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New materials in electrical engineering and electronics
SPIN CURRENT IN (110)-ORIENTED GaAs QUANTUM WELLS

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ABSTRACT

We consider a possibility of generation of the stationary spin current in (110) – oriented GaAs-based symmetric quantum well due to the nonlinear response to external periodic electric field. The model includes the Dresselhaus spin-orbit interaction and the random Rashba spin-orbit coupling.

Key words: spin current, spin-orbit coupling, GaAs, quantum well

INTRODUCTION

Recently, symmetric GaAs (110) quantum wells (QWs) became the subject of extensive studies [1-3]. Spin orbit (SO) interaction in these systems, described by the Dresselhaus term [4], conserves the electron spin along the axis normal to the QW plane for any electron momentum $k$. As a result, the random motion of an electron does not lead to spin relaxation. In reality, this spin component relaxes very slowly, and its analysis provides a test for the rapidly developing spin-noise spectroscopy [2]. In the case of perfect $z$ to $-z$ symmetry (the axis $z$ is perpendicular to the QW plane), the Rashba SO interaction is zero. But in real structures, however, the Rashba coupling still exists in the form of a spatially fluctuating SO field (though being zero on average) [5-7]. This interaction induces spin-flip processes leading to the spin relaxation [3], and can be also responsible for generation of non-equilibrium spin density due to the absorption of external electromagnetic field [7].

In this work we propose a new possibility of exciting a steadypure spin current, thus extending the abilities of spin manipulation in real situations. In

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contrast to the conventional spin Hall effect, which is linear in external electric field, the proposed spin current is quadratic in periodic field. The effect is a result of the interplay of constant Dresselhaus and spatially non-uniform Rashba interactions. The exact mechanism of this effect does not involve real spin-flip transitions of electrons between the spin-split subbands in (110)-GaAs QW, but relies on virtual spin-flip processes renormalizing the wave functions of electrons in non-equilibrium state. This makes such an nonlinear response the physically new phenomenon, which appears if one takes into account more realistic cases than those described by the conventional Rashba and Dresselhaus models.

**MODEL AND GENERAL APPROACH**

Hamiltonian of a two-dimensional electron gas with a constant Dresselhaus term and spatially fluctuating Rashba spin-orbit interaction, subjected to external electromagnetic field described by the vector potential $\mathbf{A}(\mathbf{r}, t)$ takes the form (we use units with $\hbar = 1$)

$$H = \frac{1}{2m} \left( \nabla - \frac{i e \mathbf{A}}{c} \right)^2 - i \alpha \sigma_z \left( \frac{\nabla_x - i e A_x}{c} \right) - i \sigma_x \left\{ \nabla_y, \lambda(\mathbf{r}) \right\} / 2 + i \sigma_y \left\{ \nabla_x, \lambda(\mathbf{r}) \right\} / 2 + V,$$

Where $\alpha$ is the Dresselhaus coupling constant, $\{,\}$ denoting the anticommutator and $\lambda(\mathbf{r})$ is the random Rashba SO interaction. The term $V$ describes coupling of the electron spin to the external field $\mathbf{A}(\mathbf{r}, t)$ via the Rashba field.

Due to the assumed symmetry with respect to $z$-inversion, the spatially averaged Rashba interaction vanishes, $\langle \lambda(\mathbf{r}) \rangle = 0$. We assume that the random-Rashba field can be described by the some correlation function related to fluctuating density of impurities near the QW [5, 7].

**SPIN CURRENT**

A nonzero pure spin current can be generated by an external field in the presence of random Rashba coupling. In the following we consider the $z$-component of spin current flowing along the $x$ axis. The macroscopic spin current density is then given by

$$j_x^z = i Tr \sum_k \int \frac{d\varepsilon}{2\pi} \tilde{J}_x^z G_{k\varepsilon}$$

Where $j_x^z = k_x \sigma_z / m + \alpha$ is spin current tensor component, $G_{k\varepsilon}$ is the Green's function of the system.
Fig. 1 – Dependence of the light-induced spin current on the frequency $\omega$ for different values of the correlation length $R$.

The stationary spin current is excited by the external electromagnetic field described by $A(t) = 2A_0 \cos \omega t$. We point out that only Rashba SO interaction can generate the spin current since the field-induced perturbation in Dresselhaus term commutes with $\sigma_z$ and thus does not lead to spin dynamics. After expanding Green's function up to the first order in $\mathbf{r}$ and second order in $A(t)$ we obtain the following form of the spin current

$$j_x^z = C(\omega) \int_0^{k_F} \frac{k_{d\mathbf{q}}}{4\pi^2} \frac{q_{d\mathbf{q}}}{2\pi} |\lambda_{q}|^2$$

$$\times \left( k \frac{3q\beta_2 + 4k\beta_2^3 + 2k}{(\beta_2^2 - 1)^{5/2}} + \frac{4k^2\beta_1^2 + 2k^2 + 2q^2\beta_1^2 + q^2 + 9kq\beta_1}{(\beta_1^2 - 1)^{5/2}} \right)$$

(3)

Where $q_{c} = -k/2 + (k^2/4 + 2m\omega)^{1/2}$, $\beta_{1,2} = 2m\omega/kq \pm q/k$.

RESULTS AND DISCUSSION

Numerical results on $j_x^z$ are shown in Fig. 1 for different values of the parameter $R$. We used the parameters typical for GaAs: $m = 0.067 m_0$, $k_F = 1.8 \cdot 10^6 \text{ cm}^{-1}$ and $\mu = 18.5 \text{ meV}$.

We emphasize here that the calculated spin current is a stationary nonlinear effect proportional to the intensity of incident light, in contrast to the spin
current generated by pulse excitations, where the result is proportional to the total influence in the pulse [6]. In the flux-dependent processes the pulse changes the real occupation of the spin-up and spin-down states. The calculated current is also not related to the linear response at frequency $\omega$.

**CONCLUSIONS**

We have proposed a new effect which consists in the nonlinear generation of a steady pure spin currents in GaAs (110) quantum wells by electromagnetic wave. The spin current is proportional to the intensity of the external monochromatic radiation. Physical mechanism of the effect is related to the virtual spin reorientation of electrons filling the spin subband (split by Dresselhaus interaction) in the presence of a non-uniform Rashba coupling. As a result, a 'spin hole' virtually appears in the subband, leading to the light-induced spin current.

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**REFERENCES**

T-X-Y DIAGRAMS OF LEAD-FREE SOLDERING SYSTEMS WITH THERMODYNAMIC CONTOURS OF MINIMAL SURFACES

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ABSTRACT

Alternative principle of the phase diagrams (PD) engineering has been offered: 1) before proceeding with the assembly of hypothetical or real PD, a space scheme of monovariant reactions (three-phase regions scheme) is to be elaborated; 2) contours of the surfaces with the unruled nature are to be closed and data of thermodynamic calculations are used on this stage; 3) surfaces should be approximated as the minimal ones, like the soap films, with the minimal area; 4) all geometrical elements (points, lines, surfaces, phase regions) are designated, and their “names” contain the meaning (reason) of these designations; 5) after the computer assembling the PD space model is a useful tool to solve different fundamental and applied tasks of materials science. E.g. solidification paths are confirmed by the mass balances: a vertical one - for the given centre of masses, and a horizontal one - for the isothermal state of isopleth. As computer model of PD saves information about system in compact form and permits to receive any projection, isotherm and isopleth with the decoding of intersected surfaces and phase regions, it helps also to enquire the errors and incorrectly interpreted experimental data, especially in the cases of surfaces’ degeneration because of negligibly small sizes of homogeneous regions. To investigate a competition of tiny eutectical crystals with more large primary crystals of the same phase in the invariant reaction with melt, an idea of “disperse” tie-line is used, and as a result the microstructures can be located with large, small and with mixed type of crystals.

Key words: lead-free solders, microstructures of ceramics and alloys, 3D computer models of phase diagrams, competition of crystals with different dispersity, invariant reactions, three-phase regions with the surfaces of two-phase reactions

INTRODUCTION

Results of ESF COST 531 Project were published as T-x-y diagrams Atlas of systems, which could replace Pb-contained solders [1]. Though preparation of Atlas has been required many efforts, concerned with thermodynamic coupling of experimental data, the description of 20 ternary systems were finally reduced to liquidus projection, 2-3 isotherms and isopleths (sometimes

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in fragments) and a table of invariant reactions. Shortcoming of information is felt especially when diagrams have binary and ternary compounds only in sub-solidus. So it is necessary to reconstruct lead-free ternary systems in whole scope and to design the computer models for their T-x-y diagrams [2-3].

3D PHASE DIAGRAMS WITH KINEMATICAL SURFACES

In the process of PD computer models engineering (Figure 1) the mistakes and contradictions in their traditional explanations have been found. E.g., in three systems of eutectical type with different variants of liquid stratification cupola [4], the same error repeats with the unclosed contour of a solvus surface – lack of line $C_A^0C_E^0$ on a prism base (Figure 2).

**Fig. 1** – Forming of surface $Ae_{AB}Ee_{AC}$ with a hole $k_1mk_2n$ (a): by the fragments $Ae_{AB}(e_{AB}[e_{AB},E])([A,e_{AC}]e_{AC},)$, $k_1k_2([A,e_{AC}][e_{AC},E]), k_1(e_{AB}[e_{AB},E])([e_{AB},E]E)k_2$, $([A,e_{AC}][e_{AC},E])Ee_{AC}$ (b); and by a template (c-d) with the directing curves $k_1k_4mk_2k_5$ & $k_1k_3mk_5k_2$ on hole’s contour

**Fig. 2** – Solidus $CC_A^0C_OC_E^0C_B$ with a fold $C_A^0C_O$ and solvuses $C_B^0C_E^0C_B^0$ & $C_A^0C_E^0C_A^0C_E^0$ at auxiliary and orthogonal position of lines $C_A^0C_A^0$, $C_B^0C_B^0$, $C_E^0C_E^0$, projecting into points $C_A(C_A^0), C_B(C_B^0), C_E(C_E^0)$

Computer models of PD simplify the analysis of contradicting data on low-fusible systems with a lead and allow to predict their topological variants with decomposing of compounds and degeneration of solvus surfaces at low temperatures. Such diagrams are testing on their schemes (Figure 3-5).

Correcting the «eutectical» sections of Cd-Sn-Pb PD [5], contradicted with [6], W. Zhou [7] has given the sections of reaction $R=A+B+C$ plane too, but didn't reach a success in the phase regions visualizing (Figure 3).
Despite thermodynamic instability and decomposition at -46°, an incongruently melting compound $R_1=\text{Pb}_m\text{Bi}$ was taken as a stable one in Pb-Sn-Bi PD [8], whereas a ternary compound $R_2$ decomposes (Figure 4 and 5).

Fig. 3 – Isopleth of Cd(S1)-Sn(S2)-Pb(S3) diagram [7] and its scheme

Fig. 4 - A scheme of diagram Pb(A)-Sn(B)-Bi(C) [8]

Fig. 5 – An isotherm of real [8] and schematical (Figure 4) diagram
MASS BALANCES INVESTIGATION

New results were received for the monovariant and invariant reactions. Besides confirming a horizontal position (Figure 6) for the surface of 3-phase reaction type change [9-10], new features of subsolidus 3-phase region were found (Figure 7). Investigation was validated by the mass balances.

Fig. 6 – Horizontal plane of phase B mass increment sign changing for the parallelism of $B_1B_4$ curve tangent and common tangent of $L_1L_4$ & $A_1A_4$ curves (a); mass balances for compositions 1, 2 (b); isopleth $S_1S_2$ and surfaces cuts: $A_1L_1L_4A_4$ - curves $C_1C_2&C_3C_4$, $B_1L_1L_4B_4$ - $C_2C_3$, $A_1B_1B_4A_4$ - $C_1C_4$ (c)

Fig. 7 – Three-phase region with 6 changes of the reaction type and its vertical and horizontal sections

As each phase in the process of cooling has its own density, it is important to recognize that real item belongs either one of 3 "eutectiodal" fragments, or 3 "peritectoidal" ones (Figure 7). And every such fragment will have its individual mechanism of development of the specific gravity.

Computer model of PD simplifies the solution of problems with microstructures design [11]. Field $\text{A}_\text{AB}FS$ of reaction $L+A^0=B^0+R^0$ is broken by the lines $\text{K}A$ and $KA$ into the fragments $e_{\text{AB}}FK$, $\text{A}_{\text{AB}}K$ and $\text{ASK}$ (Figure 8a). In the top fragment $e_{\text{AB}}FK$ microstructure contains a matrix $M=R^0+B^0+B^0$ and eutectical crystals $A^c$, in bottom fragment $\text{ASK}$ – a matrix $M$ and primary crystals $A^1$. The microstructure of medium fragment $\text{A}_{\text{AB}}K$ includes both types of crystals $A$: $M+A^1+A^c$. On the fragment $\text{UH}=(A-Q)(e_{\text{AB}}Q)$ of isopleth $BV$ the horizontal (isothermal) mass balances (Figure 8b-c) are constructed, before and
after reaction $L + A^Q = B^Q + R^Q$, where in intervals $UH$ and $(e_{A^H} - K)(A - K)$ the dividing of the crystals portions is executed: $A$ into $A^c$ & $A^i$ and $A^r$ - into $A^{n1}$ & $A^{n1}$ (“$r$” means excess, «избыток» - in Russian, after the quasiperitectical invariant 4-phase reaction).

**MINIMAL SURFACES**

Main perspectives for the PD computer models are connected with the using of minimal surfaces. It is the well-known task to define a surface $Z = Z(x, y)$ with the given borders. As the first step in this direction, a smooth surface of property above the whole concentration triangle ABC, (e.g. liquidus of the continuous row of solid solutions) is considered [3, p. 98]. As a surface behavior isn’t known, it is possible to assume that its average curvature $H=0$ and to receive a one, which among all other surfaces with the same contour has a minimal area. The minimal surface searching on its given contour is named as the Plato’s problem.

Average curvature of a surface is defined as

$$H = \frac{1}{2} \frac{EN - 2FM + GL}{EG - F^2},$$

where

$$E = 1 + z_x^2; \quad G = 1 + z_y^2; \quad F = z_x z_y; \quad L = Z_{xx}/\sqrt{1 + z_x^2 + z_y^2}; \quad M = Z_{xy}/\sqrt{1 + z_x^2 + z_y^2};$$

$$N = Z_{yy}/\sqrt{1 + z_x^2 + z_y^2}.$$ If suppose $H \equiv 0$, we will receive

$$\frac{EN - 2FM + GL}{EG - F^2} = 0,$$ or

$$\frac{(1 + z_x^2)z_{yy} - 2z_x z_{xy} z_y + (1 + z_y^2)z_{xx}}{(1 + z_x^2 + z_y^2)^{2/3}} = 0.$$

As the denominator isn’t equal to zero, a problem solution is reduced to a linear differential equation of the second power with private derivatives of elliptic type

$$(1 + z_x^2)z_{yy} - 2z_x z_{xy} z_y + (1 + z_y^2)z_{xx} = 0. \quad (1)$$

Let’s place a ternary system with a smooth surface in rectangular Cartesian system of coordinates (Figure 9), where binary systems are represented by the curves, described by the equations $z_{A-B} = \phi_1(x, y)$, $z_{B-C} = \phi_2(x, y)$,
\( z_{A-C} = \varphi_3(x, y) \). On this contour it is required to find a surface \( z = z(x, y) \), which is the solution of the equation (1). It may be solved by the numerical methods. For this purpose a triangle of composition is divided by a uniform grid with step \( \lambda \), formed by the lines, parallel to the triangle sides.

Let's consider any knot with number ijk on a grid. On an axis i the content of component B changes, on j - component A, on k – component C. For again added axes a, b, c we will receive: 
\[
\frac{\partial z}{\partial x} = \frac{\partial z}{\partial a} \; ; \; \frac{\partial^2 z}{\partial x^2} = \frac{\partial^2 z}{\partial a^2} \; ; \; \frac{\partial z}{\partial y} = \frac{1}{\sqrt{3}} \left( \frac{\partial z}{\partial b} + \frac{\partial z}{\partial c} \right) ;
\]

\[
\frac{\partial^2 z}{\partial y^2} = \frac{2}{3} \left( \frac{\partial^2 z}{\partial b^2} + \frac{\partial^2 z}{\partial c^2} - \frac{1}{2} \frac{\partial^2 z}{\partial a^2} \right) \frac{\partial^2 z}{\partial x \partial y} = \frac{1}{\sqrt{3}} \left( \frac{\partial^2 z}{\partial b^2} - \frac{\partial^2 z}{\partial c^2} \right)
\]
and the equation (1) will be copied in an equation

\[
2 \left[ 1 + \left( \frac{\partial z}{\partial a} \right)^2 \right] \left[ \frac{\partial^2 z}{\partial b^2} + \frac{\partial^2 z}{\partial c^2} - \frac{1}{2} \frac{\partial^2 z}{\partial a^2} \right] + \left[ 1 + 1 \left( \frac{\partial z}{\partial b} + \frac{\partial z}{\partial c} \right)^2 \right] \frac{\partial^2 z}{\partial a^2} - \frac{2}{3} \frac{\partial z}{\partial b} + \frac{\partial z}{\partial c} \left( \frac{\partial^2 z}{\partial b^2} - \frac{\partial^2 z}{\partial c^2} \right) = 0.
\]

Let's replace the private derivatives by the central differential schemes for a point ijk:

\[
\frac{\partial z}{\partial a} = \frac{z_{i,j+1,k-1} - z_{i,j-1,k+1}}{2 \lambda} ;
\]

\[
\frac{\partial z}{\partial b} = \frac{z_{i+1,j+1,k} - z_{i-1,j-1,k}}{2 \lambda} ;
\]

\[
\frac{\partial z}{\partial c} = \frac{z_{i+1,j,k+1} - z_{i-1,j,k-1}}{2 \lambda} ;
\]

\[
\frac{\partial^2 z}{\partial a^2} = \frac{\left( z_{i,j+1,k-1} - z_{i,j-1,k+1} \right)}{\lambda^2} - 2z_{ijk} \lambda^2 ;
\]

\[
\frac{\partial^2 z}{\partial b^2} = \frac{\left( z_{i+1,j,k} - z_{i-1,j,k} \right)}{\lambda^2} - 2z_{ijk} \lambda^2 ;
\]

\[
\frac{\partial^2 z}{\partial c^2} = \frac{\left( z_{i,j,k+1} - z_{i,j,k-1} \right)}{\lambda^2} - 2z_{ijk} \lambda^2 ;
\]

A system of K equations are produced:

\[
2 \left[ \frac{1}{3} \left( \frac{z_{i,j+1,k-1} - z_{i,j-1,k+1}}{4 \lambda^2} \right)^2 \right] \left[ \frac{z_{i+1,j+1,k} + z_{i-1,j-1,k} - 2z_{i,j,k}}{\lambda^2} + \frac{z_{i+1,j+1,k+1} + z_{i-1,j-1,k-1} - 2z_{i,j,k+1}}{\lambda^2} - \frac{z_{i+1,j,k-1} + z_{i,j-1,k+1} - 2z_{i,j,k}}{\lambda^2} \right]
\]

\[
+ \frac{2}{3} \left( \frac{z_{i,j+1,k-1} - z_{i,j-1,k+1}}{4 \lambda^2} \right)^2 \times \frac{z_{i+1,j+1,k} + z_{i-1,j-1,k} - 2z_{i,j,k}}{12 \lambda^2} \left[ \frac{z_{i+1,j,k-1} + z_{i,j-1,k+1} - 2z_{i,j,k}}{\lambda^2} \right] - \frac{2}{3} \left( \frac{z_{i,j,k+1} - z_{i,j,k-1}}{4 \lambda^2} \right) \times \frac{z_{i+1,j,k+1} + z_{i,j,k+1} - 2z_{i,j,k+1}}{12 \lambda^2} \left[ \frac{z_{i+1,j,k+1} + z_{i,j,k+1} - 2z_{i,j,k+1}}{\lambda^2} \right] = 0.
\]
\[
\frac{\left( z_{i+1,j+1,k} + z_{i-1,j-1,k} - z_{i+1,j,k+1} - z_{i-1,j,k-1} \right)}{\lambda^2} = 0,
\]
where triangle sides have \( N \) equal segments and there are \( K = \sum_{i=1}^{N-2} (n-i-1) \) unknown points within a triangle.

**Fig. 9** - A surface and a central differential scheme for the equation (1)

The system solution – values of temperatures in \( K \) points within a triangle – is received by the Newton method. As initial approximation the values of temperatures in the grid knots, received for a plane, constructed on three points, are accepted: \( A(0,0,T_A), B(1/2,\sqrt{3}/2,T_B), C(1,0,T_C) \).

At algorithm realization each point \( i, j, k \) in a triangle are considered in an environment of six others: \((i-1)\) and \((i+1)\), \((j-1)\) and \((j+1)\), \((k-1)\) and \((k+1)\). Accordingly in all these points seven derivatives and values of function in a point \( i, j, k \) are calculated. Received system of the \( K \) linear equations has been dared by the using of standard procedures.

**Fig. 10** – Bi(A)-In(B)-Sn(C) T-x-y diagram
RESULTS AND DISCUSSION

The Bi-In-Sn T-x-y diagram with binary compounds R1-R6, 155 surfaces and 60 phase regions (Figure 10) had been reconstructed by the data of binaries, liquidus projection, isotherm 56°, isopleths $z_{In}=0.6$ and $z_{Bi}=0.2$. Quality of reconstruction is confirmed by coincidence of simulated isopleths and isotherms with the given sections in the Atlas.

Fig. 11 – Mass balances for composition G ($S_1S_2$ isopleth of Figure 10)

Fig. 12 - Mass balances for the isopleth $z_{In}=0.6$ at $T=60°$ (Figure 10)

Two types of mass balances are considered to analyze the microstructure forming: 1) in all temperature diapason for a given concentration G (Figure 11), to show, which phase regions are intersected by the mass centre G and the
mass portions of the coexisting there phases, 2) for isothermal states of isopleth
MN (Figure 12) to demonstrate the portions of phases in the phase regions
intersected by MN at this temperature.

CONCLUSIONS

As a solder without Pb sometimes makes worse the quality of a microelec-
tronic device, it is necessary to find methods to improve its microstructure by
means of PD computer model.

PD computer model became an important tool to investigate physico-
chemical systems. It permits to receive an adequate evaluation for the thermo-
dynamic calculation and for the interpretation of experimental data.

An analysis of crystallization schemes in the system with only one ternary
incongruently melting compound is characterized as very complicated one [12].
Meanwhile it was thoroughly interpreted by L.S. Palatnik, A.I. Landau [13]. In
similar way the crystallization paths can be considered for any ternary system
by means of computer model for its T-x-y diagram.

Computer design of materials gives a possibility to detect such nuances of
microstructure formation as 3-phase transformation type change and competi-
tion of crystals with different disoperisty.

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THERMAL REVERSIBLE BREAKDOWN AND RESISTIVITY SWITCHING IN HAFNIUM DIOXIDE

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ABSTRACT

We present a model of thermal reversible breakdown via conductive filaments (CFs) in hafnium dioxide (HfO2). These CFs appear as a result of electrical pretreatment of a metal/HfO2/metal (semiconductor) nanostructure (MIM(S)). The model is based on an assumption that the thermal reversible breakdown of a CF is due to Joule heating displaying an exponential dependence of conductivity on temperature. The corresponding current-voltage characteristic and temperature of a CF in its middle and at the interface with an electrode are calculated taking into account the heat conduction equation and boundary conditions with heat dissipation via electrodes. It is found that the current-voltage characteristic of a CF has three specific regions. The initial and final regions have turned out to be linear with respect to the current and display different slopes, while the middle region is characterized by S-shaped or ultralinear dependences which are affected by the ambient temperature and nanostructure parameters. The switching potential from high resistivity state (HRS) to the low resistivity state (LRS) was shown to decrease with the ambient temperature and with worsened heat dissipation conditions.

Key words: hafnium dioxide, thermal reversible breakdown, conductive filament, s-shaped, current-voltage characteristic

INTRODUCTION

HfO2 nanostructures are currently considered to be very promising for different applications including gate oxides in Si transistors and emerging nonvolatile memory cells such as resistive random access memory (RRAM). For RRAM development a clear understanding of switching mechanisms from a HRS to a LRS is demanding. Several models were proposed to explain the switching effect [1-3], however, they did not cover comprehensively experimental observations. It is experimentally shown by means of high resolution transmission electron microscopy that formation of CFs with diameters of 30-50 nm in HfO2 occurred by an electrical pretreatment [2]. According to experimental data [3,4] current-voltage characteristics of MIM(S) nanostruc-

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tures with HfO$_2$ are characterized by a current jump at a specific set voltage ($V_{set}$) indicating that only the current-voltage characteristic of a CF displays the S-shaped or ultralinear behavior. In order to provide an interpretation of such behavior we have developed a model of thermal switching breakdown due to the Joule heating of CFs.

**MODEL**

We have assumed a CF to be formed along the $z$ axis from $z=-L/2$ to $z=+L/2$ in a HfO$_2$ layer of MIM(S) nanostructure. The heat release and voltage drop at contacts are not taken into consideration because heat removal is expected to be uniformed and to follow the Newton law. Temperature distribution in the CF can be written as [5]

$$
\kappa_d \frac{d^2 T}{dz^2} + jF = 0, \quad (1)
$$

$$
\frac{dT}{dz} \bigg|_{z=0} = 0, \quad \kappa_d \frac{dT}{dz} \bigg|_{z=L/2} = \frac{\lambda(T_b - T_0)}{1 + \lambda \delta / \kappa_c}, \quad (2)
$$

where $\kappa_c$ is the heat conduction of a contact, $\kappa_d$ is the heat conduction of a CF, $\lambda$ is the coefficient of external heat removal, $\delta$ is the thickness of contacts, $T_0$ is the ambient temperature, $T_b$ is the temperature at the interface between the CF and the electrode. The current density and the voltage drop on the CF can be defined in a drift approximation

$$
j = \sigma_0 F \exp(-\Delta E / k_B T), \quad V = 2 \int_0^{L/2} F(z) dz, \quad (3)
$$

where $F$ is the electric field strength in the CF, $\sigma_0$ is the conductivity in the CF at $T_0$, $\Delta E$ is the trap energy in the CF, $k_B$ is the Boltzmann constant.

By solving (1)-(3), the current-voltage characteristic of the CF can be calculated in the parametric form

$$
j_R = \int_{t_b}^{t_w} \left( \int_t \exp(1/t) dt \right)^{-1/2} dt, \quad \frac{v_p^2}{2} = \int_{t_b}^{t_w} \exp(1/t) dt, \quad (4)
$$

where $v_b = (V/2) \sqrt{(\sigma_0 k_B / \kappa_d \Delta E)}$, $j_R = (\sqrt{2} / 4) jL[k_B / (\kappa_d \Delta E \sigma_0)]^{1/2}$, $t_b = t_0 + (jV / W_b)$, $W_b = (4\gamma \kappa_d \Delta E) / (k_B L)$, $\gamma = \lambda L / (2\kappa_d [1 + (\lambda \delta / \kappa_c)])$, $t_{(0,m)} = k_B T_{(0,m)} / \Delta E$, $T_m$ is the temperature in the middle of the CF at $z=0$.

We have defined the function $t_n(jV/W_b)$ at different values of $\gamma$ and $t_0$ parameters and, as a consequence, find the current-voltage characteristics and dependencies of temperature in the middle of a CF and at the interface with electrodes on voltage drop.
RESULTS AND DISCUSSION

We have found three specific regions in the current-voltage characteristic of a CF. The first region at a small voltage drop is characterized by a linear dependence of current density with a small slope. The slope is found to be slightly dependent of temperature $t_0$ and independent of the parameter of heat removal $\gamma$. The second region is a transition state which displays the nonlinear current voltage characteristic depending on $t_0$ and $\gamma$. This region is S-shaped with the following transformation to nonlinear transition area with increasing $t_0$. Finally the third region shows the linear current-voltage characteristic with a high slope and obeys the Ohm law. The shape of the current-voltage characteristic is only defined by $t_0$ and $\gamma$. At $t_0 \leq 0.3$ between the linear regions the S-shaped region appears while at $t_0 > 0.35$ there is a nonlinear area. The current-voltage characteristic shifts along the voltage drop axis with increasing the heat removal parameter $\gamma$ and the formation the S-shaped regions occurs at larger voltage drops as shown in Fig. 1.

![Fig. 1](current-voltagecharacteristics.png)

**Fig. 1** – current-voltage characteristics of the CF at $t_0 = 0.2$: $\gamma = 0.1$ (1); $\gamma = 0.5$ (2); $\gamma = 1.0$ (3).

![Fig. 2](current-voltagecharacteristics.png)

**Fig. 2** – current-voltage characteristics of the CF (1), temperatures $t_m$ (2) and $t_b$ (3) at $t_0 = 0.2$, $\gamma = 10$.

The $T_m$ and $T_b$ dependences on the voltage drop are also characterized by three regions, as it is sown in Fig. 2. We have also found that the influence of parameters of a nanostructure on this dependence is analogous to the one described above for the current-voltage characteristic. A notable difference can be traced for temperature only at the boundary of a CF. At $\gamma \leq 1$ the temperature corresponds to that in the middle of the CF. Whereas, with increasing $\gamma$ the difference has turned out to be valuable leading to compression of the $T_b(v_b)$ dependence with respect to the temperature axis. Thus, with increasing of the heat removal the temperature of the CF at the boundary decreases significantly with respect to the temperature in the middle of the CF.

The potential, at which a sharp jump in the current occurs (the switching potential from HRS to LRS, $V_{sw}$), decreases proportionally to increasing of the
ambient temperature $T_0$ according to experimental data [4] for the Pt/HfO$_2$/TiN nanostructure. The potential $V_{set}$ also decreases proportionally to the parameter $\gamma$ because of the worsened conditions of heat removal.

**CONCLUSION**

We have developed the model of conductive filament thermal reversible breakdown involving mechanisms of switching between high and low resistivity states in HfO$_2$ MIM(S) nanostructures. The current-voltage characteristics and dependencies of the filament temperature on the voltage drop, ambient temperature and heat removal parameters are also calculated. We have defined conditions of an appearance of the S-shaped current-voltage characteristic of the conductive filament with a nonlinear transition area. We have also found out that decreasing in the ambient temperature leads to magnification of the transition S-shaped region of the current-voltage characteristic while degeneration of this transition region occurs with an increasing temperetute. An increase in the heat removal shifts the current-voltage characteristic to the area of larger voltage drops and decreases the temperature at the filament/electrode interface with respect to the temperature at the middle of the conductive filament.

**Acknowledgements**

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**REFERENCES**

MANY BODY EFFECTS ON THE TRANSPORT PROPERTIES OF A DOPED NANO DEVICE

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ABSTRACT

In this article, we study the effect of electron-electron interaction in a doped nano cluster sandwich between two electrodes. The Hamiltonian of the cluster is written in the tight-binding model and electrodes are described in the wide-band approximation. The GW approximation has been used for the calculation of the exchange-correlation term in the cluster region. Our results showed that in the presence of the electron-electron interaction the transmittance gap increases and current decreases. Also, in a doped nano structure the transmission decreases and many body effect becomes more important. By considering the exchange-correlation in a doped nano cluster in the GW approximation the transmission and current decrease drastically.

Keywords: nanocluster; doping; many body theory; transport properties.

INTRODUCTION

Transportation through a nano device is an interesting topic for theoretical and experimental physicist [1-4]. In realistic systems the impurity effects are inevitable. The presence of an impurity in a nano system changes the electronic and transport properties of the device. In the one particle approach and in a tight binding approximation the Hamiltonian of cluster is written according to the on-site and hopping term between nearest neighbors in the cluster. In this approach the the impurity effects are limited in the change of tight binding parameters. But due to the electron-electron and electron-phonon interactions in the nano device, we face a complex many-body problem. The effect of electron-phonon interaction has been studied in previous works[5-8]; in this article, the effect of electron-electron interaction in a doped nano device is studied. The electron-electron interaction plays an important role in solids and responsible for the coulomb blockade and the Kondo effects [9]. Based on the Born-Openheimer approximation, the electronic and the ionic degrees of freedom are decoupled. The Hartree and Hartree-Fock (HF) methods try to deals the electron-electron interactions as a one-particle term in the total Hamiltonian. The Hartree method simply adds the classical repulsion to the one particle Hamiltonian. In the GW approximation the self-energy is approximated with the first

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term in the expansion. Many body effects beyond the GW approximation could be important in the calculation of different properties of solids [10-12] but the GW approximation is reliable in different calculations [1, 3, 13-15]. The HF approximation contains the classical electrostatic and exchange potentials but the GW approximation includes the correlation between electrons in solids [16]. In this work we investigate the many body effect in a doped nano cluster.

**MODEL AND RESULTS**

We consider a typical nano cluster with 6 atoms and attach the left and right electrodes to the cluster, as shown in Figure 1. At first the transport in a pure and doped cluster in a one-particle approach has been investigated. The total Hamiltonian of the above system contains the Hamiltonian of isolated cluster, electrodes and the interaction between them.

![Figure 1](image)

**Fig. 1** – A pure and doped nano cluster with 6 point between two electrodes

The non-interacting part of the Hamiltonian is written in the nearest neighbor tight-binding approximation as follows,

\[
H_{0C} = \sum_{i,\sigma} \varepsilon_i C_{i,\sigma}^+ C_{i,\sigma} - t_i (C_{i+1,\sigma}^+ C_{i,\sigma} + C_{i,\sigma}^+ C_{i+1,\sigma})
\]  

(1)

The index \(i\) runs over the cluster sites. The operator \(C_{i,\sigma}^+\) creates/annihilates a \(\pi\) electron with spin \(\sigma\) at the \(i\)-th site of cluster. \(\varepsilon_i\) is the onsite energy of the \(i\)-th sites and \(t_i\) denotes the hopping integral between two neighboring sites. The effect of electrodes on the Hamiltonian is fully described by specifying the self-energy of the left and right electrodes. By using the Keldysh Green’s function technique, the current running between two electrodes, through the cluster, is calculated by Meir-Wingreen relation [2, 17]. Neglecting the interaction in the central region, the Mier-Wingreen relation is simplified to the well-known Landauer-Büttiker formula [18, 19],

\[
I(V_B) = \frac{e}{h} \int_{-\infty}^{+\infty} d\omega T(\omega) \left[ f_L(\omega) - f_R(\omega) \right]
\]  

(2)
Where \( f_{L/R} = \left[ \exp \left( \beta (\omega - \mu_{L/R}) \right) + 1 \right]^{-1} \) is the Fermi distribution function in the left/right electrode with chemical potential \( \mu_{L/R} = \varepsilon_f \pm (eV_b/2) \) and Fermi energy \( \varepsilon_f \). \( T(\omega) \) is the transmission coefficient as a function of energy for electrons and can be written as follows,

\[
T(\omega) = Tr \left[ \Gamma_L G_0^r(\omega) \Gamma_R G_0^a(\omega) \right],
\]

where \( G_0^r(\omega) \) is the retarded Green’s function of the non-interacting system and is defined as,

\[
G_0^r(\omega) = \left[ \omega I - H_{0C} - \Sigma_L - \Sigma_R \right]^{-1}
\]

\( \Gamma_{L/R} \) represents the coupling between the cluster and left/right electrode. In this article, the spin-flip process has been neglected and the self-energy of electrodes has been simply described within the wide-band approximation. In this approximation, the real part of self-energy is neglected and the imaginary part of the self-energy operator is written in an energy-independent form as \([5, 20]\), \( \Sigma_{L/R} = (-i/2) \Gamma_{L/R} \). In the pure cluster we set \( \varepsilon_i = 0 \), \( \varepsilon_i = 3.0 \text{eV} \), and in the doped cluster for the dopant site we use \( \varepsilon_d = -1 \), \( \varepsilon_d = 2 \text{eV} \), and electrodes described with the following parameters, \( \Gamma_L = \Gamma_R = 0.066 \Omega \). Figure 2 shows the current voltage characteristic and transmission as functions of energy for the above clusters. In both cases the transmission peaks are correspondent to the eigenvalue of the non-interacting system.

![Figure 2](image-url)

**Fig. 2**—Current volt-voltage characteristic and transmission as a function of energy for the case of (a) pure and (b) doped nano cluster

The symmetry around the Fermi energy in the pure cluster is due to the symmetry of the Hamiltonian in the pure cluster. In the doped structure the symmetry around the Fermi energy vanishes. By increasing the applied voltage the energy window opens and the current increases. When a transmission peak enters in the energy window, current increases more rapidly which leads to a step-like form in the current-voltage curve. In the next step, we consider the interacting cluster and study the effect of electron-electron interaction on the
transport properties of a pure and doped 2D cluster in the Hartree and G\textsubscript{0}W\textsubscript{0}. The quasi-particle equation for interacting electrons can be written as [21, 22],

\[ [H_{0C} + V_H] \Psi_i (r) + \int \Sigma(r, r', \varepsilon_i) \Psi_i (r') \, dr' = \varepsilon_i \Psi_i (r) \]  

(5)

Where \( V_H \) is the electrostatic or Hartree potential of the electronic system and \( \Sigma \) is the self-energy which is a non-local, energy-dependent and non-hermitian operator containing all exchange and correlation effects beyond the Hartree approximation. In the GW method, the time-ordered self-energy operator is approximated as [1, 23, 24],

\[ \Sigma_{GW} (r, r', \omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, W(r, r'; \omega') \, G(r, r'; \omega - \omega') \, e^{-i\omega'\delta} \]  

(6)

Where \( G \) is the one-particle Green’s function, \( W \) is the dynamically screened coulomb interaction and \( \delta \) is a positive infinitesimal. The GW method can be considered as a generalization of the HF approximation, in which the bare coulomb interaction \( \nu(r, r') = 1/|r - r'| \) is replaced with the dynamically screened interaction \( W \). In this article, the Green’s function is approximated with the non-interacting Green’s function [16, 22, 25]. The screened interaction can be calculated in terms of the inverse dielectric function \( \varepsilon^{-1} \) by means of,

\[ W (r, r', \omega) = \int dr' \, \varepsilon^{-1} (r, r'; \omega) \, \nu(r, r') \]  

(7)

In the direct space, the dielectric function can be written as \( \varepsilon = 1 - \nu P \). In its simplest form, the polarization operator \( P \) can be written in the independent particle approximation as [25],

\[ P(r, r', \omega) = \sum_{i,j} (f_i - f_j) \frac{\Psi_i (r) \, \Psi_j^*(r') \, \Psi_i^*(r') \, \Psi_j (r') \, \omega - (\varepsilon_j - \varepsilon_i) + i\eta}{\omega - (\varepsilon_j - \varepsilon_i) + i\eta} \]  

(8)

Where; \( f_i \) is the occupation of the i-th state and \( i \eta \) is a small imaginary part which leads to an imaginary part of \( P \). The above equation for polarization is the form of the random-phase approximation (RPA) first used by Lindhard for the homogeneous electron gas [26, 27]. The imaginary part has peaks in \( \delta(\varepsilon_j - \varepsilon_i - E) \) which shows the conservation of energy in case of excitation of an electron from state i to state j. The retarded Green’s function can be written as,

\[ G'_C (\omega) = [\omega I - (H_{0C} + V_H - \Sigma_L' - \Sigma_R' - \Sigma_{GW}' (\omega))]^{-1} \]  

(9)

Where \( \Sigma_{GW}' \) is the retarded self-energy operator due to the electron-electron interaction. A. Ferretti and et al. proposed a Landauer-like expression for current in the presence of many-body interactions as follows[2],
$$I^{\sigma,\sigma'}(V) = \frac{e}{h} \int_{-\infty}^{+\infty} d\omega \text{Tr}[\Gamma_L^r G_C^\sigma(\omega) \Gamma_R^r \Lambda G_C^{\sigma'}(\omega)] (f_L(\omega) - f_R(\omega))$$

(10)

We set $\Lambda = 1$ and restrict the changes in the definition of the retarded Green’s function which is correspondent to the strong coupling with electrodes. Figure 3 shows the transmission as a function of energy in the Hartree and GW approximations.

![Figure 3](image)

Fig. 3– Current volt-voltage characteristic and transmission as a function of energy in the Hartree and GW approximation for the case of (a) pure and (b) doped nano cluster.

In the Hartree approximation, the $H_0$ in the equation 4 is replaced with $H_0 \rightarrow H_0 + V_H$. In the Hartree model the transmission spectrum in the pure cluster does not change. But the transmission for the doped cluster decreases and transmission gap increases with respect to the non-interacting case. A comparison between the Hartree and GW appears the many body effects in the cluster region. In the GW approximation the real part of self-energy shifts the transmission peaks and increases the conductance gap. The imaginary part of self-energy leads to decreasing transmission and broadening in the transmission peaks. Figure 3 shows the current-voltage characteristic of the cluster in Hartree and GW approximation. The exchange-correlation term described in the GW approximation decreases the transmission and current which is correspond with an additional resistance in the cluster. In the doped nano cluster the electrons are accumulate in the dopant site. As a result the many body effect becomes more important in a doped cluster, thus the transmission reduces drastically in the GW approximation.

**CONCLUSIONS**

Briefly speaking, we have considered a typical nano structure and have studied the effect of electron-electron interaction on the transport properties in Hartree and GW approximations. Our results showed that in the presence of e-e interaction, conductance gap increases and current decreases. The reduction of transmission and current is increases in a doped cluster.
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ASPHALTENS OF OIL AND OF HIDROCARBONS DISTILLATES AS NANOSCALE SEMICONDUCTORS

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ABSTRACT

The asphaltens are composed mainly of polyaromatic carbon with NSO-compounds combined with traces vanadium and nickel, which are in porphyrin structures. The asphaltens include paramagnetic centers. The concentration of free radical is $10^{19}-10^{20}$ spin /g (EPR). The experiment and calculation results indicate that the molecular complexes of the asphalt pitch substances on the nanomolecular level associates in the structural units’ formation with the charge transfer properties involved. The spectra and quantum calculations indicate that the most probable centers for the electron transfer are the structures containing the aromatic rings, heteroaromatic rings and the corresponding free radicals. [1] The calculations showed that the asphaltens structural units, containing from 6 to 13 aromatic rings have the forbidden gap size from 4.92-6.49 eV - for the molecular fragments and from 2.84 to 3.20 eV - for the free radical form. This indicates possible belonging of the asphaltens to the amorphous compensatory organic broadband semiconductors. The experiments for estimation band gap of the molecules asphaltens confirmed by of computing ab-initio methods. The Asphaltens have nanomolecular structures, that can be used as a semiconductors for nanoelectronics.

INTRODUCTION

The asphaltens are complex substances that are found in crude oil, bitumen and high-boiling hydrocarbons distillates. The asphaltens are composed mainly of polyaromatic carbon with heterocyclic compounds combined with traces vanadium and nickel, which are in porphyrin structures. The asphaltens include paramagnetic centers. The concentration of free radical is $10^{19}-10^{20}$ spin /g (EPR). Average molecular mass ascertain in diapason 500- 2500 u (mass spectrum) . The molecules of asphaltens may contain 5- 10-member bensene and naphteno rings in their structure. The oil dispersion systems which include oils itself and high-boiling oil fractions are the asphalt pitch substances (APS) colloidal solutions, represented by the resins and asphaltens. According to F.G. Unger [1] ideas, the oil resins and asphaltens represent paramagnetic metastable substances, where the paramagnetic asphaltene fragments are the micelles formation centers in dispersed hydrocarbon environments. Around the micelles core the solvate layers are grouped in the

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order of the dispersed system intermolecular interaction potentials decrease. The electron structure of asphaltenes have not been researched enough.

The aim of this work is to study the electronic structure of the heteroatomic nanoparticles of the asphaltenes molecules using the electron spectroscopy and computational chemistry. The aim of this work is to study the electronic structure of the heteroatomic fragments of the nanoparticles of asphaltene molecules using the electron phenomenological spectroscopy and computational chemistry methods

**METHODS OF RESEARCH AND ANALYSIS**

Unlike conventional method, the phenomenological spectroscopy (EPS) studies a substances as a single whole without separating the spectrum of the substance into characteristic frequencies and wavelengths of individual functional groups or components of the systems. [2,3] The electronic phenomenological spectroscopy is based on the regularities of the relations between absorptivity coefficients and physicochemical properties of the substance the values of physicochemical properties of a substance are proportional to its ultraviolet and/or visible absorption [2].

Let us consider the method, which was proved in our previous works [1]. The ionization potential (PI) and electron affinity (EA) are estimated according to empirical dependences which links these characteristics with integral index of absorption $\Theta$ (1).

![Figure 1](image_url)

**Figure 1.** Absorption spectrum of asphaltene toluene solutions in UV and VIS area: 1 – asphaltenes of Surgut oilfield, 2 - asphaltenes of Ust-Balyksk oilfield, 3 - asphaltenes of Petelinsk oilfield, 4 - asphaltenes of Arlan oilfield, 5 - asphaltenes of Radaevsk oilfield
The test subjects are asphaltenes, separated from crude oils, oil fractions and solid deposits, including paraffins. The solid deposits were processed by benzene, filtered out from the impurities and paraffins. Then the asphaltenes were isolated from the samples properly by sedimentation with the n-heptane excess by Marcusson method.

The electronic absorbance spectrums were registrated on the double-beam spectrometer in the range of 280 ... 760 nm in the dilute toluene solutions at the asphaltenes concentrations of 1.10 gram-mol / m³. The spectra in the visible and ultraviolet range have no clear absorption fields (Figure 2).

Ab initio RHF/3-21G** method (Restricted Hartree-Fock method) with the minimal basis of Gaussian functions and full geometry optimization [4] was used to calculate the molecules.

RESULTS AND DISCUSSION

Further calculation of IP and EA average values were based on the correlations [2,3] between the electronic states energies and oscillators integral strengths (OIS):

\[ E = \alpha_1 + \alpha_2 \theta \]
\[ \Theta = \int_{\varepsilon_1}^{\varepsilon_2} \int_{\lambda_1}^{\lambda_2} E_{\lambda} d\lambda \]  

where: \( E \)— effective IP or EA, eV; \( \alpha_1, \alpha_2 \)— empirical coefficients, depending on the orbital type, permanent in this series, respectively eV, eV·gram-mol·m⁻³ (for IP— \( \alpha_1 = 9.495 \), \( \alpha_2 = -2.38 \), for EA — \( \alpha_1 = 0.11 \), \( \alpha_2 = 0.98 \); \( \theta \)— OIS logarithmic function, m³·10⁻¹⁰·gram-mol⁻¹.

OIS logarithmic function was calculated on the area under the absorption curve by the trapezoid method:

\[ \theta = \int_{\lambda_0}^{\lambda_f} \lg k_{\lambda} d\lambda \approx \frac{\lambda_f - \lambda_0}{n} \left[ \frac{\lg k_0 + \lg k_n}{2} + \lg k_1 + \lg k_2 + \ldots + \lg k_{n-1} \right] + \frac{\lambda_f - \lambda_0}{n} \lg M \]  

where: \( \varepsilon_{\lambda} \)— molar absorption coefficient at specific wavelengths in the near ultraviolet and visible spectrum area, m²·gram-mol⁻¹·m⁻¹; \( n \)— number of the spectrum sampling points in the radiation absorption area.; \( \lambda_0, \lambda_f \)— the spectrum boundaries, nm; \( M \)- molecular weight, gram/mol.

It was revealed, during the study of different asphaltenes and hydrocarbon systems origin data, that asphaltene fraction is a strong electron donor and acceptor at the same time (IP=4.37-5.8 eV, EA=1.65-2.66 eV). This means, that the processes in asphaltenes solutions and concentrates, including those related to ARPD (asphalt, resin and paraffin deposits), may be described by the formation of molecular charge-transfer complexes.
**Table 1** – Donor-acceptor properties of asphaltenes and resins by the electronic spectroscopy data

| Asphaltenes and resins of Radaevsk oilfield | 5.70   | 1.85   | 3.85   | 1.93   |
| Asphaltenes of Surgut oilfield             | 5.20-5.70 | 2.10-2.50 | 3.10-3.20 | 1.55-1.60 |
| Asphaltenes of strait-run stoks             | 4.37-5.27 | 2.44-2.50 | 1.93-2.77 | 0.96-1.38 |
| Asphaltenes of tar                          | 4.70-4.90 | 2.10-2.15 | 2.60-2.75 | 1.30-1.38 |
| Asphaltenes of Kushkul oilfield             | 5.20   | 1.90   | 3.30   | 1.65   |

**Table 2** – IP and EA values, computed on the base of the model fragments of resins and asphaltenes molecular and stable free-radical forms

<table>
<thead>
<tr>
<th>Model structure</th>
<th>Molecular form (M)</th>
<th>Free-radical form (R) without hydrogen (H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
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<tr>
<td><img src="image" alt="Model 1" /></td>
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<tr>
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<tr>
<td><img src="image" alt="Model 6" /></td>
<td>6.55</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Our studies assume that the asphaltenes in the liquid phase decompose into free radicals, according to the equations [1]:

\[ M_n = \cdot R + \cdot R_{n-1} \] \hspace{1cm} (3)

where \( M_n \) - the asphaltenes molecular form, \( R_n \) and \( R_{n-1} \) - the asphaltenes free radical forms. The oil resins and asphaltenes model fragments were selected to feature the elementary structural units in the associates decay scheme (3). In order to simulate the resins the polycyclic aromatic structures with the molecular masses of 276-379 amu (compounds 1-4) were used. Structures with molecular masses of 398-512 amu and the number of aromatic rings from 6 to 13 reflect the asphaltenes (compounds 5-9).

The empirical dependence, which connects the calculated values of the highest occupied molecular orbital energy (\( E_{HOMO} \)) and the experimental values of the ionization potentials (\( IP_{mol} \)) is:

\[ IP_{mol} = A_1 * E_{HOMO} + A_2 \] \hspace{1cm} (4)

where \( A_1 = 0.83 \); \( A_2 = 1.51 \) eV.

For the calculated values of the lowest unoccupied molecular orbital energy (\( E_{LUMO} \)) and the experimental values of the affinity to the electron (\( EA_{mol} \)) the following empirical dependence is applied:

\[ EA_{mol} = A_3 * E_{LUMO} + A_4 \] \hspace{1cm} (5)

where \( A_3 = -0.46 \); \( A_4 = 1.45 \) eV.

The correlation coefficients equal 0.93 and 0.97 respectively. The dependences (4) and (5) were obtained for the polycyclic aromatic hydrocarbons.

It is necessary to calculate the free-radical fragments, taking into account the high concentration of the asphaltenes paramagnetic centers and the modern views onto their free-radical structure. Unfortunately, the quantum chemistry methods do not make correct IP and EA assessments for the free radicals that is
why we used the semi empirical correlation for calculating the ionization potentials ($IP_{\text{rad}}$) and free radicals affinities ($EA_{\text{rad}}$) to the electron.

$$IP_{\text{rad}} = A_5 \cdot E_{\text{HOMO}} + A_6,$$

where $A_5 = 0.72$; $A_6 = 0.36$ eV.

$$EA_{\text{rad}} = A_7 \cdot E_{\text{LUMO}} + A_8,$$

where $A_7 = -0.60$; $A_8 = 2.78$ eV.

The correlation coefficients equal 0.90 and 0.83 respectively.

The results, calibrated for the experiment, are shown in Table 2.

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Table 3 – Computed and experimental ranges of IP and EA

<table>
<thead>
<tr>
<th>Data</th>
<th>IP, eV</th>
<th>EA, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>By UV and VIS spectrums [5]</td>
<td>4.37-5.70</td>
<td>1.85-2.50</td>
</tr>
<tr>
<td>Computed molecular fragments (RHF/3-21G** method)</td>
<td>6.36-7.56</td>
<td>0.54-1.65</td>
</tr>
<tr>
<td>IP and EA estimation of free-radical fragments by equations (4)-(6)</td>
<td>4.92-5.79</td>
<td>1.78-2.45</td>
</tr>
</tbody>
</table>

The exciton formation energy can be estimated by the half of the forbidden gap value (quasi-Fermi level). The quasi-Fermi level for the resins molecular fragments values from 2.54 to 3.10 eV, for the asphaltenes molecular fragments - from 2.46 to 3.25 eV; for the free radical fragments of resins - from 1.51 to 1.77 eV, for the free radical fragments of asphaltenes - from 1.42 to 1.60 eV.

According to the calculations for the molecular fragments of the resins the IP range is about 6.44-7.25 eV, the EA range is about 0.81-1.65 eV. For the free radical fragments the IP changes from 4.99 to 5.57 eV, the EA changes from 1.78 to 2.29 eV. For the asphaltene molecular fragments the IP changes from 6.36 to 7.03 eV, the EA changes from 0.54 to 1.52 eV. For the free radi-
cal fragments the IP changes from 4.92 to 5.41 eV, the EA changes from 1.86 to 2.45 eV.

The calculations results are confirmed by the APS spectroscopic data (Table 3). According to the experimental estimates, IP values are in the range from 4.37 to 5.70 eV, EA - in the range from 1.85 to 2.50 eV. Thus, the best agreement with the experiment is observed in the free radical fragments.

**CONCLUSIONS**

The experiment and calculation results indicate that the molecular complexes of the asphalt pitch substances on the nanomolecular level associates in the structural units’ formation with the charge transfer properties involved. The spectra and quantum calculations indicate that the most probable centers for the electron transfer are the structures containing the aromatic rings, heteroaromatic rings and the corresponding free radicals. The calculations showed that the asphaltenes structural units, containing from 6 to 13 aromatic rings have the forbidden gap size from 4.92-6.49 eV - for the molecular fragments and from 2.84 to 3.20 eV - for the free radical form. This indicates possible belonging of the asphaltenes to the amorphous compensatory organic broadband semiconductors [4].

The experiments for estimation band gap of the molecules asphaltenes confirmed by of computing ab-initio methods. The Asphaltenes have nanomolecular structures, that can be used as semiconductors for nanoelectronics.

**REFERENCES:**


A STUDY of INELASTIC ELECTRON-PHONON INTERACTION ON TUNNELING MAGNETORESISTANCE IN POLYACETYLENE

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ABSTRACT

In this research, we study the effect of inelastic electron-phonon interactions on magneto-transport properties of a sandwiched Polyacetylene molecule between two ferromagnetic electrodes by using a modified Green's function method. The molecule is described with the well-known Su–Schrieffer–Heeger Hamiltonian in the tight binding form. The self-energy of electrodes is written in the wide-band approximation and spin-flip is neglected during conduction process. Our calculation results show that with increasing of voltage current increases and tunneling magnetoresistance (TMR) is decreased. The changes in TMR due to the inelastic interaction is limited in a small bias voltage interval and can be neglected in the other bias voltages. These results confirm the neglecting of inelastic interactions in previous theoretical works.

Keywords: tunneling magnetoresistance; Green's function; Polyacetylene; inelastic electron-phonon interaction.

INTRODUCTION

Due to its application in electronic devices, transport trough molecule has been studied in detail, both theoretically and experimentally. Theoretical and experimental works confirm that conducting polymers can act as spin-polarized materials [1-4]. We have use the SSH Hamiltonian which a well-known Hamiltonian for the calculation of electronic and transport properties of organic semiconductors [1,4,5]. In the presence of magnetic field, the magnetic of electrodes are oriented in the same direction and the scattering for spin up decreases while increases for spin down. By considering a parallel circuit in conduction with different spins, the presence of magnetic field can make a short circuit and as a result conduction of system decreases. In this work, we study spin dependent transport in a Polyacetylene molecule in the presence of inelastic electron-phonon interactions. We sandwiched a Polyacetylene molecule between two cobalt electrodes as we have schematically shown in Figure 1. Because of the weakness in spin-orbit coupling and hyperfine

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interactions in the organic materials, spin relaxation length is long and spin-flip process during conduction can be neglected [2, 6]. The presence of phonon in the finite temperature changes the transmission mechanisms which is neglected in many previous works. Here, we study the effect of inelastic interactions in the central region and neglect the interaction in leads. Walczak developed a Green’s function approach to study the electron transport through DNA molecule in the presence of electron-phonon interactions [7, 8]. We had used the same formalism to study the inelastic electron phonon interaction in organic molecules. In this work we will use the same approach for the Polyacetylene molecule.

**MODEL AND METHODS**

The electronic part of Hamiltonian can be written as,

\[
H = \begin{pmatrix}
H_L & H_{L,C} & 0 \\
H_{L,C}^+ & H_C & H_{R,C}^+ \\
0 & H_{R,C} & H_R
\end{pmatrix}
\]  

(1)

where \( H_{L/R} \) denotes Hamiltonian of left/right electrode and \( H_C \) represents molecular Hamiltonian. Other matrix elements show the coupling between electrodes and scattering region. Both electrodes are described in the wide-band approximation [7,8].

![Fig. 1 –Schematic representation of Polyacetylene molecule sandwiched between two electrodes](image)

The Polyacetylene molecule which is considered as a quasi-one-dimensional chain with \( N \) pair of carbon atoms can be described by means of modified SSH Hamiltonian as follows [1,9],

\[
H_M = -\sum_{n=1}^{2N} \sum_\sigma \left[ (t_0 + \alpha(u_n - u_{n+1}))(d_{n,\sigma}^+ d_{n+1,\sigma} + d_{n+1,\sigma}^+ d_{n,\sigma}) \right]
\]  

(2)

where \( t_0 \) is the hopping integral in a undimerized molecule and and \( u_i \) is the displacement of the \( i \)th Carbon atom. The index \( i \) runs over the orbitals of Carbon chain of molecule. The operator \( C_i \) (\( C_i^+ \)) creates/annihilates a \( \pi \) electron with spin \( \sigma \) at the \( i \)-th site of Polyacetylene molecule.
The electron-phonon coupling constant is denoted by $\alpha$. The electronic states in the Polyacetylene chain accompanied with $m$ phonons can be written as \[ |n\sigma, m\rangle = d^+_n\alpha (a^+_m)^m |0\rangle \]

where $a_i$ and $a_i^+$ are phonon creation and annihilation operators, respectively, and $|0\rangle$ shows the vacuum state. For the sake of simplicity, we consider only one phonon mode with energy $w$. In this new basis the Hamiltonian of the Polyacetylene can be written as,

\[
H_M = \sum_{n,j,\sigma} \left[ \varepsilon_{n\sigma} - \lambda (a_j + a_j^+) \right] d^+_n\alpha d_{n,\sigma} - [(t_0 + \alpha(u_n - u_{n+1}))(d^+_n\alpha d_{n+1,\sigma} + d^+_{n+1,\sigma}d_{n,\sigma})]
\]

where $\lambda$ is the energy of electron-phonon interaction, in this work we assume that $|\lambda| = |\alpha|$. In the absence of inelastic electron-phonon interactions during conduction process, electron states will be changed from $|1, m\rangle$ to $|4N, m\rangle$. But in the presence of inelastic interactions, electrons can absorb/emit phonon and conduct between two levels with different number of phonons, for such a process we can write transmission coefficient as \[ T_{\sigma, \sigma'}^{\sigma, \sigma'}(E) = \Gamma^\sigma L \Gamma^\sigma R |G^\sigma L |G^\sigma R|^{2} \]

where $\Gamma^\sigma_{L/R} = 2\pi |\gamma^\sigma_{L/R}|^2 \rho^\sigma_{L/R}$ ($\gamma_a$ is the coupling strength between molecule and electrodes, $\rho^\sigma$ is the density of state in the electrodes for spin $\sigma$) and the Green's function is defined as follows \[ 1, 7, 8\],

\[
G^\sigma(\varepsilon) = [E - H_M - \Sigma^\sigma_L - \Sigma^\sigma_R]^{-1}
\]

All the off-diagonal terms in the Hamiltonian which are described the interaction between molecule and leads are compressed in the self-energy terms. The real part of self-energy is simply a shift in energy axis but the imaginary part describes the coupling of molecule with electrodes. In the wide-band approximation the real part of self-energy is neglected and the imaginary part is assumed an energy independent term which is written as $\Sigma^\sigma_{L/R} = \frac{i}{2} \Gamma^\sigma_{L/R}$. The total transmission can be defined as a sum over all incoming/outgoing channels with different number of phonon in the initial and final sites. Each transmission mechanism is weighted by an appropriate factor $P_m$, which is the Boltzmann distribution function \[ 7, 8\].

\[
T_{Tot}(\varepsilon) = \sum_{m, \sigma} P_m T_{\sigma, \sigma'}^{\sigma, \sigma'}(\varepsilon)
\]
From the above equation the elastic part of transmission occurs when \( m \) and \( m' \) are equal and can be written as [7, 8],

\[
T_{\text{ele}}(\epsilon) = \sum_{m,\sigma} P_m T_{m,m}^{\sigma,\sigma}(\epsilon)
\]  \hspace{1cm} (8)

The total current through junction is derived as follows,

\[
I_{\text{tot}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\epsilon \sum_{m,m',\sigma} T_{m,m}^{\sigma,\sigma} T_{m,m}^{\sigma',\sigma'} \left[ P_m f_L^m (1-f_R^m) - P_{m'} f_R^{m'} (1-f_L^{m'}) \right]
\]  \hspace{1cm} (9)

The elastic part of current can be obtained from the above equation by the assumption of \( m = m' \) [7,8],

\[
I_{\text{ele}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\epsilon \sum_{m,\sigma} T_{m,m}^{\sigma,\sigma} P_m \left[ f_L^m - f_R^m \right]
\]  \hspace{1cm} (10)

where \( f_L^m \) is the Fermi function of the left/right electrode in applied voltage \( V \), with chemical potential \( \mu_{L/R} = \epsilon_f \pm (eV/2) \) and Fermi energy \( \epsilon_f \).

We calculate transmission coefficient in the presence \( T_{\sigma,\sigma}^{\sigma,\sigma} \) and absence \( T_{\sigma,-\sigma}^{\sigma,-\sigma} \) of magnetic field. Total current and elastic part of current can be calculated from Equations (9) and (10). Finally, tunneling magnetoresistance can be defined as the change in the current due to the external magnetic field by using the following equation [11],

\[
TMR(V) = \frac{I_p(V) - I_{Ap}(V)}{I_p(V)}
\]  \hspace{1cm} (11)

where \( I_p \) (\( I_{Ap} \)) is the current in the presence/absence of magnetic field. Calculations are performed for the total current and elastic part of current and then we have compared the TMR in these two situations.

**RESULTS AND DISCUSSION**

Numerical calculations are carried out for a molecule with 15 carbon pairs (30 sites) and the parameters for a Polyacetylene chain are chosen as (given in eV): \( t_0=2.5, \ \alpha= 4.1 \ 1/\text{Å} \) and \( u=0.04 \ \text{Å}^2 \). These parameters well describe a Polyacetylene chain. We have used the following set of parameters for describing Cobalt electrodes (given in 1/eV), \( \rho^l=0.1367, \rho^l=0.5772 \), and we set \( \gamma_L = \gamma_R = 0.2 \ \text{eV}, \epsilon_f = -1 \ \text{eV} \) and \( w=0.1 \ \text{eV} \). By increasing the number of phonons in each site the Boltzmann factor tends to zero as a result considering a finite number of phonons in each site is a reasonable assumption. Here, Maximum number of allowed phonon quanta is chosen to be five and all of the calculations are done at room temperature. We also assume that the external magnetic field does not change the electronic structure of molecule and the
changes are restricted in the electrodes region. In the presence of magnetic field, density of states in electrodes and transmission coefficient through the molecule are different for each spin. The presence of inelastic interactions emission and absorption of phonons activate new transmission mechanism. These new mechanisms are spin independent phenomena and change the magneto transport through the molecule.

Figure 2 shows the current-voltage characteristic of Polyacetylene molecule in the presence of magnetic field. According to current–voltage characteristic of Polyacetylene it can be suggested as a switch in electronic circuit.

![Figure 2](image)

**Fig. 2**—The total (T) and elastic (E) part of current as a function of bias voltage for electrons with spin up (U) and spin down (D) in the presence of magnetic field

Figure 3(a) presents TMR versus bias voltage in the presence and absence of inelastic electron-phonon interactions. The difference between these them is plotted in Fig. 3(b).
As we expected, due to spin independent nature inelastic electron phonon interaction TMR decreases. In the low voltage regime the tunneling probability is near zero, current is small and TMR is constant. By increasing voltage energy-window opens and resonant tunneling occurs and as a result, current increase while TMR decreases. The polaron formation due to the electron phonon interaction shifts the current peak and reduces the conductance gap [12]. As a result the damping of TMR is occurred in a lower voltage. At higher voltages, TMR does not change with the increase of voltage. By increasing the applied voltage the energy of electrons is increases and the changes made by inelastic interactions are disappeared. A comparison between these results and our previous results for Polythiophene [13] confirms the neglecting of inelastic electron phonon interaction in the transport calculation of organic molecule, even in room temperature.

**CONCLUSIONS**

In summary, we have investigated the effect of inelastic electron-phonon interactions on the magneto transport in a Polyacetylene molecule. Our calculations indicate that the change of TMR due to inelastic interaction is limited in a small bias voltage interval and can be neglected in other bias voltages. These results confirm the neglecting of the inelastic interactions in previous theoretical works.

**REFERENCES**

STRUCTURE OF QUANTUM LEVELS FOR TWO-DIMENSIONAL ELECTRON IN THE HOMOGENEOUS MAGNETIC FIELD AND THE POTENTIAL CONFINING NEAR TO THE RING

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ABSTRACT

Studying of properties of quantum rings (nano-scaling and mesoscopic ring structures) in a magnetic field is one of directions on which there are interesting results (see, for example, [1]). Quantum transitions in such structures are accompanied by radiation on border of infra-red light, and interest is caused by periodic structures in which quantum rings are cooperate with neigh calls in pseudo-crystal. In the given work results of calculations of such structure in two-dimension statement (periodicity is provided with decomposition of the solution in Fourier series on both spatial coordinates) are presented.

METHODS OF COMPUTATION AND ANALYSIS

The solution of stationary equation Schrödinger in two-dimensional linear statement is considered. Following designations are accepted: \( m_e, B, \gamma, U \) - mass of electron, intensity magnetic field, the confining potential, \( c, e, \hbar \) - speed of light, an elementary charge, a constant of Planck, \( \Delta, \psi(x,y), E \) - two-dimensional harmonic operator, wave function from the Cartesian coordinates of electron, energy of stationary quantum state.

\[
\left( -\frac{\hbar^2}{2m_e}\Delta + i\frac{\hbar eB}{m_e c} \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) + \frac{e^2B^2}{2m_e c^2} \left( x^2 + y^2 \right) + U(x,y) - E \right) \psi = 0
\]

After introduction of magnetic scale of length \( \alpha = \sqrt{\frac{\hbar c}{eB}} \), scaling-less confining potential \( V = \frac{2m_e c}{\hbar eB} U \) and energies of quantum states \( \Lambda = \frac{2m_e c}{\hbar eB} E \) the equation (1):

\[
\left( -\alpha^2\Delta + 2i \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) + \frac{x^2 + y^2}{\alpha^2} + V - \Lambda \right) \psi = 0
\]

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The solution of a problem (2) was searched in the form of a trigonometrically polynomial (final of series on Fourier - harmonics). Let \( R, L \) is self-length of areas of periodicity and number of harmonics:

\[
\psi = \frac{1}{2R} \sum_{n,k=-L}^{L} a_{n,k} \exp \left( \frac{\pi i}{R} (nx + ky) \right)
\]

After substitutions of it in the equation (2), multiplication on \( \exp \left( \frac{\pi i}{R} (-qx - sy) \right) \) and integration on area of periodicity \( \Omega = \{ -R \leq x, y \leq R \} \) the algebraic problem on eigen values and vectors turns out.

\[
2\pi^2 \alpha^2 (q^2 + s^2) \frac{a_{q,s}}{R} + 4iR \sum_{n,k=-L}^{L} a_{n,k} \left( \delta_{n,q} \frac{(-1)^{k-s}}{k-s} - \delta_{k,s} \frac{(-1)^{n-q}}{n-q} \right) + 2R \sum_{n,k=-L}^{L} \left( B_{n-q,k-s}^0 + B_{n-q,k-s}^0 \right) a_{n,q} - 2R \lambda a_{q,s} = 0 ; \, q, s = -L, ..., L
\]

Here \( \delta_{n,k} \) - symbol of unit matrix, \( B_{n,k} = \frac{1}{4R^2} \int_{\Omega} V(x, y) \exp \left( \frac{\pi i}{R} (-nx - ky) \right) dx dy \) - Fourier-harmonics of decomposition of the confining potential, and a harmonic of decomposition of symmetric component of a magnetic field whereas

\[
\frac{1}{4R^2} \int_{\Omega} \frac{x^2 + y^2}{\alpha^2} \exp \left( \frac{\pi i}{R} (-nx - ky) \right) dx dy = \begin{cases} 
\frac{2 \left( \frac{R}{3} \alpha \right)^2}{n = k = 0} \\
\frac{2 \left( \frac{R}{\pi n^2} \alpha \right)^2}{n \neq 0, k = 0} \\
0 : n k \neq 0
\end{cases}
\]

designations \( \rho = \left( \frac{R}{\alpha} \right)^2 \), are represented so:

\[
B_{0,0}^0 = \frac{2}{3} \rho ; \quad B_{0,n}^0 = B_{0,n}^0 = \frac{2(-1)^n}{\pi^2 n^2} \rho : n \neq 0 ; \quad B_{n,k}^0 = 0 : n k \neq 0
\]

Having designated following
we receive, that the solution of an algebraic problem (2) is reduced to a finding of eigen numbers and vectors of Hermetic matrix \( C = \{C_{j,p}\} \) with physically scaling-less elements,

\[
\begin{align*}
\left( C_{jp} = A_{n,k,q,s} : j = k + L + 1 + (n + L)(2L + 1), p = s + L + 1 + (q + L)(2L + 1) \right) \\
n, k, q, s = -L, \ldots, L.
\end{align*}
\]

For a finding of eigen values and vectors for this matrix it is used QL - algorithm with shift [2]. Eigen-vectors consist of Fourier - decomposition terms of eigen-functions \( D^j = (v^j_p : p = 1, \ldots, (2L + 1)^2) \).

On presented below graphs (fig.1) are presented the confining potential with a sign "minus" and squares of modules of first seven eigen-functions (are signed by their numbers \( j \)). Horizontal coordinates «\( x, y \)» are specified in % from the spatial period «2R», vertical the coordinate is scaled according to a norm-condition.

It is calculated own 37 values, since the least, they are located by way of increases, according to numbering of own functions):

\[
0.6497803; 9.086677; 9.597447; 9.700025; 10.52466; 18.94184; 19.91620; 21.60274; 22.66856; 37.10139; 37.11093; 37.34475; 37.61111; 47.99970; 48.18777; 48.34706; 49.18681; 52.59499; 52.60853; 52.97558; 53.71998; 78.64438; 78.96074; 81.34107; 81.78598; 83.75708; 83.81923; 83.87377; 84.10400; 96.76934; 96.79221; 96.90021; 97.14402; 103.6655; 103.8549; 103.9458; 103.9949 (it is \( A_j \) for \( j=1, \ldots, 37 \)).
\]

Infringement of symmetry of the confining potential (its deviation from a figure of rotation) less than 1% in relation to the maximal absolute value, and it leads to infringement of frequency rate eigen-numbers with a relative error of the same order (apparently from resulted above values). Value of parameter \( \rho = 1 \), that is \( R = \alpha \), number of harmonics \( L=7 \).
**Fig. 1** – Confining potential (with sign “minus”) and square of modules of eigenfunctions with number “j”

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**References**


NUMERICAL STUDY OF NEGATIVE-REFRACTIVE INDEX FERRITE WAVEGUIDE

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ABSTRACT

Consider a magnetized ferrite-wire waveguide structure situated between two half free spaces. Ferrites to provide negative permeability and wire arrays to provide negative permittivity. The structure form left-handed material (LHM) with negative refractive index. The transmission of electromagnetic waves through the structure is investigated theoretically. Maxwell's equations are used to determine the electric and magnetic fields of the incident waves at each layer. Snell's law is applied and the boundary conditions are imposed at each layer interface to calculate the reflected and transmitted powers of the structure. Numerical results are illustrated to show the effect of frequency, applied magnetic fields, angle of incidence and LHM thickness on the mentioned powers. The analyzed results show that the transmission is very good when the permeability and permittivity of the structure are both simultaneously negative. The frequency band corresponding to this transmission can be tuned by changing the applied magnetic fields. The obtained results are in agreement with the law of conservation of energy.

Key words: Applied magnetic fields, Electromagnetic waves, ferromagnetic material, frequency, Reflected power, transmitted power.

INTRODUCTION

Metamaterials (sometimes termed left-handed materials (LHMs)) are materials whose permittivity ε and permeability μ are both negative and consequently have negative index of refraction. These materials are artificial and theoretically discussed first by Veselago [1] over 40 years ago. The first realization of such materials, consisting of split-ring resonators (SRRs) and continuous wires, was first introduced by Pendry [2, 3]. Regular materials are materials whose ε and μ are both positive and termed right handed materials (RHMs).

Magnetized ferrite is an additional alternative to SRR to provide negative permeability. Consequently, a LHM can be achieved by inserting a periodic continuous wires into the ferrite material [4-7]. ε and μ of this LHM have tuna-

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ble properties by changing the applied bias magnetic fields and both exhibit negative values at certain frequency band. Y. He et al [8] have studied the role of ferrites in negative index metamaterials. M. Augustine et al [9] have formulated a theoretical analysis of ferrite-superconductor layered structures. H. Zhao et al [10] have studied a magnetotunable left-handed material consisting of yttrium iron garnet slab and metallic wires. R. X. Wu [11] has shown the effect of negative refraction index in periodic metal-ferrite film composite. F. J. Rachford et al [12] have performed simulations of ferrite-dielectric-wire composite negative index materials. Q. X. Chu et al [13] have shown a novel left-handed metamaterial with wire array in a ferrite-filled rectangular waveguide.

In this paper we consider a magnetized ferrite-wire structure inserted in vacuum. A plane polarized wave is obliquely incident on it. $\epsilon$ and $\mu$ of the structure can easily be tuned by changing the applied magnetic fields and negative refractive index of it is achieved at a certain frequency band to make the structure LHM. Maxwell's equations are used to determine the electric and magnetic fields in each region. Then, Snell's law is applied and the boundary conditions of the fields are imposed at each interface to obtain a number of equations with unknown parameters. The equations are solved for the unknown parameters to calculate the reflection and transmission coefficients. These coefficients are used to determine the reflected and transmitted powers of the structure. The effect of many parameters like frequency, applied magnetic fields and angle of incidence etc. on the mentioned powers is studied in detail. It is demonstrated that, if both $\epsilon$ and $\mu$ of the ferrite-wire structure are both positive and both negative, then the electromagnetic waves can propagate through it. On the other hand if either $\epsilon$ or $\mu$ of the structure is negative, the incident radiation will be reflected and no transmission of the waves will be through the structure. Moreover the frequency band of zero or nonzero transmission of the waves can be tuned by changing the applied magnetic fields due to the tenability of $\epsilon$ and $\mu$ of the structure. To check the validity of the performed computations the law of conservation of energy given by [14, 15] is satisfied for all examples.

**THEORY**

Consider a rectangular ferrite-wire waveguide structure located between two half free spaces and a dc applied magnetic field acts on it along the X axis [4, 5]. A plane polarized wave is incident on the plane $y = 0$ at angle $\theta$ relative to the normal to the boundary (fig. 1). The effective permeability of the ferrite is given by [4, 5]:

$$\mu_f = \frac{\eta^2 - K^2}{\eta}$$ (1)
Where \( \eta = 1 + \frac{\omega_m(\omega_o - i\alpha\omega)}{(\omega_o - i\alpha\omega)^2 - \omega^2} \), \( K = \frac{\omega_m\omega}{(\omega_o - i\alpha\omega)^2 - \omega^2} \), \( \omega_o = \gamma B \), \( \omega_m = \gamma M \)

\( \gamma \) is the gyromagnetic ratio, \( B \) is the intensity of the applied magnetic field, \( M \) is the saturation magnetization, \( \omega \) is the angular frequency and \( i = \sqrt{-1} \).

The effective permittivity of the structure is considered to be [4, 5]:

\[
\varepsilon_f = \varepsilon_r - \frac{\sigma_{\text{eff}}}{\omega\varepsilon_o[i + (1.57 \times 10^{-6}\omega\sigma_{\text{eff}})(3.18\mu_o + 0.413\mu_f)]}
\]

(2)

Where \( \varepsilon_o \) and \( \mu_o \) are the permittivity and permeability of free space respectively, \( \varepsilon_r \) is the relative permittivity of ferrite material and \( \sigma_{\text{eff}} \) is the effective conductivity of wire arrays.

![Fig. 1 – Oblique incidence of electromagnetic wave on a ferrite-wire structure embedded in vacuum](image)

The transverse components of the electric and magnetic fields in each region of Fig. 1 are [9, 16]:

**Region 1:**

\[
E_{1x} = \left(Ae^{ik_{y}y} + Be^{-ik_{y}y}\right)e^{i(k_{z}z-\omega t)}
\]

(3)

\[
H_{1z} = \frac{1}{\mu_o\omega}\left[(-A k_{oy}e^{ik_{y}y} + B k_{oy}e^{-ik_{y}y})\right]e^{i(k_{z}z-\omega t)}
\]

(4)

**Region 2:**

\[
E_{2x} = \left(Ce^{ik_{y}y} + De^{-ik_{y}y}\right)e^{i(k_{z}z-\omega t)}
\]

(5)
\[ H_{2z} = \frac{1}{\omega} \left[ (Ck_c e^{ik_{fy}y} + Dk_b e^{-ik_{fy}y}) \right] e^{i(k_{cz}z-\omega t)} \]  

(6)

With:

\[ k_c = \frac{k_{cz}}{\mu_v} - \frac{k_{fy}}{\mu_f}, \quad k_b = \frac{k_{cz}}{\mu_v} + \frac{k_{fy}}{\mu_f}, \quad \mu_v = \frac{\eta^2 - K^2}{iK} \]  

(7)

Region 3:

\[ E_{3x} = Fe^{ik_{oy}y} e^{i(k_{oz}z-\omega t)} \]  

(8)

\[ H_{3z} = \frac{1}{\mu_o \omega} \left( - Fk_{oy} e^{ik_{oy}y} \right) e^{i(k_{oz}z-\omega t)} \]  

(9)

Where \( A, B, C, D, F \) are the amplitudes of the forward and backward traveling waves. \( k_o = \frac{\omega}{c} \) is the free space wave vector, \( k_f = \frac{n_f \omega}{c} \) is the wave vector inside the slab and \( n_f = \sqrt{\frac{\varepsilon_f \mu_f}{\varepsilon_o \mu_o}} \) is the refractive index of it.

\[ k_{oz} = k_{cz} = k_o \sin \theta \quad \text{(Snell's Law)} \]  

(10)

\[ k_{oy} = \frac{\omega}{c} \sqrt{1 - \sin^2 \theta}, \quad k_{fy} = \frac{\omega}{c} \sqrt{n_f^2 - \sin^2 \theta} \]  

(11)

Matching the boundary conditions for the transverse field components at each layer interface, that is at \( y=0, \ E_{1x} = E_{2x} \) and \( H_{1z} = H_{2z} \), at \( y=a \ E_{2x} = E_{3x} \) and \( H_{2z} = H_{3z} \). This yields the following equations [16]:

\[ A + B = C + D \]  

(12)

\[ \frac{k_{oy}}{\mu_o} (- A + B) = Ck_c + Dk_b \]  

(13)

\[ Ce^{ik_{fy}a} + De^{-ik_{fy}a} = Fe^{ik_{oy}a} \]  

(14)

\[ Ck_c e^{ik_{fy}a} + Dk_b e^{-ik_{fy}a} = -\frac{k_{oy}}{\mu_o} Fe^{ik_{oy}a} \]  

(15)

Letting \( A=1 \) and solving these four equations for the unknown parameters enables us to calculate the reflection and transmission coefficients \( B \) and \( F \) [16]. The reflected and transmitted powers are defined as [16]:

\[ R = BB^* \]  

(16)

\[ T = FF^* \]  

(17)

Where \( B^* \) and \( F^* \) are the complex conjugate of \( B \) and \( F \) respectively.
**NUMERICAL RESULTS**

In this section the reflected and transmitted powers of the structure are calculated numerically as a function of frequency, angle of incidence, applied magnetic fields and thickness of ferrite. In our method we have used the parameters as in [17]: \( M = 4398 \) G, \( \gamma = 2.8 \text{ MHz/Oe} \), \( \alpha = .006 \), \( \varepsilon_f = 4 \). Three values of \( B \) are selected to be \( B = 500 \text{ Oe} \), \( 750 \text{ Oe} \), and \( 1000 \text{ Oe} \). The central frequency is selected to be \( 8.6 \text{ GHz} \). This frequency is chosen such that \( \varepsilon_f \) and \( \mu_f \) are both simultaneously negative for all values of the applied magnetic fields. The slab thickness is assumed to be one half-wavelength long at the central frequency.

\( \mu_f(\omega) \) with real part \( \text{Re} (\mu_f) \) and \( \varepsilon_f(\omega) \) with real \( \text{Re} (\varepsilon_f) \) are plotted as a function of frequency \( \omega \) in fig. 2 for three values of the applied magnetic fields ( \( B = 500 \text{ Oe} \), \( B = 750 \text{ Oe} \), \( B = 1000 \text{ Oe} \)). As shown from the figure the frequency ranges in which \( \text{Re} (\mu_f) \) and \( \text{Re} (\varepsilon_f) \) are negative can be changed with the applied magnetic field [8]. In the case of \( B = 500 \text{ Oe} \), \( \mu_f \) and \( \varepsilon_f \) are both negative in the frequency range of \( 6.4 \text{ GHz} – 10.8 \text{ GHz} \) and consequently the ferrite-wire structure exhibits negative refractive index (i.e. LHM) in that range. For \( B = 750 \text{ Oe} \) and \( B = 1000 \text{ Oe} \) the ferrite-wire structure exhibits LHM in the frequency ranges of \( 7.2 \text{ GHz} – 11 \text{ GHz} \) and \( 8.2 \text{ GHz} – 11.2 \text{ GHz} \) respectively.

The transmitted and reflected powers as a function of frequency are calculated in fig. 3, for \( \theta = 30^\circ \) and \( a = \lambda/2 \). The frequency is changed between 2 GHz and 12 GHz, because the simultaneously negative values of \( \text{Re} (\mu_i) \) and \( \text{Re} (\varepsilon_i) \) under the three values of \( B \) can be realized in this range. In this example it
can be seen that, if both $\mu_f$ and $\varepsilon_f$ are both positive and both negative, the transmission is very good and the electromagnetic wave can propagate through the ferrite-wire structure. This is because the propagation constant of the waves in the structure are real ($k_f^2 = \frac{\omega^2}{c^2} \varepsilon_f \mu_f$). If either $\mu_f$ or $\varepsilon_f$ is negative, the propagation constant is imaginary and then the incident radiation will be reflected and no transmission of the waves will be through the structure. The symmetry of nonzero transmission shifts in frequency to the right side when the applied field increased. This is due to the tunability of the LHM which arises from the variation of the applied magnetic fields.

Fig. 3 – The transmitted and reflected powers against frequency when the applied magnetic field changes $B = 500$ Oe, $B = 750$ Oe and $B = 1000$ Oe
Figure 4 shows the transmitted and reflected powers as a function of frequency when the incidence angle changes (θ = 0°, θ = 30°, θ = 50°) for B = 500 Oe. The frequency range and thickness of ferrite is the same as in the last example. It can be seen that the transmitted power is decreasing while the reflected power increasing with the angle of incidence. Moreover they show oscillatory behavior for θ = 30° and 50° while they show nearly no ripples for θ = 0°.

Fig. 4 – The transmitted and reflected powers as a function of frequency for three values of the angle of incidence θ = 0°, θ = 30°, θ = 50°.
Figure 5 represents the transmitted and reflected powers versus the ferrite thickness for three values of the applied magnetic fields, 30° angle of incidence and 8.6 GHz frequency of the incident waves. The slab thickness is changed from zero mm to $\frac{\lambda}{2}$ (17.44 mm). It can be observed that the reflected power shows oscillatory behavior with thickness for all values of the applied magnetic fields. The transmitted power shows the same behavior but slightly decreasing with thickness for $B = 500$ Oe and 750 Oe and considerably decreasing with thickness for $B = 1000$ Oe.

Fig. 5 – The transmitted and reflected powers versus ferrite thickness for three values of applied magnetic fields $B = 500$ Oe, $B = 750$ Oe and $B = 1000$ Oe
CONCLUSIONS

Reflection and transmission of electromagnetic waves by a magnetized ferrite-wire structure inserted in vacuum are analyzed numerically. Total reflection of the waves by the structure is obtained due to the difference in signs between $\mu$ and $\varepsilon$ of the structure. Transmission of radiations through the structure is realized when $\mu$ and $\varepsilon$ of the structure are both negative or both positive. The frequency band of reflection and transmission of the waves by the structure can be tuned by changing the applied magnetic field due to the tunability of $\mu$ and $\varepsilon$. Thus we can say that the variation of the applied magnetic field changes the reflection and transmission of the waves by the structure. Numerical examples are already presented to illustrate the paper idea and to prove the validity of the obtained results. Moreover the conservation of energy is satisfied throughout the performed computations for all examples. The discussed problem is useful for applications which require controlling of reflected and transmitted powers like antenna radome, microwave, millimeter wave and optical devices.

REFERENCES

NANOSTRUCTURED METAL-FULLERENE FIELD EMIS-
SION CATHODE

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ABSTRACT

We developed new type of metal-nanocarbon composite field emission cathodes by hot sintering of ball-milled nanostructured mixture of a copper with C\textsubscript{60} fullerene. A mixture of copper and C\textsubscript{60} was subjected to co-grinding of raw materials made in the form of about 1 \textmu m size granules in a planetary mill. The purity of raw materials was not less than 99.5%. Using the grinding we reduced the size of the copper particles down to about 10-30 nm. The content of the fullerene compound in the initial mixture was 10\% (by weight). TEM analysis showed 2 nm thick nanocarbon film covering 10-30 nm size copper nanocrystals. The metal provides a high electrical conductivity, high thermal conductivity and mechanical strength of the cathode and nanocarbon material provides its high electron emission properties. Further, the resulting material was subjected to hot pressing at a pressure of 6.5 GPa and temperatures of 850°C, 1 minute. The finally obtained material can be easily mechanically processed for shaping of a cathode for any particular design. To improve the efficiency of a field emission we used chemical and plasma etching of its working surface. The turn-on electrical field of the cathode is 10-15 V/\mu m. The Fowler-Nordheim plot of the emission current shows linear function, indicating electron field emission effect. The resulting cathode emission current density was about 20 mA/cm\textsuperscript{2} with high stability and homogeneity. Such cathodes can be used as electron sources in various electronic devices - electron guns, X-ray tubes, the amplifier and generator devices in microwave electronics, light sources, etc.

Key words: nanocomposite, fullerene, hot sintering, field emission cathode.

INTRODUCTION

One of the important properties of carbon nanostructures is their cold electron emission ability. Carbon nanotubes and other nanostructures are capable of emitting high currents at relatively low electrical fields [1-4]. They are already used in functional devices such as field emitters. The conventional method of carbon nanostructured cathodes manufacturing is thin film nanocarbon deposition using CVD process on electrically conducting substrate like metal or doped silicon plates. The alternative way of manufacturing of carbon field emission cathodes is based on a special processing of carbon microfibers or composite
materials in metal holders [5]. We used the similar approach to produce composite metal-nanocarbon material which may be easily processed and shaped to produce an effective field emission cathode which can be easily fixed in any environment.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

We employed the method of hot sintering of mixed metal-nanocarbon powder to make nanocomposite field emission cathode. Copper was used as the metal compound due to its elastic and electrical properties and availability. The next (nanocarbon) component was C\textsubscript{60} fullerene. A mixture of copper and C\textsubscript{60} was subjected to co-grinding of raw materials made in the form of about 1 \(\mu\)m size granules in a planetary mill. The purity of raw materials was not less than 99.5\%. The processing time was about 30 min. Using the grinding we reduced the size of the copper particles down to about 10-30 nm. The content of the fullerene compound in the initial mixture was 10\% (by weight). The treatment was carried out in 99.999\% argon atmosphere (the oxygen content of less than 0.1 ppm) in a glove box. After the processing in a planetary mill the material was studied by transmission electron microscope. The TEM images (Fig. 1a) showed that the copper nanoparticles are covered with \(\sim 2\) nm thick nanocarbon layer.

Further, the resulting material was subjected to hot pressing at a pressure of 6.5 GPa and temperatures of 850°C, 1 minute. The result was a composite metal-nanocarbon material whose surface after additional treatment is highly effective field-emitter. Finally we obtained \(\varnothing 3\times 2\) mm\(^3\) cylindrical samples as electron emitters. One of the plane faces (the working surface of the cathode)
was mechanically polished to roughness of about 50-20 microns. It was then followed by the chemical etching. We used an aqueous solution of the ferric chloride FeCl$_3$ as it reacts with copper and completely inert with respect to carbon compound. The chemical treatment cleaned an activate surface of the nanostructured carbon content. An additional activation of the field emission properties of the cathode was performed by processing in a hydrogen plasma at a pressure of 35 Pa with a power density of 0.5 kW/cm$^2$ and a substrate temperature 150$^\circ$C. Figure 1b shows the SEM image of the surface of the obtained cathode.

**RESULTS AND DISCUSSION**

Figure 2a shows the voltage-current characteristic of the cathode in a vacuum diode scheme with the cathode - anode distance of 300 microns. The value of the current $I$ increases approximately exponentially with the increase of bias $U$. In these measurements the field emission cathode showed high stability. Figure 2b shows the same data in a Fowler-Nordheim coordinates. It has distinctly linear part at $U>15$ V/$\mu$m (the upper part of the plot in Fig. 2b). The field emission current density was up to 20 mA/cm$^2$.

![Fig. 2 a) - A voltage-current characteristic of Cu-C$_{60}$ nanocomposite field emitter at 300 $\mu$m anode-cathode distance; b) - the Fowler-Nordheim plot of a voltage-current characteristic of Cu-C$_{60}$ nanocomposite field emitter.](image)

When using a composite with a different content of nanocarbon components results deteriorated. For example, by decreasing the content of C$_{60}$ to 5% by weight the maximum field emission current reduced by about 20%, while increasing to 20% significantly decreased the mechanical strength and the machining of the material becomes impossible.
CONCLUSIONS

We developed new type of metal-nanocarbon composite field emission cathodes by hot sintering of ball-milled nanostructured mixture of a copper with C$_{60}$ fullerene. The metal provides a high electrical conductivity, high thermal conductivity and mechanical strength of the cathode and nanocarbon material provides its high electron emission properties. Such cathodes can be used as electron sources in various electronic devices - electron guns, X-ray tubes, the amplifier and generator devices in microwave electronics, light sources, etc. The material can be easily mechanically processed for shaping of a cathode for any particular design. To improve the efficiency of a field emission we used chemical and plasma etching of its working surface. The resulting cathode emission current density was about 20 mA/cm$^2$ with high stability and homogeneity.

REFERENCES


NEW FABRICATION APPROACH to ZnO MULTIPLE NANOFIBER SENSORS

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ABSTRACT

In the presented work, ZnO nanofiber sensor structures designed and fabricated using a standard microelectronic device technology were studied. The structures in the configuration of a resistor with chemically active ZnO multiple nanofibers deposited by electrospinning method were prepared. Investigation of inclusion in the process reactive-ly sputtered AlN insulating film to improve the robustness of the nanofibres on the substrate was undertaken. Selective wet chemical etching of AlN film using photoresist developers and a photoresist mask to define the sensor active area was studied. The Ti/Au ohmic contacts were fabricated using the lift-off photolithography process. Topography of the sensor structure details was investigated using AFM. Electrical characterization by means of I-V measurements was made. Sensitivity to the physiologically relevant concentration of Bovine Serum Albumin in water solution was shown.

Key words: ZnO nanofibres, AlN film coating, biosensor

INTRODUCTION

ZnO nanofibres (NFs), as quasi one-dimensional semiconductor nanostructures, due to high surface-to-volume ratio reveal improvement of crucial sensors parameters as sensitivity and response times. ZnO NFs could be of special interest in biomedical applications due to their relatively low biological toxicity [1]. The electrospinning method of ZnO nanofibres fabrication provides relative simplicity of their positioning on a chosen substrate [2, 3]. Additionally, such deposited nanofibers are characterized by a highly developed surface induced by the nanocrystalline structure. On the other hand, a main disadvantage of the electrospinning method is a relatively weak adhesion of the NFs to the substrate after the necessary calcinations process, as well as instability and vulnerability to acid and alkaline solutions. These properties impose limitations on the use of standard electronic device manufacturing techniques such as preparation of substrates, photolithography and the lift-off pro-

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cess for contact metallization and passivation of the device which results in incompatibility of the electrospun ZnO NFs and the Si processing. Although the ZnO based nanostructures have been reported as gas and optical sensors [4, 5], their fragility in water environments requires additional chemical treatment for their commercial biosensors applications. Detection of either biological molecules concentrations and activities in physiological fluids or water containing tissue is of fundamental importance in life sciences and medical diagnostics. This led us to the study of applicability of mass production manufacturing techniques in ZnO nanofiber sensor fabrication, based on large area substrates and pattern definition obtained by photolithographic methods resulting in high yield and low manufacturing cost.

In the present work, design and fabrication of ZnO multiple nanofiber sensor structures using a standard microelectronic device technology were studied. The structures with chemically active electrospun ZnO nanofibers were prepared. Two innovative fabrication steps, were proposed. Firstly, an insulating film of reactively sputtered AlN was applied on the nanofibers surface to protect the NFs against the reactants in further processing. Secondly, selective wet chemical etching of AlN film and ZnO NFs through a photoresist mask to define the active sensor area was performed using photoresist developers. The structures in the configuration of a resistor were prepared with the Ti/Au ohmic contacts fabricated using the lift-off photolithography process. Electrical characterization of fabricated structures by means of I-V measurements was made. Sensitivity to the physiologically relevant concentration of Bovine Serum Albumin (BSA) in aqueous solution was tested. BSA, due to its native adsorption properties, was selected to demonstrate the role of the protein’s charged amino acids on the ZnO surface charge and therefore on its conductance.

**METHODS OF STRUCTURE FABRICATION AND ANALYSIS**

ZnO nanofibres were deposited on 10 x 10 mm$^2$ thermally oxidized Si substrates by electrosprinning method. The precursor containing 0.25 g of zinc acetate dehydrate (Zn(CH$_3$COO)$_2$ • 2H$_2$O) in 1.25 g solution of 10% polyvinyl alcohol (PVA, MW = 72 000) was placed in a syringe and then a constant flow rate through a syringe pump was established to obtain multiple fiber deposition at high electric potential difference of 10 kV between the syringe tip and the substrate. The fibers were formed in ambient temperature 22°C and humidity of 40%. Finally, the process of calcinations at 700°C for 4h in oxygen ambient was performed. After calcinations, the fibers showed wurtzite structure of nanometer size crystallites with average diameter from 5 nm to 30 nm [6]. The diameter of a single NF averaged at 300nm. Such prepared NFs sensor substrates were coated with a dielectric layer of AlN by pulsed DC reactive magnetron sputtering in Ar/N$_2$ (6N) gaseous atmosphere using Al target. The processing was done at total pressure of 5×10$^{-2}$ mbar with no substrate heating.
The thickness of the AlN layer was of the order of a typical thickness of a ZnO nanofiber, i.e. in the range from 200 nm to 400 nm. To improve the NFs coating, multiple processing of AlN sputtering could be performed, especially in the case of thicker or cross-linked nanofibres.

Then, a lift-off photolithography technique was used to pattern photoresist (AZ 4110) and define the area for contact electrodes. The next important step, was a precise etching of AlN layer exposed in the photoresist openings. It was done in the solution of Microposit 351 developer diluted in H₂O (1:5). Appropriately controlled photoresist opening step allowed fabrication of the ohmic contacts made of Ti/Au (50/1000 Å) evaporated in a UHV system. To protect the contacts, a layer of a photosensitive polyimide was deposited by a spin-on method and a photolithography process was used to define the active region of the sensor. The active region in between the contacts had a length of 80μm and a width of 5mm. In the final processing step the ZnO nanofibers in the active region were gradually exposed by carefully selected process of etching AlN layer also in a solution of photoresist developer. Control of the process was possible by observing change of the substrate interference colors by means of an optical microscope.

To study structure and morphology of such fabricated NFs samples AFM and optical microscope were used. Details of the active region of the NFs sensor are shown in Fig. 1.

![Fig. 1](image)

**Fig. 1** - Details of the ZnO NFs sensor active region: a) an opening patterned in the etched AlN (green) showing the SiO₂ substrate (violet) with NFs on it; b) an AFM view of an edge of the active region with a polyimide layer protecting the contacts

The structures were investigated using AFM to evaluate the coating applicability of the AlN film for good coating and covering the ZnO NFs. Standard point probe measurements were performed to check the stability of the ohmic contacts and to find I-V characteristics in different environments. To test sensing properties of the sensor structures commercially available Bovine Se-
Rum Albumin (Calbiochem product, 99.0%, pH: 7.1) was used. The BSA solution was prepared from lyophilized powder of BSA (99%) with concentration of 10 mg/ml in DI water.

**RESULTS AND DISCUSSION**

Fig. 2 presents AFM images of the ZnO nanofibers after deposition and calcinations at 700°C on SiO$_2$/Si substrate. The images were taken before and after covering the NFs with the protective AlN sputtered film. The topography image and phase images are shown with the latter of special importance, since the phase image represents component contrast of the investigated surface.

![AFM images](image)

It is seen that the ZnO NF after coating with AlN film has much smoother surface (fig.2c) in comparison to the state before coating (fig.2a). The phase images shown in fig.2b and fig.2d give information about changes of the composition of the scanned surface. On this basis we could believe, that after AlN
processing the NF is almost completely covered with AlN, since a very little shadowing was visible.

The I-V measurements have shown stability and linearity of the Ti/Au ohmic contacts to the ZnO NFs. Fig. 3 demonstrates response of the sensor device to air, pure (10Mohmcm) deionized (DI) water and a BSA water solution. The BSA solution was prepared from lyophilized powder of BSA (99%) with concentration of 10 mg/ml in DI water.

![I-V characteristics of the ZnO NFs sensor structure measured in various environments: air ambient, DI water, BSA 10mg/ml DI water solution](image)

**Fig. 3** – The I-V characteristics of the ZnO NFs sensor structure measured in various environments: air ambient, DI water, BSA 10mg/ml DI water solution

Rise of current (conductivity) in the water environment, according to a well known mechanism is attributed to decrease of the NF surface depletion layer due to removal of adsorbed oxygen atoms[7]. In case of impact of BSA molecules on the current rise several factors have been postulated, e.g. adsorption of ionized atoms present on the biomolecule surface may change the conductance of ZnO nanofibers by altering the surface charge [8].

**CONCLUSIONS**

We developed and tested ZnO multiple nanofiber sensor structures for biological application with a robust design applicable to the standard microelectronic device processing which include reactively sputtered AlN dielectric film, the lift-off photolithography and a polyimide passivation layer. Application of insulated AlN layer resulted in more reliable positioning of ZnO nanofibers on
the substrate. On the other hand, selective etching of the AlN layer did not hamper the sensing capabilities of the ZnO nanofibers. The structures have shown expected I-V characteristics and responsivity to physiologically relevant BSA concentrations in aqueous solution.

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The influence of the Si dopant concentration and its distribution through the AlGaN barrier layer of the AlGaN/GaN heterostructures on their electrical properties was studied. Three types of the heterostructures were grown by MOVPE method on sapphire substrate. Electrical properties of the Al$_x$Ga$_{1-x}$N/GaN heterostructures were determined by the impedance spectroscopy method. The carrier concentration in AlGaN/GaN heterostructure, the incremental sheet charge concentration and 2DEG sheet charge concentration were obtained and correlated with Si dopant distribution through the AlGaN barrier layer of the heterostructure.

**INTRODUCTION**

The AlGaN/GaN material system is attractive for numerous device applications [1]. The relatively well developed research areas are photonic and high-power electronic devices based on nitrides. Recently, in addition to these, new trends are emerging which indicate that chemical and biochemical sensor applications of AlGaN/GaN heterostructures could benefit from unique properties of nitrides such as their excellent chemical stability and inertness as well as the possibility of formation of high-density two dimensional electron gas (2DEG) on the AlGaN/GaN hetero-interface, even without intentional doping. Its existence near the heterostructure surface is extremely beneficial for highly sensitive detection of surface phenomena. Nitrides heterostructures are also one of the leading candidates for high frequency application up to THz range (regime). However, up to now the parameters of AlGaN/GaN heterostructures do not reached the predicted, theoretical, values. Because of the lack of commercially available bulk GaN substrates the AlGaN/GaN heterostructures are typically grown on sapphire, SiC or Si substrates. The very large mismatch of lattice parameters and thermal expansion coefficients between nitrides and these substrates causes many problems during the growth and influenced the quality of the heterostructures. The choice of the substrate results from the applications and it strongly determines the properties of AlGaN/GaN heterostructures. The
basic theoretical correlations between the thicknesses and composition of Al-GaN barrier layer, its doping level and spontaneous and piezoelectric polarization are relatively well established. It was shown that the Al content in the Al-GaN barrier of the heterostructure influenced mainly spontaneous and piezoelectric polarization and its breakdown voltage [2]. The optimization of MOVPE (Metalorganic Vapour Phase Epitaxy) growth process parameters optimization was studied extensively [3-5]. It was established that the MOVPE system configuration as well as the details of the growth process strongly influenced the obtained results. Additionally, our previous study has shown that that the 2DEG parameters of HT GaN buffer layer in a wide range of its carrier concentration [6]. It is in a good agreement with recently published results [7]. But till now it seems that many unidentified factors exist that influence the electrical properties of the AlGaIn/GaN heterostructures. One of them is the distribution of Si dopant in AlGaN barrier which influences on the 2DEG parameters at AlGaN/GaN heterointerface. To study these phenomenon three sets of AlGaIn/GaN heterostructures were grown by MOVPE in which the AlGaN layer of AlGaIn/GaN heterostructure was divided into three sub-layer of different thickness and different Si dopant concentration. The laser interferometer with 635 nm laser diode was used for in-situ characterization of the whole process growth mechanism. The electrical parameters of the heterostructures were evaluated by impedance spectroscopy method using the procedure work-out by us and verified by others [8,9]. The electrical properties of AlGaIn/GaN heterostructures such as the carrier concentration in AlGaIn/GaN heterostructure and the sheet carrier concentration of 2DEG were evaluated and correlated with Si dopant distribution through the AlGaN barrier layer of the heterostructure.

**EXPERIMENTAL**

Si doped and un-doped AlGaIn/GaN heterostructures were grown on c-plane sapphire substrates by using 3×2″ Thomas Swan Close Coupled Showerhead MOVPE system at 100 mbar. Trimethylgallium, Trimethylaluminum and NH₃ were used as a Ga, Al, and N source respectively, and monosilane (SiH₄) was used as a n type dopant. H₂ was used as a carrier gas.

The growth was performed at six main stages: 1 - sapphire substrate annealing in hydrogen atmosphere, 2 - substrate nitridation in the mixture of H₂ and NH₃ (1:1), 3 - low temperature growth of GaN nucleation layer (LT-GaN NL) at 530°C, 4 - coalescence of LT - GaN NL during temperature ramping, 5 - growth of high temperature GaN buffer layer at 1035°C, 1000 V/III molar ratio, 6 -growth of undoped and/or Si-doped AlGaN layer at 1060°C, 1200 V/III molar ratio. The schematic drawings of the MOVPE process sequence for all sets of samples are presented in Fig. 1. The laser interferometer with 635 nm laser diode was used for in-situ characterization of the growth process that
allowed us to evaluate the thickness of individual layers. Three sets of samples, with different AlGaN sub-layers, were fabricated on 2.5 µm optimized HT-GaN buffer grown on LT-GaN nucleation layer [6]. The designed arrangement of AlGaN barrier sub-layer in individual heterostructure is shown in Fig. 2.

![Diagram](image)

**Fig. 1** – The schematic drawing of the MOVPE process sequence of AlGaN/GaN heterostructures grown on LT-GaN NL

The AlGaN/GaN heterostructures #045 consists of, looking from top to bottom, 25 nm thick undoped Al$_{0.2}$Ga$_{0.8}$N barrier grown on 2.5 µm thick undoped high resistive HT-GaN buffer. In Al$_{0.2}$Ga$_{0.8}$N heterostructures #042 barrier layer was divided in to two sub-layers, from top to bottom, 10 nm thick undoped Al$_{0.2}$Ga$_{0.8}$N sub-layer and 15 nm thick Si-doped Al$_{0.2}$Ga$_{0.8}$N sub-layer (Si concentration was 2.1*10$^{18}$ cm$^{-3}$). The barrier layer of Al$_{0.2}$Ga$_{0.8}$N heterostructures #044 was divided in to three sub-layers, from top to bottom, 5nm thick undoped Al$_{0.2}$Ga$_{0.8}$N sub-layer, 20 nm thick Si-doped Al$_{0.2}$Ga$_{0.8}$N sub-layer (Si concentration was 4.2*10$^{18}$ cm$^{-3}$) and 2 nm thick undoped Al$_{0.2}$Ga$_{0.8}$N sub-layer.
RESULTS AND DISCUSSION

Electrical properties of the Al$_x$Ga$_{1-x}$N/GaN heterostructures were determined by the impedance spectroscopy method performed in the range of frequencies from 80 Hz to 10 MHz with a HP 4192A impedance meter, using a two contact mercury probe. The capacitance and conductance versus frequency characteristics of the Schottky contact to AlGaN/GaN heterostructures were measured over a range of DC biases and the results were fitted to a worked-out model. The distributed elements equivalent circuit model regarding the series resistances and the Schottky junction admittance was used to evaluate the electrical properties of AlGaN/GaN heterostructures [8]. The carrier concentration distribution through the epitaxial structure and the incremental sheet charge concentration versus bias voltage were obtained for every set of the samples (Fig. 3, Fig. 4 and Fig. 5).

In Fig. 3 the carrier concentration distributions through the AlGaN/GaN heterostructures versus the distance from their surfaces are shown. In all heterostructures the characteristic spikes of the concentration at AlGaN/GaN interface, caused by 2DEG formation, were observed. For detailed analysis the excerpt of the initial part of the Figure 3 is presented in Fig. 4. The incremental sheet charge concentration in AlGaN/GaN heterostructures versus bias voltage is shown in Fig. 5 that illustrates the depletion of the channel with voltage. Based on data shown in Fig. 3 and Fig. 5 the 2DEG sheet carrier concentration and pinch off voltage of every AlGaN/GaN heterostructure could be evaluated. In the Table 1 the values of incremental sheet charge concentration ($\Delta n_s$), the 2DEG sheet charge concentration ($n_s$), pinch of voltage ($U_p$), average mobility ($\bar{\mu}$) and maximum mobility ($\mu_{\text{max}}$) measured and evaluated for all the studies AlGaN/GaN heterostructures are summarized.

![Fig.2. – The schematic cross section of AlGaN/GaN heterostructures: # 045 (a), # 042 (b) and # 044 (c)](image-url)
Table 1 – Electrical characteristic of the heterostructures

<table>
<thead>
<tr>
<th>N°</th>
<th>$\Delta n_s$ [cm$^{-2}$]</th>
<th>$n_{s2DEG}$ [cm$^{-2}$]</th>
<th>$U_p$ [V]</th>
<th>Rs [Ω]</th>
<th>$\mu$ [cm/V*S]</th>
<th>$\mu_{max}$ [cm/V*S]</th>
</tr>
</thead>
<tbody>
<tr>
<td>045</td>
<td>2.0*$10^{12}$</td>
<td>2.0*$10^{12}$</td>
<td>-0.9</td>
<td>1732</td>
<td>1708</td>
<td>2400</td>
</tr>
<tr>
<td>042</td>
<td>3.7*$10^{12}$</td>
<td>3.1*$10^{12}$</td>
<td>-1.6</td>
<td>1592</td>
<td>1055</td>
<td>1150</td>
</tr>
<tr>
<td>044</td>
<td>6.1*$10^{12}$</td>
<td>3.6*$10^{12}$</td>
<td>-3.0</td>
<td>1423</td>
<td>719</td>
<td>1155</td>
</tr>
</tbody>
</table>

It was observed that in type #044 heterostructures the edge of depletion layer is located at AlGaN barrier and that the initial carrier concentration in AlGaN barrier (below 20 nm from the surface) is equal to the Si dopant concentration. The increase in bias voltage up to -1.1 V caused the removal of electrons from the barrier layer (Fig. 5). Above the -1.1 V bias voltage the removal of 2DEG electrons starts and at voltage bias equal to -3 V the channel is pinched off. From charge balance it could be seen that for type #044 heterostructures a part of formally evaluated as 2DEG electrons, with concentration equal to 6.1*$10^{12}$ cm$^{-2}$, are electrons at AlGaN barrier with concentration 2.5*$10^{12}$ cm$^{-2}$. The mobility of these electrons is low; they are not useful for carrier transport at the electron devices.

In #042 AlGaN/GaN heterostructures the total dose of the Si dopant was lower. In Figure 4 an initial increase in the carrier concentration could be observed. The value of charge at AlGaN barrier equal to 0.6*$10^{12}$ cm$^{-2}$ was measured. For this heterostructure the sheet carrier concentration of 3.6*$10^{12}$ cm$^{-2}$ was obtained. It means that the 2 DEG sheet carrier concentrations was 3.0*$10^{12}$ cm$^{-2}$. It seems that for these MOVPE process conditions it is the maximum value
of 2 DEG concentration that could be obtained in Si doped Al$_{0.2}$Ga$_{0.8}$N/GaN heterostructure with Al content in the barrier equal 20%.

![Graph showing incremental sheet charge concentration versus voltage bias in AlGaN/GaN heterostructures](image)

**Fig. 5** – The incremental sheet charge concentration versus voltage bias in AlGaN/GaN heterostructures

In undoped AlGaN/GaN heterostructures #045 the measured sheet carrier concentration, equal to 2.0*10$^{12}$ cm$^{-2}$, arising from the equilibrium between the charges of surface states, the charges in the channel and the charges induced by spontaneous and piezoelectric polarization.

The performed experiments showed that for Al$_{0.2}$Ga$_{0.8}$N/GaN heterostructure the maximum 2 DEG sheet carrier concentration could be obtained in the range from 2.0*10$^{12}$ cm$^{-2}$ (undoped heterostructures) to 3.6*10$^{12}$ cm$^{-2}$ (Si-doped heterostructures). The increase in the Si dopant concentration above ~ 2.0*10$^{18}$ cm$^{-3}$ is not efficient. It results in the increase of concentration of the carrier with low mobility that is useless for the electronic devices.

**CONCLUSION**

The influence of the Si dopant concentration and its distribution through the AlGaN barrier layer of the MOVPE AlGaN/GaN heterostructure on carrier concentration in the channel was studied using impedance spectroscopy measurement. It was found that for appropriate Al concentration at AlGaN barrier the optimum concentration of Si dopant exists which allows us to obtain the heterostructures with good electrical properties. Too high concentration of the Si-dopant could result in decreasing the 2DEG carriers’ mobility.
Acknowledgements

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REFERENCES

PREPARATION AND PROPERTIES OF HIBRYD ORGANIC-INORGANIC COMPOSITES BASED ON POLY- TiO\textsubscript{2}\textsuperscript{**}

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ABSTRACT

Optically transparent hybrid organic-inorganic copolymers based on the poly-TiO\textsubscript{2}, vinyl monomers and lactide or glycolide have been prepared. Optical and physical-mechanical properties of composites are depended with the ratio of components have shown. Hybrid copolymers possess photochromic properties. By the UV light excitation reversible darkening of the samples due to the transition Ti\textsuperscript{4+}↔ Ti\textsuperscript{3+} had observed. The speed of transition depends on the copolymer composition.

Key words: poly-TiO\textsubscript{2}, hydroxyethyl methacrylate, lactide, glicolide, hybrid organic-inorganic copolymers, nanocomposite, reversible photochromic properties, solid-state

INTRODUCTION

In recent decades, research to develop new polymer composites containing nanoparticles metals or their oxides, as well as nanostructured hybrid organic-inorganic composites has been in rapid progress. Interest to these objects is very strong because of by the transition from micro- to nanoparticles a qualitative change in many physical and chemical properties have taken place. Often this materials show complex of unique properties such as structural, catalytic and biological.

Among the hybrid organic-inorganic polymer composites particular interest represent the copolymers poly-TiO\textsubscript{2}. Gels of poly-TiO\textsubscript{2} have demonstrated unique optical properties. By the UV light excitation observed reversible conversion Ti\textsuperscript{4+}↔ Ti\textsuperscript{3+} which accompanied by darkening - the enlightenment of samples. However the instability and absence of shape of this gels determine the need in synthesis of solid-state samples which can withstand mechanical

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Handling. In this regard the synthesis of hybrid copolymers contained poly-
TiO2 component which stabilized by polymeric matrix organic nature are promising.

For particular interest to create optical data storage devices are composite materials based on organic-inorganic copolymers containing metal nanoparticles. Additional introduction of metal nanoparticles can change the optical properties of the samples. Copolymers containing silver nanoparticles were synthesized.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

In this work, two-stage method of synthesis samples has been used: at first - hydrolytic polycondensation Ti(OPr)i4 in organic monomer - hidroxyethyl methacrylate (HEMA) or mixture of HEMA - lactide (glycolide), and then by low-temperature radial polymerization. The components were mixed in different molar ratios. In the compositions was added dopant – AgNO3 for the formation nanoparticles. Mixture was poured into forms between the panes with a calibrated distance between them. The resulting composition was left to form a polymeric inorganic matrix. On completion of this process was judged visually by the loss of fluidity of the samples. The next stage was the polymerization for the formation of organic polymer at 70 °C in an air thermostat.

Investigation of physical and mechanical properties of hybrid models

The resulting hybrid copolymers should have dimensional stability and withstand handling. The strength and ductility of the samples with different ratio of organic and inorganic components was investigated. Studies carried out on tensile testing machine ZWICK / Roell Z005.

Investigation of changes in optical density of the hybrid composites under UV exposure and during relaxation

The samples were irradiated with a mercury lamp of high and medium pressure DRT-400. The process of change in optical density due to the transition of Ti 4+ → Ti 3+, monitored on a spectrophotometer Shimadzu UV-1650PC. After the end of UV exposure, the samples were left at room temperature and monitored for changes in the relaxation spectra of light transmission.

RESULTS AND DISCUSSION

The optical properties of hybrid organic-inorganic polymer composites with different initial ratio of organic (HEMA) and inorganic (-TiO2-) copolymer have been studied. All the composites were characterized by optical transparency, the amount of light transmission depending on the ratio of the components reaches ~ 85% at λ = 700 nm. Hybrid polymers are transparent in the visible spectrum and fully absorb light in the UV region (fig.1.).
Fig. 1 – Change spectra of transmittance for the hybrid copolymer with UV irradiation for 3 hours

For the performance of the copolymers is important to obtain samples with various and regulate plasticity. However, the samples consisting of poly-TiO$_2$ and poly-MEG are very fragile. A third component - glycolide or lactide in different ratios was added in two-component mixture to increase the flexibility of the samples. Physical-mechanical properties of composites based on a three-component mixture were investigated (Table 1).

Table 1. Physical and mechanical properties of hybrids containing glycolide and lactide

<table>
<thead>
<tr>
<th>[Ti(OPr$_i$)$_4$]/[MEG]/[x], mol</th>
<th>[x] = glycolide</th>
<th>[x] = lactide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stiffening $\sigma_{cp}$, MPa</td>
<td>deformation $\varepsilon_{cp}$, %</td>
</tr>
<tr>
<td>1:4:0</td>
<td>3,92</td>
<td>2,18</td>
</tr>
<tr>
<td>1:4:1</td>
<td>5,23</td>
<td>5,51</td>
</tr>
<tr>
<td>1:4:2</td>
<td>4,14</td>
<td>45,80</td>
</tr>
<tr>
<td>1:4:3</td>
<td>1,40</td>
<td>113,72</td>
</tr>
<tr>
<td>1:4:4</td>
<td>1,29</td>
<td>136,47</td>
</tr>
</tbody>
</table>

The data in Table 1 shows that the intake of a third component - glycolide – lead to reduction of the damaging voltage of the system from 5.23 MPa to 1.29 MPa and an increasing the deformation of the samples up to 136%. It can be concluded that the links are internal plasticizer glycolide, which are built into the structure of the copolymer and decrease the intensity of interaction between macromolecules, facilitating the mobility of their segments.

It should be noted that the transparence of samples is stay in the order of 87 % with modification of physical- mechanical properties.
The spectra of transmittance for ternary organic-inorganic copolymers containing units of TiO$_2$, HEMA and glycolide; TiO$_2$, HEMA and lactide are shown in fig.2.

![Fig. 2](image)

**Fig. 2** – The absorption spectra of the hybrid copolymer composition (a) [Ti (OPr$_i$)$_4$] / [HEMA] / [glycolide] = 1:4:4 mole; (b) [Ti (OPr$_i$)$_4$] / [HEMA] / [lactide] = 1:4:4 mole under UV irradiation of the sample: curve 1 - 0 min UV curve 2 - 3 hours of UV

*Figure 2* shows that in the copolymers, which consist of three components, remains reversible electron transfer Ti$^{4+}$ + e $\rightarrow$ Ti$^{3+}$, characteristic for gels of poly-TiO$_2$. The appearance of broad absorption bands in the 400-800 nm was observed during UV irradiation of copolymers. Optical transmission of the sample of [Ti (OPr$_i$)$_4$][HEMA]/[glycolide] = 1:4:4 mol after 3 hours of UV radiation varies from 82% to 37% at a wavelength of 700 nm, in copolymers containing lactide the light transmission is changed from 87 to 50%.

Thus, the totality of physical-mechanical and optical studies makes it possible to develop technology for organic-inorganic composite materials with controlled physical and mechanical characteristics while retaining the unique photochromic properties poly-TiO$_2$.

Of particular interest to create optical data storage devices are composite materials based on organic-inorganic copolymers containing metal nanoparticles. Additional introduction of metal nanoparticles can change the optical properties of the samples. Copolymers were synthesized on the basis of HEMA and Ti (OPr$_i$)$_4$ containing the precursor – AgNO$_3$ - in different proportions (1-3%) by weight of Ti(OPr$_i$)$_4$. Samples received a two-stage method which was described earlier.

Reducing of Ag$^+$ by UV irradiation is observed in samples. There is the emergence and growth of the absorption maximum in the region of 380-420 nm, corresponding about plasmon absorption of silver nanoparticles (*Fig. 3*).

From *fig. 3a* we can see that increasing the concentration of AgNO$_3$ shifts the absorption band at longer wavelengths, from 403 to 416 nm. That is give evidence about the formation of larger particles.
Fig. 3 – The absorption spectra of hybrid composites, containing AgNO₃: a – composition [HEMA]/[Ti(OPr)₄] = 4, with different concentrations of AgNO₃ (% by weight of Ti (OPr)₄) after UV irradiation for 120 min, the curve 1 - 1% (λ_{max} = 403 nm), 2 - 2% (λ_{max} = 411 nm), 3 - 3% (λ_{max} = 416 nm); b – Hybrid composites with initial concentration of AgNO₃ 3% (by weight of Ti (OPr)₄) and different molar ratios in the initial reaction mixture [HEMA]/[Ti(OPr)₄]: curve 1 - 4 (λ_{max} = 416 nm) curve 2 - 8 (λ_{max} = 429 nm)

Changes in the ratio of organic and inorganic components at a fixed dopant concentration also leads to changes in the size of formed nanoparticles. The maximum absorption band shifts from 416 to 429 nm with doubling content of organic component (fig. 3b). Such an increase in the size of the particles may be due to the fact that the structure of the copolymer with low content of inorganic component is less cross-linked. This is facilitating the growth process of nanoparticles to larger sizes.

It should be noted that the hybrid copolymers containing silver nitrate, is far less effective darkening associated with the electronic transition Ti⁴⁺ + e ↩ Ti³⁺. This may indicate that the priority process in these samples is the reduction of silver ions: Ag⁺ + e → Ag⁰.

**CONCLUSIONS**

The optically transparent hybrid organic-inorganic copolymers has been prepared. This copolymers retain unique photochromic optical properties of gels of poly-TiO₂. By the UV light excitation observed reversible darkening of the samples due to the transition Ti⁴⁺ ↔ Ti³⁺ had observed. The speed of transition depends on the composition of components.

**REFERENCES**

ADVANCED NANOSTRUCTURED ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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ABSTRACT

The more popular active material for negative electrode is usually flake graphite due to its excellent cycle life (up to 1000 cycles). The main disadvantage of graphite is a relatively low specific capacity, because even the theoretical value is \( QC_{th} = 372 \) mA·h/g.

Si, Sn, Al, hard carbons and some other materials are actively investigated as the alternate materials for lithium-ion batteries. However, they have not received a practical application, since their large theoretical capacity is accompanied by sharp drop of capacity (during the few cycles), high irreversible capacity (up to 50 % and more), non-horizontal shape of charge–discharge curves. The main reason of sharp capacity degradation is considerable (in 2-4 times) volume changes of these materials during intercalation-deintercalation of lithium ions.

We have formulated some theoretical principles and developed the experimental composite nanostructured anode materials for lithium-ion batteries with high level of specific capacity (up to 600 mA·h/g), quite stable cyclization, minimal irreversible capacity (ca 8 %), horizontal shape of charge–discharge curves.

Key words: nanocomposite, lithium-ion battery, negative electrode

INTRODUCTION

Lithium-ion batteries are the most promising devices for electrochemical energy storage due to their high energy density and cycle life.

The more popular active material for negative electrode is usually flake graphite due to its excellent cycle life (up to 1000 cycles). The main disadvantage of graphite is a relatively low specific capacity, because even the theoretical value of capacity is \( QC_{th} = 372 \) mA·h/g.

Si, Sn, Al, hard carbons and some other materials are able to intercalation-deintercalation of lithium ions. Nevertheless, they have not received a practical application, since a huge theoretical capacity (for example \( QS_{ith} = 4,200 \) mA·h/g for Si, \( QS_{nth} = 994 \) mA·h/g for Sn) is accompanied by sharp drop of capacity (during the few cycles), high irreversible capacity (up to 50 % and more), non-horizontal shape of charge–discharge curves. The main reason of

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sharp capacity degradation is considerable volume changes of these materials during intercalation-deintercalation of lithium ions in the structure of above mentioned active materials (AMs).

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

Composite active materials (AMs) for lithium-ion battery electrodes were prepared mainly by mixing corresponding electrochemically active components with different-type nano-structured graphite and carbon materials [1], such as thermally expanded graphite (TEG), graphitized carbon-black (GC), special types of activated coal (AC) and their mixtures. The electrodes were produced by thoroughly mixing the AM with different-type polymer fillers (polytetrafluoroethylene (PTFE), carboxymethylcellulose (CMC), polyvinylidene fluoride (PVDF) and others) followed by applying a thin uniform layer of the suspensions to metal foil with the help of a special device, “Doctor Blade”.

The lithium-ion battery assemblies were carried out in the Department of Electrochemical Power Engineering & Chemistry of Kiev National University of Technologies and Design in non-aqueous and oxygen-free atmosphere of the UNILAB (MBraun Inc., USA) glove-box.

Apart from general physical-chemical methods (light, transmission electron, scanning electron and energy-dispersion microscopy), atomic-adsorption spectroscopy with the automatic double-beam atomic-adsorption spectrometer SOLAAR S4 (ThermoElectron, USA) was used to determine the chemical composition of the materials.

Electrochemical characteristics of the materials were measured by cyclic voltammetry, chronoammetry and electrochemical impedance spectroscopy carried out with the multi-channel potentiostat-galvanostat VMP3 (Bio-Logic-Science Instruments, France).

The performance of the electrode materials and battery models in long-term operation was studied using the automatic 32-channel system for testing batteries MSTAT 32 (Arbin Instruments, Texas, USA).

**RESULTS AND DISCUSSION**

We have formulated the following principles of practical usage of above-mentioned materials for development of advanced composite anode materials for lithium-ion batteries [2, 3].

Anodes has to contain a composite of graphite with high-dispersed (as ideal – nano-dispersed) particles of AMs (like Si, Sn) as active additives;

Particles of AMs have to be surrounded by a quite elastic porous electro-conductive matrix (ECM), like amorphous carbon, Al, etc. This ECM has to compensate the considerable volumetric changes of AMs particles during the cycling. It creates the possibilities to prevent a destruction of AM particles and to reach relatively stable cyclization of electrodes.
A concentration of AMs particles has not to be very high (not more than 10%).

We made some experimental investigations in our laboratory and have developed Si/C/graphite based composite nanostructured anode materials for lithium-ion batteries with high level of specific capacity (up to 550-600 mA·h/g), quite stable cyclization (during the hundred cycles), minimal irreversible capacity (ca 8 %), horizontal shape of charge–discharge curves.

The similar results we have achieved also with Sn - based composite nanostructured anodes. Both these nanostructured composites give possibility to exceed noticeably the maximal achieved capacity of graphite anodes (ca 350-370 mA·h/g).

Fig. 2 – Specific capacity vs cycle number of the carbon coated silicon-graphite composite. Current density is 30 mA/g. The cut-off potentials were 1.5 V for charge and 0.01 V for discharge.
CONCLUSIONS

Nano-composites of graphite with silicon, tin and some other materials which can be involved in reversible intercalation of lithium ions have been developed. The use of such materials allows one to increase specific capacity of anodes of lithium-ion batteries by a minimum of 1.5-2 times and at the same time to provide the necessary stability of cycling.

Acknowledgements

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REFERENCES


FERMI LEVEL OF CARRIERS IN THE VOLUME FILLING DEFECTS STRUCTURE BASED ON HEAT-RESISTANT METALS

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ABSTRACT

The volume filling defects structure based on metals are widely used in modern nanotechnology, especially when creating high temperature sensors and structural elements based on metal foams [1]. The development of contactless and nondestructive methods for diagnosis and test control parameters of multiply connected matrix base material is a very important and interesting aspect of the application [2]. In a heat-resistant metal with the volume filling defects (VFD) (micro- and nanopores with complex topologies and sizes, see. Figure 1) it is primarily its strength and electrical and physical characteristics. Almost all rapid methods of such measurements are based on both electrical measurements data and on fundamental functional relationships establishing of the microstructure parameters and the dispersion medium carriers [3]. The influence of a disordered set of volume filling defects (VFD) (micro- and nano-pores of complex topology and various sizes, Figure 1.) is the unsolved problem on the electronic properties of the micro heterogeneous materials theory.

Key words: nanopores, electronic properties, materials with VFD.

PLASMA STATISTICAL APPROACH

The new statistical “plasma” approach is proposed in this work. This method is based on the modeling statistical concept of the heterogeneous plasma system (HPS) characteristics [3-5]. The main point of this approach is the concept of an electrically neutral cell (see Figure 2). This cell is the smallest area of the electrically inhomogeneous material released by a multiply connected surface Π extreme of instant self-consistent system electric potential [4].

The electronic component statistical equilibrium in volume filling defects of the heat-resistant metals of both nano- and mesoscopic sizes determines the level of electrochemical potential of a homogeneous volume of the sample in any its point. Statistical equilibrium of the electronic component in FVD high-temperature metal nano- and mesoscopic size determines the level of electrochemical potential of a homogeneous volume of the sample in any its point. Moreover, according to the principle of free energy minimum, F takes the smallest value. Equilibrium distribution of the local density of the electronic component in the matrix base material and...
VFD satisfies this condition and is determined by solving the effective electrostatic problem in an averaged cell \( C_{\xi}^z \) [3, 5].

Fig. 1 – Nanoporous metal foams [1]

Fig. 2 – Planar cell of the micro-hulled metal with VFD

Fig. 3 – 3-D graph of the dependence \( F = F(\Phi_0) \)

RESULTS AND DISCUSSION

The main point of this approach is the concept of an electrically neutral cell (see Figure 2). This cell is the smallest area of the electrically inhomogeneous material released by a multiply connected surface \( \Pi \) extreme of instant self-consistent system electric potential [4].

The electronic component statistical equilibrium in volume filling defects of the heat-resistant metals of both nano- and mesoscopic sizes determines the level of electrochemical potential of a homogeneous volume of the sample in any its point. Statistical equilibrium of the electronic component in FVD high-
temperature metal nano- and mesoscopic size determines the level of electrochemical potential of a homogeneous volume of the sample in any its point. Moreover, according to the principle of free energy minimum, F takes the smallest value. Equilibrium distribution of the local density of the electronic component in the matrix base material and VFD satisfies this condition and is determined by solving the effective electro-static problem in an averaged cell $C_z$ \cite{3,5}. For the hulled metal sample with VFD this equation looks like

$$
\Omega(\Phi_0, F) = \text{tg} \left( \frac{\kappa \cdot r_p}{\sqrt{2}} \right) - \tilde{\alpha} \cdot \frac{\varepsilon_p \cdot \kappa_F \cdot E_F^0}{\kappa \cdot kT} \cdot \sinh(\kappa_F \cdot \delta) = 0
$$

Here: $\Phi_0$ is potential in the center of the cell; F is the Fermi level of the carriers; $r_p, \delta$ is respectively, the size of the defect and matrix elements of metal, which belongs to $C_z$; $\kappa^{-1}$, $\kappa_F^{-1}$ is Debye length and the Fermi length of the electronic component; $\tilde{\alpha} = \frac{2}{3} \cdot \left[ (1 + F/E_F^0 + W^0/E_F^0) - 1/\sqrt{(1 + F/E_F^0 + W^0/E_F^0)} \right]$ is the parameter of the equation; $E_F^0$ and $W^0$ is the Fermi energy and electron work function of metal; $\varepsilon_p$ is metal dielectric permittivity; $T$ is temperature of the sample. Equation (1) establishes a functional relationship of electrochemical potential of the carriers with the defining parameters of the sample: temperature, geometric characteristics and concentration of VFD, the electronic parameters of the base material, and particularly with the equilibrium value of the local electrostatic defects potential (Figure 3.) stabilized. The external electric field $\Phi_0$ influence on the electrons density distribution in the sample VFD was determined in the computer experiment. The possibility of creating of the sensitive temperature sensors based on heat-resistant metal with nano-VFD was discussed in details.

**REFERENCES**


CHEMO-EMF IN THE SILICON SOLAR CELL EXPOSED TO LOW-ENERGY HYDROGEN ATOMS

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\textbf{ABSTRACT}

A new reactive gas-semiconductor system is experimentally found and examined for the electron-hole pairs (e-h pairs) generation in the semiconductor due to exoergicity of a surface chemical reaction. This system is “atomic hydrogen-crystalline silicon”. The p-n silicon homojunction was used to produce chemo-emf and chemicurrent in the semiconductor system due to e-h pairs creation. The ideal geometry of the semiconductor system would require the top semiconductor layer be of a nanosized thickness since only the upper layer of the semiconductor is involved in chemical excitation. To make the beginning of a research we howere harnessed the commercial silicon solar cell fabricated with the certain technological changes to have a bare semiconductor surface. A special procedure was worked out to prepare the silicon surface free of the blocking layer of silicon oxide.

The chemo-emf in the open circuit up to a few mV and the short circuit chemicurrent up to the record 700 nA were achieved that are the promising magnitudes to pave a way for direct chemical energy to electrical energy conversion by semiconductor systems.

\textbf{Key words:} nanostructures, energy conversion, p-n junction, silicon, atomic hydrogen, solar cells.

\textbf{INTRODUCTION}

The problem of renewable and ecological (“green”) sources of energy requires searching for the new approaches to overcome a number of challenges on this way. For instance the fuel cells energy production still encounters the high cost of the up to date devices [1, 2].

Recently a new direction has been started based on direct chemical-to-electrical energy conversion on metal-semiconductor Schottky nanostructures (see e.g. [3-7] and references therein). In Schottky nanodiodes the exoergic chemical events on the ultrathin (nanosized) metal film, forming the top part of the Schottky diode, give rize to kinetically hot electrons in the metal layer. The hot electrons cross ballistically the metal film, then surmounting the Schottky barrier and (after entering semiconductor) producing electric current in the

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external circuit. This direction was pioneered by the authors of [3,4]. However the nonadiabatic nature of the energy transfer from the “heavy” systems (nuclei of the reagents on the surface) to the “light” system (electrons in the solid) requires breaking of the adiabatic approximation of Bohr-Oppenheimer and leads to relatively low efficiency of the energy conversion process [3, 7].

We are developing an alternative concept of direct chemical energy-to-electricity conversion using the semiconductor p-n junctions [8]. Here the exothermic chemical reaction produces by its exothermic steps the electron-hole (e-h) pairs in the uppermost semiconductor layer, contacting with the chemically active ambience. The nonequilibrium carriers move to the junction region and produce chemo-emf when the components of e-h pairs are separated by the electric field of the junction. The working near-surface semiconductor layer operating in this fashion has a nanometer thickness due to intrinsic mechanisms of the chemical energy transfer. The semiconductor region between this working near-surface layer and the junction itself plays a role of a certain “buffer”, where the e-h pairs could be lost because of the recombination process. Thus the thinner top layer of the semiconductor structure the better performance expected.

The principle of the operation of the device in question needs that a semiconductor-reagents system be possible to transform the chemical energy into e-h pairs energy on the first stage of the energy conversion process. The urgent task to advance the problem is to find the suitable semiconductor-reactants systems with high e-h pairs yield. Unfortunately at present only a few systems are known satisfying the requirements described (see [9] and references therein).

Here we addressed the promising and widely used semiconductor - silicon. The previous attempts to use Si for the above purpose failed because of the existing of the blocking silicon oxide layer on the Si-surface. We managed to solve this problem by an appropriate surface preparation procedure. As a testing reaction in searching for the system needed we traditionally have applied the reaction of recombination of hydrogen atoms. Besides we examined here the reaction of recombination of H+O atoms.

The standard silicon solar cell was here utilized since the technology of such devices is well developed for the sunlight-to-electricity conversion. It is worth notice that both the chemical energy and the light energy conversion into electric current on semiconductors are similar in its operation principles.

**EXPERIMENTAL**

Though only of nanosized-thickness top layer will be optimal as a semiconductor for our purpose to minimize the recombination of carriers, we confined ourselves here for the initial stage of research to examinations of the standard silicon solar cell. The latter was produced by the Public Joint-Stock Company
“Kvazar” (Ukraine). The upper n – layer of the p-n junction is formed by diffusion of phosphorus into the silicon wafer, and the base p – layer is doped by boron. The Ohmic contacts were made by an Ag – technology. However the changes in the technology of the solar cell fabrication were brought so as to remain bare the top layer of the semiconductor. The silicon (111) surface morphology characterized using the scanning electron microscope is shown in the Fig.1.

The schematic sketch of the measurements is displayed in the Fig. 2.

The hydrogen atoms of thermal energies were produced by H₂ - dissociation in HF- discharge (40 MHz) and the fluxes j (m⁻² s⁻¹) incident on the sample were measured by an isothermal wire platinum microcalorimeter.

The chemo-emf signal produced from the sample 2 × 2cm² was registered by the measurement circuit composed of the laboratory-made instrumental electrometric direct current amplifier, and an analogue-digital converter (ADC) supplied with the pre-amplifier.

Fig. 1 – Morphology of the silicon top layer surface of the solar cell

Fig. 2 – A schematic sketch of the chemo-emf measurements in the silicon solar cell exposed to low-energy hydrogen atoms: 1- microheater, 2- sample, 3- mica plate, 4- instrumental amplifier, 5- analog-digital converter, 6- power supply unit, 7- personal computer
The signal from the ADC was displayed on the monitor of a PC to be then processed and analyzed. Both the current and the voltage regimes were applied.

The sample was subjected to HF-chemical etching before placing in a vacuum chamber. After mounting on the microheater and pumping the sample was treated in a special procedure composed of a sequence of bombardment by low-energy Ar+ ions (produced by an ion-gun) and atomic hydrogen exposure at varying temperatures.

**EXPERIMENTAL RESULTS AND DISCUSSION**

The as-fabricated oxidized sample of a solar cell with the durable SiO$_2$ layer did not show any effect under exposure to hydrogen atoms.

After the proper preparation of the Si-surface, as indicated above, the admission of the atomic flux to the sample (by switching on the HF-discharge) revealed the chemo-emf ($\varepsilon_{\text{ch}}$) generation. The kinetics of $\varepsilon_{\text{ch}}$ is illustrated in the fig.3. The $\varepsilon_{\text{ch}}$ value quickly reached almost steady state magnitude (within 1-1.5 s) and this state was stable during at least 25 min (the time of observation).

The “switching off” the atomic flux turned its value to the initial zero level. Appearance of $\varepsilon_{\text{ch}}$ unambiguously implies that e-h pairs are generated in chemical H-atoms – semiconductor interaction, since only an ambipolar process can be responsible for chemo-emf production. The quick jump up in the $\varepsilon_{\text{ch}}$ value at the beginning of the H-atoms – surface interaction, when the surface is pure after Ar$^+$ ions bombardment (free of adsorbed H-atoms), clearly indicates that the process of H-atoms adsorption (the most intensive at the unoccupied surface) is active in the e-h pairs production. This is in a qualitative agreement with the heat of adsorption $q_1$ of H-atoms on the (111) surface of silicon: $q_1 \approx 3$ eV > $E_g$ = 1.17 eV [10] ($E_g$ is the silicon bandgap). The event of the atomic recombination (abstraction) itself is probably insufficiently energized to ionize the silicon lattice.

![Fig. 3](image)

**Fig. 3** – The typical kinetics of chemo-emf $\varepsilon_{\text{ch}}$ produced in the Si solar cell under exposure to hydrogen atomic flux ($T=300K, j \approx 10^{20} m^{-2} s^{-1}$). The moments of the flux “switching on” (↓) and “switching off” (↑) are indicated.
The total cycle of the reaction may be represented as follows:

\[ H + H + Si \xrightarrow{q_{1}} H + His \xrightarrow{q_{2}} H_{2} + Si \]

(the quantities above arrows show the exoergic effect of the corresponding reaction event, \( q_{1} + q_{2} + Q = D_{g} \) where \( D_{g} = 4.48 \text{eV} \) is the heat of dissociation of the \( H_{2} \) – molecule in the gas phase, \( Q \) – is the energy carrying away if any from the surface by desorbing vibrationally excited \( H_{2} \)-molecule). Hence a deficit of energy \( (q_{2} < E_{g}) \) may occur for the e-h pair excitation in the recombination event.

The stationary state existing does not contradict to inactive character of the \( H + HSi \rightarrow H_{2} + Si \) abstraction stage for electronic excitation, since the stationary process of atomic recombination includes the continuously repeated adsorption stage.

The dependence of the \( \varepsilon_{ch} \) on the atomic flux is shown in the Fig. 4 (the absciss is represented in logarithm scale).

The \( \varepsilon_{ch} \) increases with the temperature increase, Fig. 5. The activation energy cannot be determined since this dependence is strongly deviated from the exponential one. The most probable explanation of this dependence is the coverage-dependent activated interaction of atoms with the silicon surface.

The short-circuit current in our system achieved the magnitude of 700nA. To our knowledge this is a record value for n-p junction systems up to now. The open circuit voltage was about 1.1mV.

The results represented is promising for the further advancing the semiconductor system in question for transformation of chemical energy into electric current through e-h pairs generation.

![Fig. 4 – Dependence of \( \varepsilon_{ch} \) in the solar cell on the atomic flux (T=300K)](image-url)
Even more pronounced effect of chemo-emf generation was found for a mixed flux of $H+O$ atoms, produced by passing the $(H_2+O_2)$ mixture through HF-discharge ($P \approx 1\,\text{Pa}$). The respective $\varepsilon_{\text{ch}}$ kinetics is demonstrated by fig. 6. Here the entire flux is only approximately estimated by Pt calorimeter because of different heat of recombination of $H$ and $O$ atoms (for the latter $D_g=5.12\,\text{eV in gas phase}$) and different catalytic properties of Pt with respect to $H$ and $O$ atoms.

On the whole this kinetics is similar to that observed for $H$-atoms alone, though a new feature appears at the initial part of the kinetics in the form of a initial peak.
This feature may help to kinetically separate an involvement of the recombination stage in e-h pairs production in this case. The latter would be possible due to higher exoergicity of the reaction O+O (5.12 eV).

These studies to be advanced in more detail fashion targeted to harness all the achievements of the third-generation photovoltaic solar cell nanotechnologies.

**CONCLUSIONS**

The paper addressed the problem of direct chemical energy conversion into electricity. An approach based on the concept of hot electrons in metal – semiconductor Schottky nanodiodes developed in last decade in Germany and the USA has met a serious challenges because of low efficiency of hot electrons production on metal surface in the surface chemical reactions. The common fuel cell is yet expensive enough as current sources. We used a new approach to the problem in question harnessing the convenient semiconductor p-n junctions using them in a manner similar to that utilized in photovoltaic solar cell devices. The nonequilibrium electron-hole pairs on the top part of the p-n system was produced in the chemical interaction of hydrogen atoms and separated by the junction electric field, producing chemo-emf. We found for the first time that silicon can serve as an active material of the converter. The standard solar cells are promising devices for the chemical energy-to-electricity conversion.

**REFERENCES**

Nanopolymers, fullerenes and nanotubes
COMPARISON OF THE STRUCTURAL CONFIGURATION OF Co NANOPARTICLES ON TiO$_2$ AND TNT SUPPORTS

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**ABSTRACT**

In this study, two cobalt based catalyst samples were prepared on titania and titania nanotubes supports using the deposition precipitation method. Their structural configurations were characterized and compared using BET, and TRP analyses. The BET analysis showed that the surface area of TiO$_2$ is much higher than that of TNT which was due to their structural differences. Analyses of the results obtained revealed that the surface area of the 10%Co/TNT catalyst sample is higher than that of the 10%Co/TiO$_2$. The TPR analysis showed that it is much easier to reduce 10%Co/TiO$_2$, than 10%Co/TNT. This is attributed to be due to the fact that the cobalt particles were adsorbed on the surface of the TiO$_2$, and formed covalent bonds with TNT. Therefore reduction temperature was higher with TNT than TiO$_2$. The investigation of structural changes of these catalysts when they were coated with carbon, using chemical vapour deposition method was also conducted. The catalyst prepared on TNT support showed better properties in terms of average pore diameter, pore volume and surface area than the catalyst sample prepared on TiO$_2$ support when the two samples were exposed to carbon environment for the same period of time.

**Key words:** catalyst, configuration, TNT, TiO$_2$, support

**INTRODUCTION**

A catalyst can either be heterogeneous or homogeneous, depending on whether it exists in the same phase as the substrate. Most heterogeneous catalysts are solids that act on substrate in a liquid or gaseous reaction mixture, and the total surface area of solid has an important effect on the reaction rate. Thus the smaller the catalyst particle size the larger the surface area for a given mass of particles and the higher the reaction rate [1]. Supports provide a platform from which heterogeneous catalysts, can act to change the rate of a reaction without being consumed during the reaction. The support material may or may not take part in the catalytic reaction. The support is usually a surface such as a metal oxide or carbon material. The support and catalyst may bond together in such a way to enhance the reactivity of the catalyst. In other cases, the support...
may be inactive and provide a high surface area substrate to increase the collisions of the reactants with the catalysts. For example, in catalytic converters, a ceramic honeycomb acts as a high surface area support for a catalyst such as platinum, rhodium, or palladium for changing pollution gases from the engine to environmentally friendly products. In fuel cells, platinum catalysts are located on a carbon support, which provides a means for conduction of the electrons for the electrocatalytic reactions [2, 3].

TiO$_2$ is used in heterogeneous catalysis as a photo catalyst, in solar cells for the production of hydrogen and electric energy, as gas sensor, as white pigment, as a corrosion-protective coating, as an optical coating, in ceramics, and in electric devices such as varistors [4]. TiO$_2$ is not suitable as a structural support material, but small additions of titania can modify metal-base catalysts in a profound way. A strong-metal support interaction is in part due to encapsulation of the metal particles by a reduced TiO$_x$ over layer [5]. The support provides a high surface area substrate to increase the collisions of the reactants with the catalysts which increase the reaction rate; it also gives a good dispersion of a catalyst which results in an optimal surface area. Previous studies have shown the performances of TiO$_2$ as support for different metal catalysts [6]. It has been known that the Co/TiO$_2$ catalyst is considered to have a strong metal support interaction (SMSI) and shows a high activity in CO hydrogenation reactions [6,7]. This interaction is an important factor used for determining the properties of a Co/TiO$_2$ catalyst such as cobalt dispersion and reduction behavior [8].

The synthesis of highly dispersed cobalt on a TiO$_2$ support requires the strong interaction between cobalt and support. However a too strong interaction can produce a Co-support compound as a suboxide at an interface that is highly resistant to reduction [9 – 11]. It has been reported that Co-support compound formation (Co-SCF) during standard reduction resulted in a lower reducibility of a Co/TiO$_2$ catalyst. It has been known that the dominant surface sites of TiO$_2$ support consists of two main sites Ti$^{4+}$ and Ti$^{3+}$ [6, 12 – 16]. The effect of surface sites on the formation of Co-SCF has not yet been investigated. This study is therefore aimed at loading cobalt particles on both TiO$_2$ and TNT supports using the deposition precipitation method for catalyst preparation, coating the supports TiO$_2$ and TNT with carbon (TiO$_2$-C and TNT-C) using chemical vapour deposition method and use characterization methods to compare the structural configurations of the two supports and catalysts.

**EXPERIMENTAL**

A 2.5 g of a hydrated cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O) sample was mixed with 0.76 g of urea respectively and 5 ml of deionised water was added to dissolve the solid mixture. A few drops of deionised water were added in a beaker with 5 g of the TiO$_2$ support, in an oil bath at 90$^\circ$C while stirring. A
solution of urea and \( \text{(Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}) \) was added drop-wise into the support using a burette, while stirring until the mixture was dry. The sample was then dried overnight at 120°C in an oven. This catalyst precursor was then calcined at 350°C for 6 hours in air. The same procedure was adopted to impregnated Co particles on TNT.

A chemical vapour deposition (CVD) reactor was used to coat the TiO\(_2\) and TNT samples with carbon. The description of this reactor has been reported elsewhere [3, 17, 18]. Acetylene was used as a source of carbon for coating TiO\(_2\) and TNT. About 0.2 g of each sample was placed in a small ceramic boat placed at the middle of the quartz tube that is about 80 cm in length. The tube was then passed through the ceramic tube of the horizontal furnace. Nitrogen gas (Afrox, 99.99%) was introduced while heating the sample at a rate of 10°C/min to 900°C. This was done to ensure an inert atmosphere in order to avoid some side reactions. At 900°C, acetylene was introduced to replace nitrogen gas and the process was done for 60 minutes.

Reducibility behavior of all the calcined catalysts were studied using an in-house designed TPR. A 0.2 g catalyst sample was placed in a U shaped quartz reactor on top of quartz wool which is used as a catalyst bed. Pure nitrogen gas (for degassing) was first passed through the quartz reactor while heating the reactor at the rate of 10°C/minute from room temperature to 150°C. The temperature was kept at 150°C for thirty minutes to ensure that all the moisture content was driven off. The reactor was then cooled to room temperature after degassing the sample, 5% hydrogen in argon gas was introduced at the rate of 30 ml/minute and nitrogen gas was then turned off. Temperature was adjusted from room temperature to 900°C at 5°C/minute. The temperature profiles were collected from a computer.

TGA analyses were conducted on a Perkin Elmer TGA 4000. After placing ~20 mg sample in a ceramic pot it was heated at 10°C/minute from room temperature to 900°C under a constant flow of air (20 ml/minute). The weight loss as a function of temperature was monitored on a computer.

Nitrogen adsorption measurements were performed at -196°C using a Micrometrics Tristar adsorption analyzer. The samples (mass~0.2 g) were loaded in the Micrometrics tubes and degassed at 150°C for overnight in nitrogen (99.99% purity). The tubes were then attached to the Tristar analysis and run overnight.

**RESULTS AND DISCUSSION**

Figures 1a, b show the typical structures of the titania nanotubes and titania supports respectively. It can be seen that the titania nanotubes have tubular structure while the titania has a spherical structural configuration. The titania nanotubes also show a well–ordered structure with relatively simple compositions are formed by titania materials [19]. The tubular structure of the titania
nanotubes is similar to those of carbon nanotubes and it is expected that they will possess exceptional physical, mechanical and electrical properties such as the latter.

![Fig. 1 – Structures of (a) titania nanotubes and (b) titania catalyst supports](image)

The surface area property is very important in the preparation of catalyst because it is responsible for the distribution of the catalyst particles on the support. The larger the surface area of the support, the better it is for good distribution of the catalyst particles and the better the activity of the resulting catalyst. The tubular structure of the titania nanotubes gives it a larger surface area than their titania counterpart. This is confirmed by the comparative surface areas results of the two structures as shown in Table 1.

Table 1 shows the BET analysis of the two supports and their respective catalyst samples which reveals the pore volume, pore diameter and the surface area of the samples. The average diameters of the supports and the Co-loaded catalysts exist within the nano–range of the 10.2 and 35.5, which shows that the particles are fine enough to give even distribution and subsequent good catalytic activity for hydrogen oxidation and oxygen reduction reactions [20]. The preparation method is also a crucial method in the size of the particles; TNT was prepared from the TiO$_2$ and the average diameter of the nanotube material is smaller than that of the initial material.

**Table 1 – BET analysis of the supports, and 10%Co/TNT & 10%Co/TiO$_2$ catalyst samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>35.5</td>
<td>0.420</td>
<td>47.2</td>
</tr>
<tr>
<td>TNT</td>
<td>10.2</td>
<td>0.370</td>
<td>231</td>
</tr>
<tr>
<td>10%Co/TiO$_2$</td>
<td>28.2</td>
<td>0.379</td>
<td>53.8</td>
</tr>
<tr>
<td>10%Co/TNT</td>
<td>12.9</td>
<td>0.484</td>
<td>150</td>
</tr>
</tbody>
</table>
Similar trend is observed in the Co loaded samples of the TiO$_2$ and TNT in which the latter has a smaller size compared to the former. It can also be observed that the surface area and the pore volume of a 10%Co/TNT sample were much higher than that of a 10%Co/TiO$_2$ sample. This can be attributed to the structural change of TNT support when it was prepared from TiO$_2$ of surface area 47.2 m$^2$/g that resulted in a very high surface area of 231.1 m$^2$/g.

The temperature programmed reduction (TPR) profile (Figure 2) indicates the behaviour of a cobalt oxide loaded on TiO$_2$ and TNT supports. These catalysts were both prepared using the deposition precipitation method. Urea is used as a cobalt particles precipitator and is believed to be favourable for the production of small metal particles as well as acted as a reducing agent during the catalyst preparation. The prepared catalyst samples were heated to 1000°C at the rate of 5°C, and held at 1000°C for two hours followed by slow cooling in static air. The form of heat treatment is an important and necessary step in the preparation of the catalysts because it has a significant impact on the Co metal particle size and distribution, particle surface morphology, and Co particle distribution on the supports [21]. The calcination or thermal treatment, removed the volatile compounds contained in the catalysts and removed the undesirable impurities resulting from the early preparation stages, to allow a uniform dispersion and stable distribution of the Co particles on the supports, and therefore improves the electrocatalytic activity of the synthesized catalysts.

![Fig. 2 – TPR profile of 10%Co/TiO$_2$ and 10%Co/TNT catalyst samples](image-url)
The TPR profile shows that the reduction temperature of a 10%Co/TNT occurred at 360°C and 650°C while the reduction temperature of 10%Co/TiO₂ occurred at 360°C and 500°C (Table 2). This suggests that it is easier to reduce 10%Co/TiO₂ catalyst sample than 10%Co/TNT catalyst sample. This could be due structural metal surface interface (SMSI), because the structural configuration of Co when loaded on TiO₂ shows that the Co particles adsorbed on the surface of the TiO₂, while the structural configuration of Co loaded on TNT support indicates a bond between the cobalt oxide and the TNT support.

**Table 2 – Reduction temperatures of 10%Co/TNT and 10%Co/TiO₂ samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C) first peak</th>
<th>Temperature (°C) second peak</th>
<th>Other peaks (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>-</td>
<td>500 – 900</td>
</tr>
<tr>
<td>TNT</td>
<td>-</td>
<td>-</td>
<td>500 – 900</td>
</tr>
<tr>
<td>10%Co/TiO₂</td>
<td>360</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>10%Co/TNT</td>
<td>376</td>
<td>446</td>
<td>-</td>
</tr>
</tbody>
</table>

The height of both peaks was dependent on the consumption of a H₂ that was measured using the TCD detector that was connected to an amplifier. The faster the quantity of H₂ consumed the higher the height of the peak. From the Figure, the peak of the 10%Co/TiO₂ sample is higher than that of 10%Co/TNT catalyst sample which can be due to the distribution of cobalt oxide particles on the TiO₂ support. The reason for the shorter peak of 10%Co/TNT catalyst sample is attributed to the fact the rate of H₂ consumption is slower than that of 10%Co/TiO₂ because the cobalt oxide particles are not close to each other as with 10%Co/TiO₂.

On 10%Co/TNT graph two more peaks appears on the far end of the graph, which was due to the structural change of the TNT support, this is further emphasized in Figure 3a. The change occurred at 500°C and 900°C, this is the same with a TiO₂ Figure 3b.

![Graphs](image_url)
Table 3 shows the average pore diameters, the pore volumes and the surface areas of a TNT-C\textsubscript{60minutes} and TiO\textsubscript{2}-C\textsubscript{60minutes} samples coated with carbon for 60 minutes. The two samples both spent the same period of time (60 minutes) in the furnace to obtain carbon coating from acetylene. It can be observed that the surface area and the pore volume of TNT-C\textsubscript{60minutes} sample were higher than that of the TiO\textsubscript{2}-C\textsubscript{60minutes} sample. This can be attributed to the difference in the configurations of the TNT structure; the distribution of carbon on the TNT support left some space in between as the structure has a certain value of length, and when it was distributed on TiO\textsubscript{2} the carbon particles did not leave some space, as it is believed that the TiO\textsubscript{2} has a spherical structural configuration as previously indicated.

Table 3 – BET analysis of carbon coated TiO\textsubscript{2} and TNT supports

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore diameter (mm)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}-C\textsubscript{60minutes}</td>
<td>30.4</td>
<td>0.019</td>
<td>2.4</td>
</tr>
<tr>
<td>TNT-C\textsubscript{60minutes}</td>
<td>12.2</td>
<td>0.026</td>
<td>3.9</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The loading of 10% cobalt particles on TiO\textsubscript{2} and TNT supports using the deposition precipitation method was carried out in this investigation. The structural configurations of the resulting catalyst samples were characterized and compared using TGA, BET, and TRP analyses. BET analysis showed that the surface area of TNT is much higher than that of TiO\textsubscript{2} which was due to the tubular structure of the nanotubes as compared to the spherical structural configuration of the TiO\textsubscript{2}. The surface area of the 10%Co/TNT catalyst sample also is higher than of the 10%Co/TiO\textsubscript{2} catalyst sample. The TPR analysis showed that it is easy to reduce 10%Co/TiO\textsubscript{2}, than 10%Co/TNT. This is due to the fact that the cobalt particles were adsorbed on the surface of the TiO\textsubscript{2} and formed covalent bonds with TNT. Therefore reduction temperature was higher in TNT than TiO\textsubscript{2} support. The investigation of structural changes of these catalysts when they were coated with carbon, using chemical vapour deposition method was also conducted. The catalyst prepared on TNT support showed better properties in terms of average pore diameter, pore volume and surface area than the catalyst sample prepared on TiO\textsubscript{2} support when the two samples were exposed to carbon environment for the same period of time.

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NANOPOROUS Ag-Cnts FOAMED ELECTRODE FOR LITHIUM INTERCALATION

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ABSTRACT

Intercalation of lithium into Ag-CNTs sample is reported here. We have used a nano-porous silver foam as a frame for deposition of the CNTs inside the pores by electrophoresis deposition (EPD) technique. By using chronopotentiometry method, we have noticed that the Li storage capacity of the prepared Ag-CNTs electrode was improved noticeably in comparison with literature. In addition, a very good functional stability for the prepared electrode has been tested during subsequent cycles of charge / discharge (C&D) procedures. By scanning the cycle’s regulated current from 0.2 up to 1.0 mA, it was shown that in the range of 0.4 - 0.6 mA the Li storage capacity and reversibility of the C&D cycles became optimum, as well.

Keywords: Carbon nanotubes; Li intercalation; Foamed Ag; Electrophoresis deposition

INTRODUCTION

Li-Ion batteries have been widely used in portable electronic devices due to their high energy density, high operating voltage and excellent charge and discharge (C&D) cyclic stability [1–3]. For these applications, it is critical that Li-Ion batteries should have high capacity and good rate performance [3]. Carbon materials [3–5], such as CNTs have been widely used as conductive additives in fabrication of the battery's working electrode because of their high electrical conductivity. To effectively utilize the active materials in the electrode, the contents of these CNT additives should be often reach up to 10~20 wt.%. On the other hand, some unexpected new symptoms such as electrochemicalagglomeration, unstable SEI film formation [6] and so on, lead to significant capacity fading due to deteriorated electric contact between particles. Therefore, it would be the most promising approach to make improvement in dispersing carbonaceous particles well on some substrate materials in order to attain better cycling stability [7].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Our aim was to fabricate higher performance working electrodes in electrochemical applications from mechanical and electrical point of view. The

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effective strategy was that to pin the CNTs into the nano- scaled pores of the silver foam substrate (see Fig. 1) by using electrophoresis deposition (EPD) technique [8]. The defused CNTs inside pores of the silver foam made better inter-junctions with it, therefore; the charge exchange process on the surface of the electrode has been facilitated in electrochemical usages. In spite of higher weight percentage of the CNTs content, such a structure of the porous silver electrode is beneficial to buffer the volume variation of the CNTs during lithium adsorption (charging) and desorption (discharging) periods [9].

![Fig. 1– left- TEM image of the Ag foam surface with nano-scale porosity, Right- magnified image of the foam surface](image)

Finally, we have tried to optimize the lithium storage capacity in the working electrode by scanning the applied cyclic current in the chronopotentiometry measurements and the optimum Li storage capacity was achieved in the range of 0.4 - 0.6 mA of the current.

**RESULTS AND DISCUSSION**

Fig. 2 shows the typical voltage profiles of first, sixth and eleventh charge and discharge cycles for the Ag-CNTs electrode according to the regulated currents as: I = 0.2, 0.4, 0.6, 0.8 and 1 mA. In the case of I = 0.2 mA upon the first discharge process the cell voltage initially drops rapidly until it reaches about 0.8V where there is a plateau for a considerable amount of time. The plateau has been reported for the influence of amorphous forms of carbon previously [10, 11] and this removes gradually during subsequent cycles, probably because the interconnections between the silver frame and the CNTs have been stabilized after several times of lithiating and delithiating.

In battery's terminology, "reversible capacity ratio" (RCR) defines as the ratio of capacity displayed in the charging half to total discharge capacity and here, during the first cycle it was about 0.40 and for subsequent cycles reached to about 0.50. This increasing of the RCR can be attributed to re-arrangement
procedure of the CNTs inside the pores of the Ag foam during the next C&D cycles.

By scanning the regulated current, with steps of 0.2 mA, up to 1 mA and running 11 cycles in each step, it can be seen that the discharge profiles behave in the aforementioned general trend. However, a noticeable point occurs in the range of: I = 0.4-0.6 mA, because the cycle profiles were converged and coincidental and also the reversible discharge capacity became optimized at I = 0.4 mA.

**Fig. 2** – Regulated current C&D voltage profile scans for: I = 0.2, 0.4, 0.6, 0.8 and 1.0 mA. Numbers on the graphs show the corresponding cycle numbers

**CONCLUSION**

Improvement of functional performance of CNTs contain electrodes for electrochemical lithium storage applications e.g. Li-Ion batteries, has been considered.

In this ground, foamed Ag substrate has been used for EPD process to deposit CNTs inside its pores. By this method, it is expected a higher amount loading of the CNTs and also better interconnections between them and the silver frame.

On the other hand, Chronopotentiometry measurements show that i: Li storage capacity of the foamed silver is several times more than the plane Ag electrode, ii: the prepared Ag-CNTs working electrodes have very notable functional stability during successive C&D cyclic applications without any disintegration of the CNTs from the foamed silver frame. Because the porous structure of the electrodes have ability to buffer the volume variation of the electrodes during lithium charging (expansion) and discharging (contraction) periods.
In addition by scanning the regulated current from 0.2 up to 1mA, there was a convergence between C&D cyclic voltage profiles in the range of 0.4-0.6 mA and also, an optimization on reversible Li storage capacity has been observed in this range for the electrodes. This optimized behavior of the prepared electrodes could be interpreted as a result of dependency of the SEI film formation (near surface of the Ag-CNTs electrode) to the regulated current values during the C&D cycles.

REFERENCES

EFFECT OF SURFACTANT ADDITION ON THE MWNT SUSPENSIONS STABILITY IN ORGANIC SOLVENTS

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ABSTRACT
It is shown that multi-walled carbon nanotubes (MWNT) form stable suspensions in isopropanol solvent as a result of influence of ultra-sound in the weight range of concentrations from 0.0001% to 1% by weight. Nonionic surfactant Triton X-165 affects the microstructure of the MWNT aggregates in isopropanol, a small amount of surfactant increase the intervals between the aggregates and accelerate the sedimentation process. MWNT suspension in and toluene shows unstable behavior, their total precipitation time is less than $10^4$ sec. Addition of 0.4% Triton X-165 to suspension of MWNT in p-xylene leads to its stabilization. Also, addition of 0.6% Triton X-165 leads to partial stabilization of suspensions of MWNT in toluene.

Key words: multi-walled carbon nanotubes, surfactant, Triton X-165, sedimentation, isopropyl alcohol, p-xylene, toluene

INTRODUCTION
Dispersion of MWNT are used in the production of composite materials, films, filters, conductive coatings and fillers [1]. The creation of suspensions is one of ways to produce MWNT dispersions. The stability of MWNT in liquids and their densities, viscosities, polarities and other physical and chemical properties are reflected in the most important characteristics of the final product [2]. Organic liquids often wet carbon materials better than water-based suspensions; therefore suspensions of MWNT in many organic solvents are sufficiently stable [3]. Furthermore, the addition of surfactants can contribute to dispersions stabilities [4].

METHODS OF SAMPLE PREPARATION AND ANALYSIS
MWNT are produced by "Spetsmash", Ukraine. The length of the nanotubes 5–10 microns, average diameter is approximately equal to 18 nm, the average number of layers - 14, the distance between the layers - 0.34 nm. Dispersive medium is isopropyl alcohol (chemically pure, "Alfarus", Kiev).

The dispersion of MWNT in the suspension produced by ultrasonic disperser UZDN-2T (Russia), the power of 450 W, frequency 22 kHz. It was pre-

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pared a few samples of suspensions with different mass concentrations of MWNT, from $C=0.0001\%$ to $C=1\%$.

The nonionic surfactant Triton X-165 (Sigma-Aldrich) was used for determining the effect of surfactants on stability of the suspension. Surfactant was added to the suspension during ultrasonic treatment.

Optical transmission of dispersion was studied by photoelectric colorimeter KFK-2MP (LOMO, Russia). Electrical conductivity was measured using the multimeter LCR-819 (Instek, Taiwan) with alternating current frequency of 1 kHz and an effective voltage 0.25 V.

The sample in the cell with optical path length 10 mm was photographed through the eyepiece of an optical microscope Biolar ZM-50 (PZO, Poland) with an increase 125x with camera Canon A580 (Taiwan). The studies were conducted at a temperature of 298 K.

**RESULTS AND DISCUSSION**

_Suspensions of MWNT in isopropanol._ It is shown that MWNT can form a stable suspension in isopropanol a result of influence of ultra-sound irradiation in the investigated concentration range. The aggregates of nanotubes are visible with an optical microscope in a suspension starting from concentration of about 0.01\%. Bridges between the aggregates appear when the concentration reaches 0.1\% by weight. The rapid growth of electrical conductivity to a value of about $10^{-4} (\Omega \cdot M)^{-1}$ occurs at this concentration.

![Fig. 1 – The change of optical transmission of suspension ($\Delta T$) during 6000 sec from the end of ultrasonic treatment with the surfactant concentration 0.04\% in dependence of the concentration of MWNT ($C$). Inset: dependence of the optical transmission $\Delta T$ suspension of the surfactant concentration ($Cs$) for different mass concentrations of MWNT $C$: 1) $C = 0.00023\%$; 2) $C = 0.00092\%$; 3) $C = 0.0036\%$; 4) $C = 0.006\%$; 5) $C = 0.01\%$](image-url)
Adding a surfactant Triton X-165 results in a slight reduction and fragmentation of aggregates of nanotubes, but also speeds up the sedimentation process in the suspension. Time of deposition decreases with increase the surfactant concentration.

*MWNT suspension in p-xylene.* MWNT suspension in p-xylene is not stable, complete sedimentation time is c.a. 4000 sec, regardless on concentration of MWNT. Addition a surfactant strongly reduces the initial transmission and decelerate sedimentation processes. Surfactant suspension becomes stable when the mass fraction becomes of about 0.4%.

Addition the surfactant does not affect evidently the microstructure of aggregates MWNT. This fact entails the conclusion that the surfactant prevents sedimentation process in the suspension.

*Suspensions of MWNT in toluene.* Suspensions of MWNT in toluene are instable, the complete sedimentation finishes for 6000 sec. Sedimentation MWNT in toluene occurs in one and a half times longer than in p-xylene.

Addition a surfactant slightly stabilizes the suspension MWNT in toluene, but it is not such effective as in p-xylene. Optical transmission of suspension after addition the surfactant grows slowly. The microstructure of samples of the suspension, containing the surfactant does not differ from the samples which do not contain surfactant. The greatest effect of addition of surfactant observed when it’s mass fraction becomes of about 0.6%.

![Fig. 2](image-url) – The change of optical transmission of suspension ($\Delta T$) during 6000 sec of the end of ultrasonic treatment in p-xylene (1) and toluene (2) in dependence of the surfactant concentration ($Cs$). Concentration of MWNT in suspensions is 0.0015%
**CONCLUSIONS**

Suspensions of multi-layer carbon nanotubes in isopropanol in the range of concentrations by weight of 0.0006% to 1% form stable suspensions without any addition of surfactants under influence ultrasound radiation. MWNT suspensions in p-xylene and toluene are unstable, and their total precipitation time is less than $10^4$ sec.

Addition of 0.4% Triton X-165 to suspension of MWNT in p-xylene leads to its stabilization. Also, addition of 0.6% Triton X-165 leads to partial stabilization of suspensions of MWNT in toluene. But addition of Triton X-165 into the suspension on the basis of isopropanol leads to its rapid sedimentation. Nonionic surfactant Triton X165 reduces slightly the size of aggregates of MWNT in isopropyl alcohol.

**REFERENCES**

IN SITU MONITORING OF C$_{60}$ HYDROGENATION

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ABSTRACT

Kinetics and pathways of C$_{60}$ reaction with hydrogen gas were studied in a broad temperature interval and over extended periods of time. Specifically, hydrogenation was monitored in situ at high temperature and high hydrogen pressure conditions using gravimetric method. The shape of gravimetric curve was found to depend on hydrogenation temperature: at 350-400°C saturation of the sample weight was achieved, whereas at 420-440°C the sample weight reached the maximum and decreased upon prolonged hydrogenation. The weight decrease is due to fullerene cage fragmentation with formation of light hydrocarbons evaporating from the sample. Hydrogenation products were studied by X-ray diffraction, APPI FT-ICR mass spectrometry, and elemental analysis. Hydrogenation pathways (from C$_{60}$H$_{18}$ up to C$_{60}$H$_{56}$) and possible mechanisms of hydrogenation-induced fragmentation of fulleranes are discussed.

Key words: fullerene, hydrogenation, hydrogenated fullerene, fragmentation, mass spectrometry.

INTRODUCTION

Fulleranes (hydrogenated fullerenes) are products of the reaction of fullerenes with hydrogen and were considered as promising materials for hydrogen storage application [1]. However, high temperature required for hydrogenation/dehydrogenation of fullerenes [2] and partial collapse of fullerene cage upon heat treatment required for the release of hydrogen [3] are the main obstacles for the hydrogen storage application. One of the most important methods for preparation of bulk amounts of fulleranes is a direct reaction of C$_{60}$ with hydrogen gas at elevated temperatures and pressures [1-10]. Direct hydrogenation of C$_{60}$ typically leads to formation of a complex mixture of fulleranes with broad distribution of hydrogen content. One of the main obstacles to the synthesis of pure highly hydrogenated fulleranes is fragmentation and collapse of the fullerene cage during prolonged reaction [9-11]. However, none of the fragmented hydrogenated fullerenes has been isolated in a pure form so far due to the complexity of the obtained mixtures. To isolate a certain isomer of ful-
lerane or fragmented fullerane, it is important to prepare less complex samples, e.g., by variation of the P-T reaction conditions.

Fundamental understanding of the reaction pathway and kinetics is required to achieve selective synthesis of fullerenes with certain compositions. In this study we apply weight measurements of solid $C_{60}$ powder for *in situ* monitoring of hydrogenation reaction at high temperatures (350-450°C) and high hydrogen pressure (50 bar). Detailed *ex situ* characterization of hydrogenated samples was performed to evaluate the hydrogenation reaction pathways at various temperatures and to estimate conditions required for $C_{60}$ fragmentation under hydrogenation.

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

Typical experiments were performed using 300mg of $C_{60}$ powder (sublimed, >99.9% pure, purchased from MER corporation, city, USA) loaded in a stainless steel container. Rubotherm gravimetric system (Rubotherm, Germany) modified for high temperature experiments was used for the *in situ* monitoring of hydrogenation reactions. The precision of weight measurements according to specifications of the balance was ±0.02mg which gave an error less than ±0.01 Wt% considering typical weight of the sample (300mg) (more information about the experimental set up could be found in the previously published articles [12]). Hydrogenation of $C_{60}$ was performed in the temperature range of 350-440°C at 50 bar hydrogen pressure. Gravimetric data were used for qualitative analysis of the reaction kinetics and for evaluation of hydrogen uptake. X-ray powder diffraction data were collected using Siemens 5000 diffractometer and CuKα radiation. Elemental compositions of the samples after hydrogenation experiments were determined using a flush combustion gas chromatography (MIKRO KEMI AB, Uppsala, Sweden). High-resolution APPI FT-ICR MS was performed with a hybrid 12 T linear ion trap FT-ICR MS (LTQ FTMS, Thermo Scientific, Bremen, Germany) [13].

**RESULTS AND DISCUSSION**

A reaction of hydrogen gas with solid $C_{60}$ is expected to result in a sample weight increase. As it can be seen in the *Figure 1*, hydrogenation at 50 bar $H_2$ pressure and temperatures up to 400°C shows gradual weight increase. The data demonstrate that hydrogenation at 400°C and below proceeds without $C_{60}$ collapse and fragmentation. When temperature of the reaction was increased up to 420°C-440°C the kinetics of the process changed dramatically.

After the initial increase the weight of the sample started to decrease. The downturn in the gravimetric curve can be explained only by suggestion that some light hydrocarbons are formed in the process of the hydrogenation reaction and evaporate from the sample. Content of hydrogen deduced from gravimetical curves was in good agreement with data obtained by elemental analysis for samples hydrogenated at 350°C and 375°C (see *Table 1*).
Table 1 – Summary of the elemental analysis and its comparison with results deduced from gravimetrical data

<table>
<thead>
<tr>
<th>Synthesis T, °C</th>
<th>C content, elem. analysis, wt.%</th>
<th>H content, elem. analysis, wt.%</th>
<th>H content, gravim. analysis, wt.%</th>
<th>Number of H per C₆₀, elem. analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>97,4</td>
<td>1,7</td>
<td>1,67</td>
<td>10</td>
</tr>
<tr>
<td>375</td>
<td>96,4</td>
<td>2,9</td>
<td>2,73</td>
<td>20</td>
</tr>
<tr>
<td>400</td>
<td>94,9</td>
<td>4,4</td>
<td>3,96</td>
<td>31</td>
</tr>
<tr>
<td>420, max.weight</td>
<td>95,0</td>
<td>4,0</td>
<td>3,40</td>
<td>28</td>
</tr>
<tr>
<td>440, max.weight</td>
<td>94,9</td>
<td>3,8</td>
<td>3,11</td>
<td>27</td>
</tr>
<tr>
<td>420, long</td>
<td>94,3</td>
<td>4,9</td>
<td>N/A</td>
<td>35</td>
</tr>
<tr>
<td>440, long</td>
<td>94,0</td>
<td>4,7</td>
<td>N/A</td>
<td>33</td>
</tr>
</tbody>
</table>

However, for higher reaction temperatures (e.g., 400°C, 420°C, and 440°C) elemental analysis showed higher content of hydrogen compared to the expected. Samples hydrogenated at 420°C and 440°C had the highest hydrogen content despite the negative total weight change. The negative total weight change could be due to the partial collapse of C₆₀ fullerene cage and release of some light hydrocarbons while higher hydrogen content can be expected if some solid hydrocarbons are formed due to C₆₀ fragmentation or collapse [7, 9-10]. Hydrogenated samples prepared were studied ex situ by X-ray diffraction. All samples had fcc cubic lattice as pristine fullerene C₆₀ but with the increased cell parameter (see Figure 2). All samples were also studied by high resolution APPI FT-ICR MS in order to get detailed information about products of hydrogenation reactions. MS analysis indicated that sample synthesized at 350°C mostly consisted of C₆₀H₁₈ (data not shown).
Fig. 2 - X-ray diffraction patterns of fullerenes hydrogenated at different temperatures: a) pristine C\(_{60}\), b) T=350ºC, c) T=375ºC, d) T=400ºC, e) T=420ºC (max. hydrogenation), f) T=440ºC (max. hydrogenation). A (111) reflex from Si was used for the calibration (marked with an asterisk).

The mass spectrum of the sample synthesized at higher temperature, 375ºC, is more complex. Besides the main peak assigned to C\(_{60}\)H\(_{18}\), a set of low intensity peaks was present in the higher mass range with local maxima at C\(_{60}\)H\(_{36}\) and C\(_{60}\)H\(_{44}\) compositions (see Figure 3). After hydrogenation at 400ºC most of the material was converted into highly hydrogenated species with rather broad mass distribution with the most abundant atoms at C\(_{60}\)H\(_{36}\), C\(_{60}\)H\(_{44}\), C\(_{60}\)H\(_{52}\), and C\(_{60}\)H\(_{18}\). Moreover, the spectrum showed minor fraction of fragmented fullerenes with a loss of 1-2 carbon atoms of the C\(_{60}\) cage, the most abundant ion corresponding to C\(_{59}\)H\(_{44}\). Mass spectrum of the sample hydrogenated at 420ºC showed peaks mostly from fragmented fullerenes, e.g., C\(_{59}\)H\(_{44}\), C\(_{59}\)H\(_{42}\), C\(_{58}\)H\(_{44}\), and C\(_{58}\)H\(_{42}\).

The sample hydrogenated at 440ºC had a similar mass spectrum but the material showed higher degree of fragmentation. Analysis of the MS data shows that some hydrogenated fullerenes prevailed at certain synthesis conditions while others were not observed. For example, C\(_{60}\)H\(_{18}\) was synthesized at 350ºC while higher temperature of 375ºC was needed in order to start the synthesis of C\(_{60}\)H\(_{36}\) or C\(_{60}\)H\(_{44}\) (Figure 3). All other hydrogenated fullerenes had substantially lower abundance. Therefore, we consider C\(_{60}\)H\(_{18}\) as the first step of hydrogenation. Upon increase of the synthesis temperature up to 375ºC additional peaks assigned to C\(_{60}\)H\(_{36}\) and C\(_{60}\)H\(_{44}\) appeared in the mass spectrum while other peaks were significantly less pronounced. We assume that C\(_{60}\)H\(_{36}\) is the second major step in the hydrogenation of fullerenes and formation of...
C\textsubscript{60}H\textsubscript{44} is the third main step. As it could be seen in Figure 3 C\textsubscript{60}H\textsubscript{18} was almost completely transformed into C\textsubscript{60}H\textsubscript{36} and C\textsubscript{60}H\textsubscript{44} upon hydrogenation at 400°C. Moreover, a new strong peak due to C\textsubscript{60}H\textsubscript{52} was found in the mass spectrum which we consider as forth main step in hydrogenation. Hydrogenated fullerenes with number of hydrogen atoms up to 56 were observed in mass spectra but with rather low abundance.

Therefore, we assume that synthesis of C\textsubscript{60}H\textsubscript{52} is critical step in the hydrogenation of fullerenes, and further hydrogenation is either not possible or (most likely) results in a collapse of the fullerene cage. The main steps of the hydrogenation reaction of C\textsubscript{60} can be summarized as following:

\[
\text{C}_{60} \rightarrow \text{C}_{60}\text{H}_{18} \rightarrow \text{C}_{60}\text{H}_{36} \rightarrow \text{C}_{60}\text{H}_{44} \rightarrow \text{C}_{60}\text{H}_{52}.
\]

In principle, synthesis of reasonably pure C\textsubscript{60}H\textsubscript{52} could be expected after sufficiently long duration of hydrogenation reaction following chain of reaction suggested above. However, synthesis of final products of the chain is complicated by a “side reaction” of fullerene cage fragmentation which starts for C\textsubscript{60}H\textsubscript{x} with X over 36. Using the mass spectrum of the sample hydrogenated at 440°C we propose two fragmentations models. Those models suggest reforming some dangling bonds (formed when carbon atom is taken off the cage) into new C-C bonds (models are summarized in Figure 4).

First proposed fragmentation pathway (see Figure 4, top) suggests to explain the loss of a single carbon atoms while keeping the same number of hydrogen atoms (e.g., from C\textsubscript{60}H\textsubscript{44} to C\textsubscript{59}H\textsubscript{44}). This reaction can be performed either in one step (1) or in two steps (2, 3) with the same final product. Second possible fragmentation pathway suggests slightly different consequence of dangling bond reformation (see Figure 4).
As it was observed in our previous experiments the fragmentation of fullerenes always could be described by the total loss of either –C or –CH$_2$ [10]. Both pathways 1 and 2 proposed in this study would satisfy observed results. Additional experiments are required to establish which fragmentation mechanism (or may be both of them) is valid for a certain hydrogenation reaction of C$_{60}$.
CONCLUSIONS

The reaction of solid C$_{60}$ with hydrogen gas was studied in situ and ex situ in the temperature interval of 350ºC-440ºC and at 50 bar of hydrogen pressure. Advantages of in situ monitoring of hydrogenation reactions using gravimetric method are demonstrated. A set of hydrogenated fullerenes with different content of hydrogen was prepared and main products of reaction analyzed. Despite rather broad distribution of hydrofullerene compositions, some of the products had significantly higher abundance which allowed suggesting the following reaction pathway: C$_{60}$ → C$_{60}$H$_{18}$ → C$_{60}$H$_{36}$ → C$_{60}$H$_{44}$ → C$_{60}$H$_{52}$. Prolonged hydrogenation at 400ºC-440ºC resulted in the fullerene cage fragmentation and formation of hydrogenated fragmented fullerenes. Several mechanisms of fragmentation with the loss of up to 7 carbon atoms were discussed.

REFERENCES

INTERACTION BETWEEN NUCLEOSIDE AND NUCLEOTIDE WITH CARBON NANOTUBES

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ABSTRACT
Carbon nanotubes (CNTs) possess a number of unique properties; they are successfully applied as fillers for improving the mechanical, electric, thermophysical, and optical properties of composite materials. At present, CNTs are intensively used in the development of biosensor devices and materials designed for pharmaceutics and diagnostics. Functionalization of CNT surfaces with molecules playing important roles in biological processes, including proteinforming peptides, nucleic acids, etc., makes it possible to produce new systems capable of identifying biological objects. CNT surface can serve as a platform for the targeted transport of different molecules, including drugs (antibiotics or protein). Efficiency of this transport is governed by the unique adsorption ability of CNTs and the specific interaction of molecules with their surface.

The idea of this work was to investigate the adsorption of a number of biological molecules with different numbers of phosphate groups from aqueous solutions onto the surface of multiwall CNTs. Adsorption isotherms for adsorbate concentration range C = 0–10⁻³ mol/dm³ were plotted.

Experimentally observed positive adsorption of adenosine (AN), adenosine triphosphate (ATP), and adenosine monophosphate (AMP) from aqueous solutions onto the surface of multiwall CNTs takes place because of the presence of adenine fragments in the studied com-pounds. At the same time, the data obtained indicate that, in the case of monomolecular adsorption, the molecular packing is rather loose and the packing density is higher for compounds containing phosphate groups. The observed behavior of the adsorbates seems to reflect the intensification of lateral interactions in the adsorption layers. In the region of polymolecular adsorption at high adsorbate concentrations in solutions (C > (5–6) × 10⁻⁴ mol/dm³), the adsorption reduced in a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these com-pounds in water.

Key words: adenosine, AMP, ATP, carbon nanotube, adsorption isotherm

INTRODUCTION
Carbon nanotubes (CNTs) possess a number of unique properties; they are successfully applied as fillers for improving the mechanical, electric, thermo-

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physical, and optical properties of composite materials [1]. At present, CNTs are intensively used in the development of biosensor devices and materials designed for pharmaceutics and diagnostics [2–4]. The functionalization of CNT surfaces with molecules playing important roles in biological processes, including proteinforming peptides, nucleic acids, etc., makes it possible to produce new systems capable of identifying biological objects [5]. A CNT surface can serve as a platform for the targeted transport of different molecules, including drugs (antibiotics or protein). The efficiency of this transport is governed by the unique adsorption ability of CNTs [7] and the specific interaction of such molecules with their surface [2].

**EXPERIMENTAL**

AN, AMP, and ATP produced by Sigma-Aldrich Co. (the United States) were applied in the experiments.

Multiwall CNTs (Spetsmash, Ukraine) had a specific surface area of 190 m$^2$/g, a diameter of 10–30 nm, a length of 1–10 µm, and a content of mineral impurities of less than 1% [9]. AN, AMP, and ATP were adsorbed from an aqueous physiological solution (infusion solution with NaCl concentration of 0.9 wt %, Novofarm-Biosintez, Ukraine). Initial samples of adsorbate solutions were prepared by the gravimetric method with following dilution. The adsorption was performed in dark at 293 K and were continuously stirred on a water bath shaker.

The concentration of biomolecules was measured spectrophotometrically with a Specord UV Vis spectrophotometer (Germany). Spectra were registered in the wavelength $\lambda = 250–357$ nm with the absorption maximum at $\lambda = 260$ nm.

The initial region of a adsorption isotherms (in the range of the monolayer filling) was approximated by the Langmuir equation.

The surface area per a molecule was found from the relation $s = A/a_mN_A$, where $A$ is the specific surface area of nanotubes occupied by an adsorbate and $N_A$ is Avogadro’s number.

**RESULTS AND DISCUSSION**

Typical time dependences of the normalized values $a/a_x$ for AN, AMP and ATP adsorption on CNTs are presented in Fig. 1. Here, $a_x$ corresponds to the adsorption value at $t \to \infty$, and all dependences are obtained for initial solution concentrations $C$ of approximately $2.3 \times 10^{-4}$ mol/dm$^3$. Similar $a(t)/a_x$ dependences were observed for other $C$ values.

As a rule, adsorption equilibrium was established within 1 h. Note that, during 2 h, the equilibrium of the reversible hydrolysis of AMP and ATP remained nonshifted, thus indicating a relative stability of the examined biomolecules in aqueous solutions.
Figure 2 illustrates the isotherms of AN, AMP and ATP adsorption measured at room temperature. The initial regions of the isotherms correspond to the process of the formation of adsorbate monolayers on the CNT surface. When equilibrium concentration \( i \) is increased to the value that corresponds to the complete CNT surface coverage with the monolayer of a substance, a horizontal region is observed. As the adsorbate concentration in a solution is further increased, all three substances exhibit the behavior typical of polymolecular adsorption [10] (Fig. 2).

In the case of AN, the onset of the monolayer formation is observed at lower concentrations than for AMP and ATP. Polymolecular layers of AN, ATP and AMP are formed at \( C > 2.5 \times 10^{-4}, 3.5 \times 10^{-4} \) and \( 4.5 \times 10^{-4} \) mol/dm\(^3\). The longest horizontal region of the monomolecular adsorption is observed for AMP (\( n = 1 \)), thus indicating the most complete coverage of the CNT surface with the adsorbate monolayer; for AN (\( n = 0 \)) and ATP (\( n = 3 \)) shorter regions are seen. Table 1 presents the calculated values of the surface areas per a molecule \( s \) and free energy \( G \), which characterize the monomolecular adsorption of the examined biomolecules.

Table 1. Surface areas \( s \) per a molecule and standard adsorption free energies \( G \) for AN, AMP, and ATP molecules on CNT surface

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>( s ), nm(^2)</th>
<th>( k \times 10^{-3} )</th>
<th>-( G ), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>1.80±0.17</td>
<td>4.13±0.21</td>
<td>31.5±0.1</td>
</tr>
<tr>
<td>AMP</td>
<td>1.50±0.12</td>
<td>1.71±0.18</td>
<td>29.4±0.2</td>
</tr>
<tr>
<td>ATP</td>
<td>1.71±0.15</td>
<td>1.65±0.20</td>
<td>29.3±0.1</td>
</tr>
</tbody>
</table>
After the CNT surface is completely covered with an adsorbate layer, the adsorption value spiked. A further increase in C causes the appearance of additional horizontal regions that seem to reflect the formation of adsorption bilayers, etc. (Fig. 2). At higher C values, a increases with C.

The studied compounds are amphiphilic, and their hydrophobic–hydrophilic balance is governed by the size ratio between adenosine and phosphate fragments. Hence, AN, AMP, and ATP are adsorbed on the hydrophobic surface via the adenine fragments, which have a relatively high hydrophobicity parameter \( \log P = -0.3 \) [11]. The decrease in the adsorption free energy in the aforementioned series of the biomolecules in the initial regions of the isotherms (Table 1), which is symbate to the increase in the solubility, confirms this conclusion.

At high concentrations of adsorbate solutions (\( C > (5–6) \times 10^{-4} \) mol/dm³), the adsorption diminished in a series AN > AMP > ATP, with the weakest a(C) dependence being observed for ATP. This character of the polymolecular adsorption absolutely corresponds to the enchance in the hydrophilicity and solubility of these compounds in the aforementioned series.

Note that the obtained surface areas \( s \) per molecules of AN and AMP exceed the theoretically estimated value of the total area of the largest molecule (ATP), which is equal to nearly 1.0–1.2 nm² [12]. Hence, the molecular packing of AN and AMP on the CNT surface in the case of the monomolecular coverage is rather loose. This fact seems to reflect the peculiarities of the interaction between adenine fragments of these biomolecules and the aromatic surface of CNTs.

Taking into account that AN molecules have the smallest areas, it may also be concluded that the packing of this adsorbate molecules on the CNT surface is loosest. The analysis of the chemical shifts in the \(^1H\) NMR spectra of adenine and D-ribose fragments [8] led us to conclude that hydrophobic and \( \pi-\pi \) interactions take place between adenine fragments and CNT surface. The denser packing of AMP and ATP molecules in the adsorption monolayers may be assumed to reflect a stronger lateral attraction between molecules of these adsorbates compared to AN molecules due to the appearance and elongation of the phosphate fragment. The differences in the character of the polymolecular adsorption that are observed for AN, ATP, and AMP (Fig. 2) are likely to reflect the differences in the character of their molecular association in aqueous solutions.

**CONCLUSIONS**

The experimentally observed positive adsorption of AN, ATP, and AMP from aqueous solutions on the surface of multiwall CNTs takes place because of the presence of adenine fragments in the studied compounds. At the same time, the data obtained indicate that, in the case of monomolecular adsorption, the
molecular packing is rather loose and the packing density is higher for compounds containing phosphate groups. The observed behavior of the adsorbates seems to reflect the intensification of lateral interactions in the adsorption layers. In the region of polymolecular adsorption at high absorbate concentrations in solutions (C > (5–6) × 10^{-4} \text{ mol/dm}^3), the adsorption reduces in a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these compounds in water.

REFERENCES
EXCIPLEXES OF FULLERENE C\textsubscript{60} WITH AROMATIC SOLVENTS

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ABSTRACT

The solvent induced spectral shift method is applied to study stacking interactions between aromatic solvents molecules, such as benzene and toluene from one side, and solute fullerene C\textsubscript{60}. Ratios of high-energy transitions shifts to calculated shifts under dispersion interactions are considered. It is concluded that in contrast to aromatic molecules containing two or three rings which do not form complexes with aromatic solvents, fullerene forms exciplexes with high-energy excited states involved in more strong interactions rather than low-energy one. The higher is excited state, the stronger is interaction.

Key words: fullerene C\textsubscript{60}, exciplexes with aromatics, spectral shift in a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these compounds in water.

INTRODUCTION

Recently we have shown [1, 2] that apolar aromatics with a few rings, such as naphthalene, phenanthrene and anthracene, do not demonstrate symptoms of stacking interactions with aromatic solvents. Fullerene C\textsubscript{60} has more complex system of conjugated bonds than any of mentioned molecules. So, it looks interesting to know, if molecule C\textsubscript{60} posses the same property. The study carries out with spectral shift method.

SOLVENT INDUCED SPECTRAL SHIFT

A shift of an electronic spectrum of molecules in a solvent from the spectrum in the gas phase is:

\[ \Delta \nu = \Delta \nu_{\text{disp}} + \Delta \nu_{\text{elst}} + \Delta \nu_{\text{oth}}, \]  

where \( \Delta \nu_{\text{disp}} = -C(\alpha_i - \alpha_0)\phi(R, r)f(n) \), \( C \) is a positive factor dependent on solute properties, \( \alpha \) is polarizability of the solute in the \( i \)-th or in the \( 0 \)-th electronic states, \( \phi(R, r) \) is a geometrical factor, it is \( R^3/[r^3(2R - r)^3] \) in the quasi spherical approximation, \( R \) is an effective radius of the cavity occupied by a

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solute molecule whose effective radius is \( r \), \( f(n) = (n^2 - 1)/(n^2 + 2) \), \( n \) is refractive index of solvent, \( \Delta v_{\text{elst}} = -0.5(\alpha_i - \alpha_0)\Sigma E_k \), \( E_k \) is electric field created by the k-th origin (ion, dipole,...) on the solute, and \( \Delta v_{\text{oth}} \) is a contribution of all other sources into the shift. Eq. (1) is valid when the electronic state in consideration does not depend on other ones. It is readily seen from Eq. (1) that for different electronic transitions of an apolar molecule

\[
\eta = \Delta v_0/\Delta v_0 = (\alpha_i - \alpha_0)/(\alpha_i - \alpha_0)
\]

if \( \Delta v_{\text{oth}} = 0 \).

One may rewrite equation for the shift

\[
\Delta v = -C_kf(n) + \Delta v_{\text{elst}} + \Delta v_{\text{oth}}
\]

in the cases when \( R \) keeps constant for all solvents in study. Here \( k \) indicates the transition in consideration. So it is expedient to compare relations

\[
\eta_k = \Delta v_k/[-C_kf(n)]
\]

EXPERIMENTAL

Spectrophotometers Specord UV Vis (Germany) and Perkin Elmer lambda 3S (UK) were used for recording spectra. Fullerene was produced in Institute of Surface Chemistry NASU. Solvents of chemical grade were made in Novocherkassk Chemical Plant (Russia).

RESULTS AND DISCUSSION

As it is shown in ref. [3], aromatic molecules dissolved in n-alkanes show linear dependence of \( \nu \) on solvent function \( f(n) \) which extrapolates to wave number in the gas phase at temperature of solvents. Similar dependences for some bands of \( C_{60} \) electronic spectrum are as follows. Assignment is taken from ref. [4].

Band \( \gamma_0 \), transition \( 1^1T_{1g} \leftarrow 1^1A_g^\prime \): \( \nu_{\gamma0} = -1363.3f(n) + 16444 \) cm\(^{-1}\), correlation factor \( \rho = 0.998 \), root-mean-square uncertainty for the factor at \( f(n) \), \( \sigma_\nu = 88.8 \) cm\(^{-1}\), and the similar value for free term, \( \sigma_B = 22 \) cm\(^{-1}\).

Band \( \gamma_2 \), \( 1^1T_{1g} \leftarrow 1^1A_g \) or \( 1^1T_{1u} \leftarrow 1^1A_g^\prime \): \( \nu_{\gamma2} = -1463.5f(n) + 17064 \) cm\(^{-1}\), \( \rho = 0.998 \), \( \sigma_\nu = 99.3 \) cm\(^{-1}\), \( \sigma_B = 24.4 \) cm\(^{-1}\).

Band \( \gamma_3 \), \( 1^1T_{1g} \leftarrow 1^1A_g \) or \( 1^1T_{2g} \leftarrow 1^1A_g^\prime \): \( \nu_{\gamma3} = -1695.9f(n) + 17341 \) cm\(^{-1}\), \( \rho = 0.999 \), \( \sigma_\nu = 86.6 \) cm\(^{-1}\), \( \sigma_B = 21 \) cm\(^{-1}\).

Two last bands are prominent enough for watching them. Nevertheless, they merge together due to broadening under aromatic solvent influence (Fig. 1). Therefore we use a half of the sum of these bands frequencies for comparison maxima positions of broadened bands:
\[ v_{23} = \frac{(v_2 + v_3)}{2} = -1579.7f(n) + 17202.5 \text{ cm}^{-1} \]

Band A, \( ^1T_{1u} \leftarrow ^1A_g \): \( v_{A1} = -1616f(n) + 25182 \text{ cm}^{-1}, \rho = 0.992, \sigma_A = 201.7 \text{ cm}^{-1}, \sigma_B = 49 \text{ cm}^{-1} \).

Band C, \( ^3T_{1u} \leftarrow ^1A_g \): \( v_C = -2490.9f(n) + 31122 \text{ cm}^{-1}, \rho = 0.999, \sigma_A = 95 \text{ cm}^{-1}, \text{ and } \sigma_B = 23 \text{ cm}^{-1} \).

One can see from the Table that all values of \( \eta_g \) equal to unity with uncertainty which does not exceed 0.001. This fact means that all interactions between solutes and solvents except for dispersion ones may be neglected for this transition.

Table – Spectral shifts and ratios \( \eta_k = \Delta v_k/[Cf(n)] \)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(-\Delta v_{g23}, \text{ cm}^{-1})</th>
<th>(-A_g f(n), \text{ cm}^{-1})</th>
<th>(\eta_g)</th>
<th>(-\Delta v_{A1}, \text{ cm}^{-1})</th>
<th>(-A_{A1} f(n), \text{ cm}^{-1})</th>
<th>(\eta_{A1})</th>
<th>(-\Delta v_C, \text{ cm}^{-1})</th>
<th>(A_C f(n), \text{ cm}^{-1})</th>
<th>(\eta_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₅H₁₂</td>
<td>346</td>
<td>346.4</td>
<td>0.999</td>
<td>352</td>
<td>354.4</td>
<td>0.993</td>
<td>547.5</td>
<td>546.3</td>
<td>1.002</td>
</tr>
<tr>
<td>n-C₆H₁₄</td>
<td>362</td>
<td>361.7</td>
<td>1.001</td>
<td>372</td>
<td>370.1</td>
<td>1.005</td>
<td>568.5</td>
<td>570.4</td>
<td>0.997</td>
</tr>
<tr>
<td>n-C₇H₁₆</td>
<td>372</td>
<td>372.5</td>
<td>0.999</td>
<td>383</td>
<td>381.1</td>
<td>1.005</td>
<td>589</td>
<td>587.4</td>
<td>1.003</td>
</tr>
<tr>
<td>n-C₈H₁₈</td>
<td>381</td>
<td>381</td>
<td>1.000</td>
<td>393.5</td>
<td>389.6</td>
<td>1.010</td>
<td>599.5</td>
<td>600.6</td>
<td>0.998</td>
</tr>
<tr>
<td>n-C₁₀H₂₂</td>
<td>392</td>
<td>391.6</td>
<td>1.001</td>
<td>397</td>
<td>400.6</td>
<td>0.991</td>
<td>616.5</td>
<td>617.5</td>
<td>0.998</td>
</tr>
<tr>
<td>n-C₁₁H₂₄</td>
<td>397</td>
<td>397.4</td>
<td>0.999</td>
<td>403.5</td>
<td>406.6</td>
<td>0.992</td>
<td>627.5</td>
<td>626.7</td>
<td>1.001</td>
</tr>
<tr>
<td>n-C₁₃H₂₈</td>
<td>404</td>
<td>403.9</td>
<td>1.000</td>
<td>415</td>
<td>413.2</td>
<td>1.004</td>
<td>636</td>
<td>636.9</td>
<td>0.999</td>
</tr>
<tr>
<td>n-C₁₅H₃₂</td>
<td>410</td>
<td>409.8</td>
<td>1.001</td>
<td>420</td>
<td>419.2</td>
<td>1.002</td>
<td>647.5</td>
<td>646.1</td>
<td>1.002</td>
</tr>
<tr>
<td>c-C₆H₁₂</td>
<td>405</td>
<td>405.2</td>
<td>1.000</td>
<td>412</td>
<td>414.5</td>
<td>0.994</td>
<td>643</td>
<td>638.9</td>
<td>1.006</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>466</td>
<td>465.8</td>
<td>1.000</td>
<td>558</td>
<td>476.6</td>
<td>1.171</td>
<td>1187</td>
<td>724.6</td>
<td>1.616</td>
</tr>
<tr>
<td>C₆H₄CH₃</td>
<td>465</td>
<td>461.4</td>
<td>0.999</td>
<td>565</td>
<td>472</td>
<td>1.197</td>
<td>1214</td>
<td>727.6</td>
<td>1.669</td>
</tr>
</tbody>
</table>
One can readily see from the table that high-energy transitions suffer additional shifts under aromatic solvents influence comparing to those under n-alkanes. The higher electronic level is situated, the higher the addition is. So, interaction affects rather upper states then lower ones. Hence the staking interaction consists in formation of exciplexes in high-energy states.

REFERENCES

POSITRON LIFETIME AND COINCIDENCE DOPPLER BROADENING STUDIES OF GRAPHENE OXIDE – POLYANILINE NANOCOMPOSITE

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ABSTRACT

In this work, we report about the results of a detailed investigation comprising of measurements of positron lifetimes and coincidence Doppler broadening of the electron-positron annihilation gamma ray spectra on graphene oxide – polyaniline nanocomposite samples prepared with different ratios of weight and at different temperatures. The two experimental techniques are capable of providing information respectively on the electron density and momentum distribution at the specific sites of annihilation. This makes them effective in identifying the different types of defects present in the composite matrix. The magnitudes of the positron lifetimes were commensurate with the expectation of very large size defects in the form of vacancy clusters within the atomic composition of the composite material. The average defect size apparently reduced when the relative abundance of polyaniline increased that led to increased reduction of graphene oxide to graphene. The reduction also resulted in the shrinkage of the graphene oxide matrix and the free volume thereby released added to the overall defect concentration. The variation of the positron lifetime and its intensity with the temperature of synthesis suggested an optimum temperature suitable for the process.

Keywords: graphene, polyaniline, defects, vacancy clusters, positron annihilation, nanocomposites.

INTRODUCTION

Graphene, the enchanting monolayer of graphite, is fast growing as a material of great scientific importance due to the high promises it holds for technological applications [1, 2]. Research using a number of experimental techniques is rapidly progressing with a view to explore its many versatilities and many of these studies have already poured in very exciting information on its structural aspects and remarkable properties.

With a single monolayer composition and the necessity to have atomic arrangement as perfect as possible, it is often required to detect and characterize the structural defects in the graphene or graphene-related systems with preci-
sion and accuracy. Positron annihilation is the best option as it has the potential to reflect the electronic environment around vacancy-type defects through measurable changes in the energy and momentum of the annihilation gamma rays [3]. The lifetime of a positron emitted from a radioactive source (say, for example, 22Na) and simultaneously entering into a material medium is related to the density of electrons through the relation

\[ \tau = \left( \frac{\pi r_0^2 c \xi n_e}{2} \right)^{-1} \]  

(1)

where \(r_0\) is the classical electron radius, \(c\) is the velocity of light and \(n_e\) is the electron density at the site of annihilation. \(\xi\) accounts for the local enhancement in the electron density due to Coulomb interaction between the positron and the neighbouring electrons before it eventually gets annihilated by one of them.

The gamma rays resulting from electron-positron annihilation normally experiences Doppler shift due to the momentum of the electron and hence the 511 keV gamma ray spectrum recorded using a high pure Ge detector will suffer from broadening and the lineshape of the spectrum will represent the electron momentum distribution in the material [3].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Graphene oxide (GO), bearing oxygen functional groups on the basal planes and edges of graphene, have been used for the preparation of graphene oxide – polyaniline (PANI) composite with different relative abundances. The weight of PANI was fixed as 102 mg and graphene oxide in different amounts, viz., 51, 26, 10.2, 5.1 and 1 mg, were used for preparing samples of the different compositions. The relative abundance \((x)\) is calculated as the percentage by weight of PANI. Thus, five samples with \(x = 66.7, 80, 90.9, 95.2\) and 99% were prepared in one set. The reaction temperature had been 268K. In another set, samples with \(x = 90.9\%\) were prepared at three more different temperatures, viz., 283, 298 and 313K. All the samples were studied using different experimental techniques such as electrochemical analysis, X-ray diffraction and Raman spectroscopy. For positron annihilation measurements, a 22Na radioactive source taken within a ultra-thin Ni foil was sandwiched by the sample sheets. The sandwich as a whole was further sandwiched by two Si pellets to prevent the positrons from escaping into air. To prevent moisture condensation and gas absorption, the sandwich as a whole was kept under vacuum (~ \(10^{-3}\) mbar) while data were acquired for prolonged intervals of time. Positron lifetime measurements were done using a gamma-gamma coincidence spectrometer with prompt time resolution (full width at half maximum) 180 ps. The contributions from the source material (22NaCl), the supporting foil (Ni) and the backing Si samples were carefully estimated and removed before the spectrum were
analyzed for the different positron lifetimes in the sample [4]. Coincidence Doppler broadening measurements were carried out using two high pure Ge detectors with resolution 1.2 keV at 511 keV [5].

**RESULTS AND DISCUSSION**

The positron lifetime spectra due to annihilations taking place within the graphene oxide – PANI nanocomposite samples gave two lifetimes $\tau_1$ and $\tau_2$ (with relative intensities $I_1$ and $I_2$) in which the latter is a true representation of the nature and size of the predominant positron trapping site present in the sample. The first component $\tau_1$ is described in positron literature as an admixture of the bulk positron lifetime ($\tau_b$) and the Bloch state residence time ($\tau_n$), as a result of which $\tau_1 < \tau_n$. Since an ideal sample with absolutely no defects in it even in trace amounts is difficult to achieve, an estimate of $\tau_b$ can be obtained from the trapping model equation [3]

$$\tau_b = \frac{\tau_1 \tau_2}{\tau_1 I_2 + \tau_2 I_1} \tag{2}$$

Initially a sample was prepared by reducing the graphene oxide to graphene and then using it to make the composite with PANI. In this case, we obtained $\tau_1 = 63$ ps and $\tau_2 = 402$ ps (with relative intensities $I_1 = 30.9\%$ and $I_2 = 69.1\%$). Using the above equation (2), we get $\tau_b = 151$ ps. Although this is lower than that for crystalline graphite (215-225 ps [6]), it is consistent with that obtained in a similar way for multi-wall carbon nanotube-embedded polyacrylonitrile samples [7]. More important is the presence of a very large defect-characteristic lifetime $\tau_2$ of 402 ps with a large intensity $I_2 = 69.1\%$. This indicates a high defect concentration of the vacancy cluster-type within the composite.

As the relative abundance of PANI increased, $\tau_2$ got reduced, as shown in fig. 1a. The positron lifetime in pure PANI has been reported as between 360-380 ps [8]. The combined positron lifetime will decrease with increasing percentage of PANI. What is noteworthy is an enhancement in $I_2$ (fig. 1), which is not unexpected since PANI itself is of a structure that has rich concentration of free volume defects associated with it. With increasing abundance of PANI, more positrons may get trapped in these defects. Further that PANI has the ability to reduce graphene oxide to graphene also contributes to shrinkage in the occupied volume whereby free volume cavities are generated within the PANI matrix. Both these factors must have resulted in the increase in $I_2$.

It may be mentioned that a third positron lifetime $\tau_3$ (~ 2 - 5 ns) also resulted in the analysis. This was attributable to the formation of positronium atoms, which are metastable bound states of one electron and positron each [3]. This happens within the free volume defects in PANI but, since the intensities of this component were negligibly small (< 1%), it is not further discussed.
Fig. 1 – (a) The defect-characteristic positron lifetime $\tau_2$ and its intensity $I_2$ versus $x$. (b) The variations of the two parameters with sample preparation temperature.

The coincidence Doppler broadening measurements help to suggest the relative variation in the annihilation of positrons with electrons of different elements present in a sample matrix. Fig. 2 shows the characteristic peak of annihilation with carbon electrons. The peaks appear at an electron momentum $p_L = 9.8 \times 10^{-3} m_0 c$ ($m_0$ is the electron mass) whereas the intensities of the peaks display variations with samples changing their PANI abundance ($x$).

Fig. 2 – The ratio curves obtained from coincidence Doppler broadening spectra of some of the samples.
Finally, we also performed measurements in a few samples with fixed $x (= 90.9\%)$ but synthesized at different temperatures. In this case, we found an initial decrease followed by a substantial increase in both the lifetime $\tau$ and intensity $I_2$ (Fig. 2). While the temperature helps in migrating and condensing isolated smaller vacancies with the existing larger vacancy clusters, thereby directly enhancing the value of the positron lifetime, the corresponding rise in $I_2$ is incomprehensible as it points towards the production of additional defects. These and additional details are currently under serious consideration and need better understanding through advanced measurements and analysis.

**CONCLUSIONS**

Positron annihilation spectroscopy is rather unusual but innovative for novel material systems. In one of the very few attempts made so far to study graphene systems using defect spectroscopic techniques, we report in this paper the results of conventional positron lifetime measurements in graphene oxide – PANI composite to understand the types of defects inherently built in it. Notwithstanding the controlled experimental conditions including ambient temperatures used in the preparation, we observed very large lifetimes for positrons injected into the samples indicating the presence of void-like cavities. With increasing abundance of PANi in the nanocomposite, there is a distinct reduction of positron lifetime and the generation of additional defects. It indicates the shrinkage when graphene oxide is successfully reduced to graphene by the reducing agent. The observations also call for more stringent methods of experimentation while synthesizing such samples for spectroscopic investigation. The variation arising from difference in sample preparation temperature is also to be noted, since it points towards an optimum reaction temperature, say for example, 283K in this case (fig. 1b).

**REFERENCES**

THE ANALYSIS OF THE ELASTIC PROPERTIES OF ARMCHAIR AND ZIGZAG SINGLE-WALLED CARBON NANOTUBES

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ABSTRACT

Computational simulation is a powerful tool for predicting the mechanical properties of carbon nanotubes. In this paper we present analytical molecular mechanics models of elastic properties of armchair and zigzag single-walled nanotubes. The aim of this work is investigation and comparison of Young’s modulus, shear modulus and Poisson’s ratio variations of armchair and zigzag tubes as functions of diameter. We obtained a set of concise, closed-form expressions for the size-dependent elastic modulus, shear modulus and Poisson’s ratio of armchair \((n, n)\) and zigzag \((n, 0)\) nanotubes, which are basic for constructing mathematical models of elastic properties of SWNTs. We investigated armchair nanotubes with chirality \((3, 3)–(40, 40)\) and zigzag \((3, 0)–(40, 0)\) with diameters \(4.2–54.2\ \text{Å}\) and \(2.4–31.3\ \text{Å}\) respectively. We calculated Young’s modulus to be \(0.26–2.95\ \text{TPa}\) for armchair and \(0.5–3.7\ \text{TPa}\) for zigzag nanotubes. The shear modulus calculated for armchair nanotube appeared to be in the range of \(0.2–2.0\ \text{TPa}\) and for zigzag one in the range of \(0.2–2.7\ \text{TPa}\). Specifically, it was inverse dependences of Young’s modulus and shear modulus on diameter. The Poisson’s ratio was in range from \(0.28\) to \(0.42\) and from \(0.27\) to \(0.39\), respectively. Results of this research can be used for design, analysis and evaluating of nanotubes functioning and creating new materials based on CNTs.

Key words: carbon nanotubes, Young’s modulus, shear modulus, Poisson’s ratio

INTRODUCTION

The advancement of science and technology has evolved into the era of nanotechnology. Carbon nanotubes (CNTs) have stimulated great interest and extensive research with regard to the measurement of their exact mechanical properties [1, 2] and the search for potential structural applications [1] ever since their discovery by Iijima [3].

Specific characteristics, such as the exceptionally high stiffness and strength, which are in the range of TPa, the extreme resilience, the ability to sustain large elastic strain as well as the high aspect ratio and low density [1, 4], make CNTs the ideal reinforcing material for a new class of superstrong nanocomposites. That is why the accurate assessment of the mechanical properties

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of the nanotubes is an important first step towards the potential development of the structural composites. Investigation of the properties of those structures has a lot of experimental difficulties arising from their nanoscale, necessity for complicated and expensive equipment and apparatus with large resolution. Computational simulation is a powerful tool relative to the experimental difficulties. In this paper we present two mathematical models, based on classical mechanics and molecular mechanics approach, for investigating the difference between properties of armchair and zigzag single-walled CNTs (SWNTs).

**METHODS OF INVESTIGATION**

The methods of molecular dynamics (MD) and molecular mechanics (MM) based on the molecular nature of nanotube structure are often used for simulation [4-6] of their mechanical properties. In this work we used MM approach based on modern continuum mechanics and elasticity theory. It allows to calculate the geometry of the frame with sufficient accuracy and to model some physical processes in nanotubes under influence of external factors: the deforming forces, external electromagnetic fields, etc.

We used some basics of molecular mechanics [4, 5] which is based on the concept of molecular force field for this investigation. This approach was based on a link between molecular and solid mechanics. Using the harmonic energy functions the nanotube was modeled as a frame structure and a closed-form elastic solution was obtained.

Let $a_1$ and $a_2$ be unit vectors of the two-dimensional graphene sheet, $(n, m)$ be a pair of integers that indexes the atomic structure of CNT uniquely determining the size of the SWNT. Then a pair $(n, m)$ corresponds to a lattice vector $C_h = na_1 + ma_2$ on the graphite plane. If $m = 0$, then such a tube is called zigzag, and when $n = m$ it is an armchair tube. Based on rolling graphene sheer model the diameter $D$ of nanotube can be determined as follows:

$$D = \frac{\sqrt{3}b}{\pi} \sqrt{(n^2 + m^2 + mn)},$$  \hspace{1cm} (1)

where $b$ is the carbon-to-carbon bond length. This parameter was taken as 0,66 Å [4].

For armchair and zigzag tubes diameter is equal to $D_1$ and $D_2$ respectively:

$$D_1 = \frac{3bn^2}{\pi}, \quad D_2 = \frac{\sqrt{3}bn}{\pi}. \hspace{1cm} (2)$$

Given the effective wall thickness $t$ of SWNTs which corresponds to the thickness of the graphene layer, the effective diameter $D_{\text{eff}}$ is equal to $D_{\text{eff}} = D_i + t$, where the parameter $D_i (i = 1, 2)$ is taken by $D_1$ for an armchair tube, and $D_2$ for a zigzag tube. Effective thickness $t$ was taken as 0,66 Å [4].
We have analyzed the forces and geometrical relations for an armchair tube. Also we have used the assumption that all atomic interactions in a molecular structure of nanotubes satisfy the potential laws, so they can be described by using molecular mechanics. Regarding aforementioned we have build the following relations which comprise our model.

Young’s modulus of armchair and zigzag nanotubes is expressed as follows:

\[ E = \frac{\lambda_i K^\theta K^\rho}{3b^2 K^\rho + 9\lambda K^\theta} \left( \frac{16\sqrt{3}D_i}{D_{eff}} \right), \]

where parameters \( \lambda_i, D_i, D_{eff} \) (i = 1, 2) are taken by \( \lambda_1, D_1, D_{eff 1} \) for an armchair tube, and \( \lambda_2, D_2, D_{eff 2} \) for a zigzag tube; \( \lambda_i \) is the elongation, equaled to the ratio of total nanotubes elongation \( \delta l \) to its length \( l_0 \) before deformation:

\[ \lambda_i = \frac{16 + 2\cos^2 \gamma}{4 - 3\cos^2 \gamma}, \]

where \( K^\rho, K^\theta \) are force constants, which depend on the force field. \( K^\rho = 97800 \) kcal/mole/nm2, \( K^\theta = 126 \) kcal/mole/rad2, \( \gamma = \pi/2n \) is the angle, related to the curvature effect.

Shear modulus is given by

\[ G = \frac{D_{eff i}^{\frac{4}{3}} - 16 \left( \frac{D_{eff i}}{2} - t \right)^4}{tD_{eff i}^4} \left( \frac{\sqrt{3}}{b^2 K^\rho + \lambda K^\theta} \right). \]

Poisson’s ratio is defined as:

\[ \nu = \frac{b^2 K^\rho - \lambda_i K^\theta}{b^2 K^\rho + 3\lambda_i K^\theta}. \]

Mathematical models of elastic properties of armchair and zigzag tubes have been obtained in the form of equations (2), (3), (5) and (6) with taken \( i = 1 \) for an armchair tube, and \( i = 2 \) for a zigzag tube.

**RESULTS AND DISCUSSION**

The elastic properties of two main types of CNT — armchair and zigzag — were investigated and discussed in this paper. We can say that calculated values of elastic properties largely depend on the assumption of the wall thickness \( t \) of SWNT. There are other information about different wall thickness such as 6,9 Å, 5,7 and 3,4 Å [4-6]. In this investigation \( t \) was taken as 0,66 Å [4].
It was build application for investigation elastic properties using software Delphi 7 and mathematical models of SWNTs. It makes possible to estimate Young’s modulus $E$, shear modulus $G$ and Poisson’s ratio $\nu$ of armchair $(n, n)$ or zigzag $(n, 0)$ tubes with any specified diameter $D$.

For example, we investigated armchair tubes with chirality from $(3, 3)$ to $(40, 40)$ and zigzag tubes from $(3, 0)$ to $(40, 0)$. Those armchair tubes had diameter from 4.2 to 54.2 Å and zigzag tubes – from 2.4 to 31.3 Å. The values of Young’s modulus ranged from 0.26 to 2.95 TPa for armchair and from 0.5 to 3.7 for zigzag nanotubes. We calculated that shear modulus of armchair nanotubes was in the range of 0.2–2.0 TPa and of zigzag was in the range of 0.2–2.7 TPa. Young’s and shear moduli have shown inverse chirality and diameter dependences. The Poisson’s ratio was ranging from 0.28 to 0.42 and from 0.27 to 0.39 for an armchair and zigzag tubes, respectively. Those results agree well with reported results in literature [3, 4, 6].

**CONCLUSIONS**

In this paper we present the approach for investigation the elastic properties of SWNTs, based on molecular mechanics. The mathematical models for simulation Young’s modulus, shear modulus and Poisson’s ratio of armchair and zigzag tubes were built. Those parameters were investigated as functions of the nanotube size and structure. According to the presented models we calculated values of Young’s modulus, shear modulus and Poisson’s ratio for armchair and zigzag CNTs. It can be seen that predicted values of Young’s and shear modulus for zigzag tube are larger than for armchair tube, especially for smaller tubes, but they both decrease rapidly while the diameter increases. With diameter increasing Young and shear modulus of the both type of tubes begin to have the same value. As for Poisson’s ratio, we can say that zigzag tube is more sensitive to the diameter than that of the armchair tube.

**REFERENCES**

INFRARED CHARACTERIZATION OF SILICON CARBIDE NANOWIRES

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ABSTRACT

Silicon carbide nanowires have been obtained via combustion synthesis route. X-ray diffraction analysis confirmed that the synthesized material is the 3C polytype of silicon carbide with zincblende unit cell. Detailed investigations of such SiC 1D nanostructures were carried out exploiting Fourier transform infrared spectroscopy. IR measurements we performed using BRUKER HYPERION FT-IR microscope. For the purpose of comparison, a series of powder samples were examined, including raw synthesis product, purified SiC nanowires and several commercially available micro- and nanopowders (from Alpha Aesar and PlasmaChem). Comprehensive comparative analysis of the MIR spectra has been performed.

Key words: silicon carbide, nanowires, infrared spectroscopy.

INTRODUCTION

Silicon carbide (SiC) is one of the important wide band gap semiconductors exhibiting high electron mobility, high Debye temperature and large breakdown voltage and thus having some technological advantages as compared to other materials of this class [1]. Several polytypes of SiC has been identified, including the most common ones: 3C, 4H and 6H. In the present report we focus on the 3C polytype (band gap 2.39 eV) [2] and will discuss the synthesis of novel 3C-SiC nanostructures and further infrared spectroscopy characterization of the obtained nanomaterials.

EXPERIMENTAL DETAILS

For the purpose of detailed FTIR studies we have prepared several powder samples. These include raw sponge-like combustion synthesis product contain-

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ing SiC nanomaterial and the product of the purification of the first sample. In order to compare the IR spectra of the obtained nanowires with those of other SiC nanostructures, SiC nanoparticles, bought from different companies, were also studied.

Typical SEM image of the investigated nanowires of silicon carbide is shown in Fig. 1.

![Fig. 1 – A typical SEM image of the synthesized SiC nanowires](image)

For the purpose of IR characterization using BRUKER HYPERION FT-IR microscope investigated powders we mixed with KBr and pressed into pellets (the contamination of the SiC in the pellets was 0.1%). IR measurements were performed in the reflection mode with 2 cm$^{-1}$ resolution in the wave-numbers range of 600 to 3000 cm$^{-1}$.

**RESULTS AND DISCUSSION**

MIR spectra of the synthesized 3C-SiC nanowires are presented in Fig. 2. Spectra of the selected commercial silicon carbide nanomaterials are shown on the same plot.

From Fig. 2 it follows that commercial nanoparticles of silicon carbide exhibit typical feature peaked slightly above 800 cm$^{-1}$. It is obviously the manifestation of the fundamental Si and C sublattice corresponding to the reststrahl band of the SiC single crystal observed in the range of 770 to 1000 cm$^{-1}$.

In case of the synthesized nanowires one observes a different profile of the reflectivity peak which is strongly dependent on the purity of the material under study.
Fig. 2 – MIR spectra of the synthesized SiC nanowires and some commercial SiC nanopowders.

For the raw synthesis product the main peak is damped by strong background absorption. Generally, SiC nanowires show sharper reflectivity maximum than those of the nanoparticles. Both commercial samples have similar IR reflectivity spectra; slight difference might be due to different nanoparticle size distribution in these samples.

CONCLUSIONS

FTIR technique which is known to be highly sensitive to silica and a perfect method for the monitoring the surface structure and reaction analysis on sub-micrometer powders has been applied to study novel silicon carbide nanostructures.

Room temperature reflectivity spectra were recorded for unpurified and purified SiC nanowires and compared with the spectra of commercial SiC nanoparticles. The differences in the infrared spectra profiles of the nanowires and nanoparticles are emphasized.

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PERSPECTIVES OF APPLICATION OF NANOTUBES IN MODERN COMPOSITE BUILDING MATERIALS

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ABSTRACT

There are described the perspectives of application a carbon and hydro silicate nanotubes in modern building compositional materials …

Key words: carbon and chrysotile nanotubes, compositional building materials, reinforcement.

ACTUALITY OF THE TOPIC

Modern technology is in need of materials, including construction, for usage in extreme conditions. This requires the creation of new materials with properties that are absent for those natural and traditionally used. The combination of materials with different properties led to the creation of composite materials with new technological and performance properties. The most important advantage of composite materials is the possibility of creating products with given properties that best correspond the conditions of use in a best way. Composite materials can have properties practically unattainable using traditional construction materials. Composite materials consist of a binder that provides the integrity of the material and various fillers (reinforcing, weighting, or conversely, lightening (gases), etc.), providing various required functional characteristics of products. Depending on the type of reinforcing filler (fibrous, flake, ribbon or powder-like), composite materials are divided into fibrous, flake, dispersion-hardened or mixed-reinforced. The efficiency of obtaining the material with the desired properties depends on the proper selection of fillers and matrix (and their compatibility). Basis for efficient production of new composite materials is knowledge of the physicochemical nature of phenomena and the ability of purposeful formation of required and unique performance characteristics at nanoscale level. The level of binding energy between the neighboring crystals predetermines the future strength of polycrystalline materials. The influence of mineral fillers on the processes of hydrate formation is expressed in different ways, often in a more rapid

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formation of gel-like products of different composition or in the formation of specific structures (calcium hydrocarboaluminate and others). Practical research of the influence of mineral additives on structure formation of cement concrete [1] shows us that the use of microfillers improves concrete strength by 1.5-2 times at a constant water-cement ratio. This is because the smallest particles of microfiller which are similar in size to the colloid ones and are located between the grains of cement or near them, form new centers of crystallization. This speeds up this process and increases the strength of cement stone and concrete. At a certain ratio of the particle size of cement and filler there is an effect of hardening of binding [2]. It is determined that, in dense concrete, depending on the given tasks and properties of original materials, it is wise to substitute from 20 to 50% of cement for microfillers. Associating of a properly chosen microfiller into the concrete compound provides reducing water demand of cement produced as well as saving the proper rheology and adhesion properties of cement paste. A given strength of cement and concrete is provided and at the same time setting qualities and creeping of concrete are reduced[3]. Comprehensive study of hydration of the separate clinker minerals and Portland cements showed us that in all cases, milled mineral fillers accelerate the processes of hydration (an increase of volume of the hydrates formed and an increase of intensity of the process) significantly (for about 1.5-2 times). During the process the period of formation of individual hydrates is shifted to an earlier stage. A similar effect of fillers can be explained by high surface energy that is spent on formation of thermodynamically stable state by means of the phenomena of chemisorption and the subsequent formation of crystalline hydrate nuclei[4]. Thus, by applying mineral agents, we can control the structure formation of cement stone and get the best structure and properties of concrete under specific operating conditions.

It has long been known that the use of fibers as a reinforcing component can solve many problems, dramatically increasing the strength properties of products and constructions at the nanoscale level and as a result in the whole volume while reducing the consumption of materials and thermal heat capacity at the same time. The higher the dispersion of the particle is, the greater activity should be expected from it. An interest to nanoparticles can be explained by their unique properties. Nanoparticles, in particular carbon and silica nanotubes, which have very high tensile strength, are characterized by a huge surface potential concentrated in nanovolume. Their use as one of the components of the polycrystalline composite materials can serve as a promoter intensifying of the process of forming in a matrix of smaller crystals. The number of these crystals is much bigger than without them. The strength of microcrystalline materials is higher than that of coarse-crystallines. In the production of special high-strength composites the fine-grained fibrous (reinforcing) fillers such metal, carbon, silicate are used. Despite the extremely
high publication activity on the application of carbon fibers, which indicates their importance, the data on their use in technology of building materials are very poor due to low volumes of their production. Building materials require thousands of tonnes of them. At the same time, Russia has the world's largest reserves of fibrous mineral – chrysotile which has nanotubes with the diameter of ≈ 30 nm aggregated into threads, which are a natural composite material. It easily splits into filaments. (Fig. 1) By techno-economic indicators this mineral at present day is out of competition. Chrysotile is a layered magnesium hydrosilicate, it has a tubular morphology crystals, which consist of a twisted in tube and condensed between each other tetrahedral (silica oxygen) and octahedral (brucite) layers (Fig. 2). Twisting the layers into a tube is explained by the fact that the unit cell parameters of brucite layer are a bit bigger than those of silica oxygen. Compensation of tenses in the condensed layer leads to the formation of the tube, the outer layer of which is brucite - Mg (OH)₂. Magnesium (an alkaline-earth element) causes an alkaline reaction of aqueous suspension of chrysotile asbestos, while the surface hydroxyl groups cause an increased reactionary reactivity of chrysotile as a filler.

![Fig. 1 – View of Bazhenov fiber commercial chrysotile P-3-60](image1)

![Fig. 2 – Electron-microscopic picture of a cross section of chrysotile fibers [5]](image2)

Currently researchers are paying great attention to disperse reinforcement [6-8] and to nanomaterials [9-12]. Nanotubes in a fiber concrete are nanoreinforcing elements of a cement matrix. The consequence is an increase of its compressive strength, tensile and impact strength. The uniqueness of the application of carbon nanotubes astralenes with the diameter of <1 nm is in effect on the growth of the strength of cement stone at dosages of hundredths or even thousandths of a weight percent of cement [13].

Unfortunately, very little attention is wrongly paid to nanosilicates. In this work it is only possible to briefly describe the most effective ways of application nanotubes, especially of those with the modified surface. The representative of the silicate nanofibrous reinforcing fillers is a modified by thixotropic appretams fine-grained chrysotile "Silodeks Sx24" by VR Grace.
Co., Ltd. Firm. It was designed to give thixotropic properties to high-strength polymer composites. It should be noted that the range of possible uses of nanofibers in the development of nanomaterials technology is expanding rapidly.

The most promising is the reinforcement of cement matrix of concrete on micro and nanoscale levels. While doing this the fiber concrete is received. Fiber concrete, as well as traditional concrete is a composite material including additional distributed in a volume fiber reinforcement [14] That means that during preparing the concrete mix the correct proportion of natural, artificial, synthetic or metallic fibers of a special section are added into it. The properties of fiber concrete as a composite material are determined by the properties of its components. Steel or non-metallic (carbon, silicate or polymer) fiber is one of the most important components of fiber-reinforced concrete. Dispersed reinforcement by a fiber allows to offset the major shortcomings of concrete to a higher extent. They are low tensile strength and brittle fracture. Fiber-reinforced concrete have several times higher characteristics such as: compressive strength, axial tension, bending tension, the initial modulus of deformation, shear strength, frost resistance, water resistance, crack resistance, heat resistance, fire resistance, abrasion, fatigue strength, resistance to cavitation, impact strength (toughness)

The most important characteristic of fiber reinforced concrete is a tensile strength. It is not only a direct characteristic of the material, but also indirect and it shows its resistance to other influences, as well as its durability.

A very important characteristic of fiber-reinforced concrete is an impact strength (toughness), which depending on the material and the degree of reinforcement is from 3 to 20 times greater than conventional concrete in terms of destruction, which ensures its high technical and economic efficiency when used in building structures and their repair.

**PURPOSE OF THE REPORT**

The aim of our development is the creation of high-strength compositions for use in extreme conditions.

To achieve this goal we should have got a fibrous silicate nanofillers that improve the technological and operational properties of composite materials, i.e, allowing to get more qualitative products from original materials.

The original materials and the composites obtained were studied by modern methods of analysis - X-ray phase and structural, transmission and scanning electron microscopy, photoelectron spectroscopy, electron microdiffraction, chemical, pH-testing, derivatography, infrared spectroscopy.

For serial large-scale production of nanoreinforced building materials with new and unique technological and operational properties some items are required:
large-scale production of nanofibers with low cost with given technological characteristics;
- development of technologies of introduction of the nanofibers in the technological mixes;
- studying the properties of nanocomposite construction materials and development of production technologies

Hardening of composite materials is achieved by selecting the efficient composition of components and strengthening of ties between them. In studying the influence of the degree of filling of the composite material by the fibrous component it was found that by increasing the mass content of fiber of the same length the tensile strength and elastic modulus increase compared to the unfilled matrix. For example, for a composite with a fiber length of 3 mm the increase in strength is the highest concentrations of filler up to 10%, at a concentration of 10 to 40% of filler the strength of samples is increased lesser. The increase of fiber content of more than 40% does not lead to a further increase in the strength of the samples.

For samples with equal mass content of fibers of various lengths (from about 25 microns to 10 mm), we saw an increase in tensile strength with increasing fiber length, which can be explained by an increase in force that holds the fiber matrix, which, in turn, reaches a maximum and a further increase of length of the fibers doesn’t lead to its increase. Characteristic ratio (the ratio of fiber length to its diameter) depends on the type of the matrix and is chosen empirically.

We worked out the dispersion technologies of chrysotile production to nanofibers and their introduction into the concrete mixtures. We made structural and morphological studies of changes in the hydration products of cement clinker minerals and formation features of their structure with the introduction of nanofibers. We obtained materials with higher technical and economic indicators. The application of nanochrysotile allows to receive high-strength concrete with a compressive strength of 100 MPa or more. Basing on these data we can reasonably say about the influence of nanotubes on a grade (at the age of 28 days.) strength of the composite cement and a very substantial increase in its hardening on the early stages This reduces energy costs in manufacturing from the concrete of handling strength. Application of nanoconcretes reduces the turnover forms (in production) and the formwork (in-situ concreting of building structures), increasing economical effectiveness efficiency. In addition, nanoreinforcing of porous [15], constructional heat-insulating and heat-insulating concretes provides a significant increase in their strength, which is one of the major problems of building materials science.

**Perspectives** for further practical use. Traditionally they have paid and continue to pay particular attention to the influence of fillers on the mechanical strength of the product, but the fillers can improve also technological
properties. They can regulate flow (giving thixotropy to mixtures and, consequently, improving their stability of shape and moldability), reduce the chemical and thermal contractions in volume (the elimination of cracking). Fillers can change the electrical, magnetic and thermal properties, reduce flammability (flame resistance), to change the friction coefficient, optical properties (color and coloration), density, porosity, hardness (wear resistance), corrosion resistance, permeability, tensile strength, bending and impact and of course, the cost [16]. We created nanoreinforcing filler for using it in composite materials operating in extreme conditions, but it can be successfully applied in all economic sectors, particularly in high voltage electric-power industry, because in addition to the properties listed, it has high-arc resistance.

The following areas of rational use of nanofiber concretes can be possible (construction and repair):

- Monolithic design, construction and spatial coverage: fortifications, explosive and burglar structures, baffle dams, lining of tunnels and irrigation canals, water tanks and other liquids, highways, industrial floors and bridge decks, fire-retardant plaster, etc.;
- Prefabricated elements and structures: piles, railroad ties, pipes, beams, stairs, wall panels, roof panels and roof tiles, floating dock modules, offshore structures, plates of airfield, road, walkway covers and mounting channels, curtain elements of bridges, piling, heating elements, the elements of spatial surfaces and structures, ornamental accessory.

CONCLUSIONS:

Production of building materials of new generation with nanodispersed reinforcement is one of the most promising branches. The effectiveness of the introduction of nanotubes of chrysotile as a krentyi agent with high surface energy in the cement composition is based on lowering the energy threshold of the beginning of crystal formation from an aqueous solution, which is saturated with ions of cement clinker minerals, as a result of its interaction with water.

The studies confirm the probability of the impact on hydration and physical and mechanical properties of hardening cement compositions using aggregates and fillers of specific nature.

For composite materials used in various fields of modern and advanced equipment, the technology of production of fine-grained chrysotile with desired properties (nanofiller) was investigated. It reduces shrinkage deformation and prevents the formation of cracks in thin-walled and large-sized products.

Tests showed us that the designed filler can be successfully used in building compositions, including porous materials, adhesives, mastics, putties, high-strength mortar concrete, concrete shielding of nuclear reactors and other.

The observed effect of the length of reinforcing fillers is of great importance in the technology of composite materials: no need to seek for
maximal filling of the matrix by only one fiber and the fiber should not be used much longer than required for optimal composition.

The commercial production of nanofiller, production of composite materials and products from them for a modern and projected technology is organized.

In the future, for targeted development of new construction of nanocomposites with desired properties in-depth studies aimed at developing new technologies of surface modification of nanofibril are needed because the fibrous morphology of the nanocrystals substantially increase the strength of the matrix of composite materials. By modification of the filler we can obtain the required technological properties of the mixtures and properties of indurated compositions.

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ENVIRONMENT FRIENDLY INDUSTRIAL NANOTECHNOLOGIES

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ABSTRACT

One of the most interesting and perspective directions in material engineering of the last years is development of technology of nanocomposite materials consisting from two or more phases with precise interphase border and nanostructured materials based on interpenetrated polymer network. Israel is one of leaders in nanotechnology, not only in fundamental academic researches but mainly in industrial researches and founding start-up companies. Some important results in the nanotechnology material engineering field in Israel are summarized in the paper.

Key word: Nanotechnology, Nanocomposites, Nanostructured material, Israel

INTRODUCTION [1-6]

The economic, security, military, and environmental implications of molecular manufacturing are extreme. Unfortunately, conflicting definitions of nanotechnology and blurry distinctions between significantly different fields have complicated the effort to understand those differences and to develop sensible, effective policy for each.

The risks of today's nanoscale technologies cannot be treated the same as the risks of longer-term molecular manufacturing. It is a mistake to put them together in one basket for policy consideration—each is important to address, but they offer different problems and will require far different solutions. As used today, the term nanotechnology usually refers to a broad collection of mostly disconnected fields. Essentially, anything sufficiently small and interesting can be called nanotechnology. Much of it is harmless. For the rest, much of the harm is familiar and limited quality. Molecular manufacturing, by contrast, will bring unfamiliar risks and new classes of problems.

Desktop nanofactories will use vast arrays of tiny machines to fasten single molecules together quickly and precisely, allowing engineers, designers, and potentially anyone else to make powerful products at the touch of a button. Although such a contraption has been envisioned in some detail for almost two decades, and although the basic concept goes back to 1959, when the physicist R.Feynman first articulated it, it’s only in recent years that technology has

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advanced to the point where we can begin to see the practical steps that might bring it into reality.

The essence of nanotechnology is the ability to work at the molecular level to create large structures with fundamentally new molecular organization. Materials with features on the scale of nanometers often have properties different from their macroscale counterparts. The prospect of a new materials technology that can function as a low-cost alternative to high-performance composites has, thus, become irresistible around the world. By this means nanotechnology presents a new approach to material science and engineering as well as for design of new devices and processes. Figures 1-3 can give some imagine of the global tendency of nanotechnology development.

As is known, composite materials are two- or multiphase with well defined interphase border. Such materials contain the reinforcing elements immersed into a polymeric, ceramic or metal matrix. Mechanical properties of composites depend on structure and properties of the interphase border. Phases of usual composite materials have micron and submicron sizes. Important among these nanoscale materials are nanocomposites, in which the constituents are mixed on a nanometer-length scale. They often have properties that are superior to conventional microscale composites and can be synthesized using surprisingly simple and inexpensive techniques.

The tendency to reduction of the phase's sizes of a filler (a strengthening element) is attributable
to decrease in its microscopic deficiency (the size of one of nanocomposite phases does not exceed 100 nm). Due to the nanometer size of the particles, which is smaller than the wavelength of visible light, the reinforced polymer remains transparent. Other characteristics of the composites include high barrier performance and improved thermal stability, which make these compounds suitable for many applications. Because of this technology of nanocomposites is one of the most perspective directions in material engineering. Specifically, nanocomposite technology is applicable to a wide range of polymers. Cutting across the material classes of thermoplastic, thermosets, and elastomers.

Israel is one of leaders in Nanotechnology, not only in fundamental academic researches but mainly in industrial researches and founding start-up companies.

In the paper we are presenting new development of one of the leader Israeli company: Polymate Ltd., International Nanotechnology Research Center (Polymate Ltd., INRC) with the branch in Berlin, Germany.

Polymate Ltd., INRC specializes in providing applied and fundamental research and development (R&D) in the scientific and technological fields of material, chemical and environmental engineering, with a focus on the development, marketing, and commercialization of the advanced nanocomposites.
Polymate Ltd., INRC successfully operates on the basis of multi-sided partnerships in many regions around the world, such as Europe, Japan, Canada, the Former Soviet Union and others. Polymate Ltd., INRC’s last elaboration Network Nanostructured Polymer System has been named a winner in the third annual NASA Nanotech Briefs®’ Nano 50™ Awards (2007) in the Technology category.

GENERAL COMMENT

Nanostructured composite materials can be categorized depending on the location of the nanoscale structure in the system (Fig. 4).

After an initial literature review, and when considering the information needed in order to describe a nanomaterial from a physical and chemical perspective when estimating the hazard of nanomaterials, we propose the following nine properties as being important:

- Chemical composition,
- Size,
- Shape,
- Crystal structure,
- Surface area,
- Surface chemistry,
- Surface charge,
- Solubility,
- Adhesion, defined as the force by which the nanoparticles and its components are held together."

NANOSTRUCTURED COMPOSITES BASED ON INTERPENETRATED POLYMER NETWORK [7-11]

This project is oriented to prepare nanocomposites based on interpenetrated polymer network (IPN), such as polyurethanes, epoxies and acrylate by way of creating nanoparticles of SiO$_2$, TiO$_2$ and other metal oxides during a technological stage from a liquid phase. Using as interpenetrating polymer networks principle in production of composite materials provides a unique possibility to regulate their both micro-and nano-structured properties. Formulation of a new class of nanocomposite materials is characterized by the absence of contaminants for a network polymers technology. As a main component of such technology we are using branched (dendro)-aminosilanes that at the first stage are curing agents for many oligomers.

The proposed dendro-aminosilane hardeners give the possibility to introduce the siloxane fragments into aromatic structure of diphenylolpropane based epoxy-amine network polymers. Additional hydrolysis of aminosilane oligomer creates the secondary nano-structured network polymer that improves the service properties of the compound. Branched (dendro) polyamine
hardeners are novel direction in epoxy and cyclocarbonate and acryl resins chemistry.

The new hardeners give rise to formation of IPN of a polymerized resin with a polysiloxane network by the hydrolytic polycondensation of silane groups. IPN network may be formed on the base of epoxy- cyclocarbonate oligomers. It was found that at least 0.1 equivalent weight of silane per epoxy resin equivalent weight may result in IPN formation. It has been known that epoxy resin has low resistance to acetone and methanol attack. IPN film provides increasing the resistance.

Novel hybrid nonisocyanate polyurethane based nanocomposites (HNIPU) was received by the following reaction:

\[
\text{R-O-CH}_2\text{-CH}_2 + \text{HNR'} \quad \rightarrow \quad \text{R-O-CH}_2\text{-CH}_2\text{-O-C-NH-R'}
\]

Pilot production of two component paints, top coatings, adhesives and floorings are obtained. Fig. 5 illustrated industrial application of the IPN flooring. The two-component compound have unique properties that combine the best mechanical properties of polyurethane and chemical resistance of epoxy binders.

![Fig. 5 – IPN flooring (Tosaf Compounding Co., Israel )](image)

**NANOCOMPOSITES BASED ON HYBRID ORGANO-SILICATE MATRIX [12-17]**

Important among nanoscale materials are hybrids or nanocomposites. They often exhibit properties superior to conventional composites. Organic-inorganic hybrid nanostuctures have generated great interest by combining optical, magnetic or electronic properties of inorganic crystals with mechanical properties and functionality of organic compounds. They suggest a variety of potential applications as electrical, optical and medicals markers.
By using a principle of forming nanostructure by creating nanoparticles during a technological process from a liquid phase, Polymate Ltd., INRC has elaborated a few of composites based on different kinds of soluble silicates. Significant increasing of silicate matrix strength and toughness was reached by incorporation of special liquid additives, such as TFS, which effect as a microcrystallizing nucleator on the technological stage and later they colmatage the pores of silicate matrix. Our last elaborations are mainly applying a novel type of soluble silicate contained organic cations, for example, the DABCO (\textsuperscript{\textbullet})-based organic alkali soluble silicate.

**POLYMER NANOCOMPONITES WUTH VERY LOW PERMEABILITY AND HIGH RESISTANCE TO AGGRESSUVE ENVIRONMENTS [18-22]**

Novel chemically resistant polymer materials were elaborated with adding nano-size inorganic active fillers that react with aggressive medium into which they are introduced, forming a new phase of high-strength hydrate complexes. This enhanced bonding occurs upon the penetration of aggressive media into active nano-fillers containing polymer material. The chemical resistant properties of the forming polymer materials are activated by harsh environmental conditions where polymer systems without additives remain defenseless to chemical corrosion.

*Polymate Ltd.*, INRC has developed an extensive product range of such active nano-fillers for upgrading the most common polymers against a wide variety of aggressive media including acids, sea water, fluorine, alkalis and more.

**NOVEL METALIC MATRIX NANOREINFORCED MATERIALS PRODUCED BY METHOD OF SUPERDEEP PENETRATION [23]**

Technological process on the basis of new physical effect “superdeep penetration” (SDP) allows to make from the known tool steels (for example, HSS) new composite materials (Fig. 6).
These materials can be used for replacement base steels in metal-cutting and stamp tools. In some cases new materials can be used for replacement of a hard metal (on the basis of WC) in the tool for mining (for example, cutters of coal and mining machines, Fig. 7). The application of the new SDP technology allows to increase the service life of the tools up to 1.5-5.0 times compared to the common used tools. The technology can be applied for the volume strengthening practically any type of instrumental steels.

Use of new physical effect SDP allows as well to obtain the special composite materials on the basis of aluminum, with the set anisotropy of physical and chemical properties. In microvolume of the aluminium matrix Electroconductivity in mutually perpendicular directions of an aluminium matrix is differ a two times. The new technology of volumetric reorganization of aluminum will find wide application at manufacture of electric installations and electronic devices.

**WATER-DISPERSION PAINT COMPOSITION WITH BIOCIDE PROPERTIES BASED ON SILVER NANO-POWDER [24]**

We have elaborated advanced bioactive coating with using silver nanoparticles. As found in numerous studies during the last two decades, particles with dimensions in nanometer scale ($10^{-9} - 10^{-8}$ m) possess peculiar properties, different from those of atoms and ions on the one hand and of bulk substance on the other. These silver nanoparticles was received by the novel BAR-synthesis. The biological activity of varnish-paint materials modified by silver nanoparticles was estimated on the following microorganisms:

- Escherichia coli (E. Coli 1257) as a conventional devices. The effect from use of a new aluminum material in electric installations and electronic control systems will make, due to reduction in expenses for expensive materials, hundred millions and billions dollars USA. Cost of process of rearrangement of structure of aluminium preparation does not exceed 40 USD/kg. By industrial production of such material its cost to decrease in 2-3 times. From individual preparation can be made tens electric and thousand electronic devices. Process SDP is high-efficiency and does not demand the expensive equipment. The new technology of volumetric reorganization of aluminum, creation zones of nano-structures, the materials received on this basis, will find wide application by manufacture of electric installations and electronic devices. model of bacterial contamination of the environment;
- Coliphage (RNA-phage MS-2) as a model of viral infection, including influenza A and B, hepatitis A, et al;
- Mold fungi (Penicillinum Chrysogenum) as a typical representative of microflora of the dwellings and a model of fungicidal contamination;
- Spores as a model of spores and other microflora.
The data of the testing confirms the significant advantages of elaborated water-born acrylic bioactive coatings.

**NANOCYTELOUSE AND BIODEGRABLE COMPOSITE MATERIALS [25,26]**

(NanoCell) with CI crystalline modification was prepared using advanced, environmentally friendly, resource-save and cheap technology. The developed technology permits producing NanoCell in pilot and industrial amounts. NanoCell product can be manufactured in the form of dispersions, high solid paste and dry powder.

The FDA-approved aqueous polymer nanostructured composition CreenCoat is applied for protective covering of paper and board. The coating layer imparts to material barrier properties against permeation of water, grease, oxygen and some other substances (*Fig. 8*).

The GreenCoat emulsion is coated on cardboard surface by means of bar - coater and dried at temperature 150-170 °C for 30-60 sec. Then the GreenCoat W glazing hot melt composition is coated on first layer by means of bar-coater at temperature 130-135 °C and air cooled.

Waste of coated material can be repulped and used in paper industry or decomposed in nature due to its biodegradability (*Fig. 9*).

**REFERENCES**

Magnetic Fine Particles
INFLUENCE OF THE INVERSE FARADAY EFFECT ON SWITCHING AND OSCILLATIONS OF MAGNETIZATION IN SINGLE-DOMAIN NANOPARTICLES

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ABSTRACT

We have performed a numerical simulation of magnetization switching and oscillations in a ferromagnetic single-domain particle in the disk form under the influence of nanosecond laser pulses with linearly and circularly polarization.

During the simulation of magnetization we have used the macrospin approximation with the generalized Landau-Lifshitz-Gilbert equation. In this model the interaction of laser with ferromagnetic metal leads to following processes: a change in energy magnetic crystallographic anisotropy and in a value of saturation magnetization, a generation of the spin-polarized current by photon pressure, an occurrence of the magnetic field induced by the magnetooptical inverse Faraday effect in the case of circularly polarized laser.

The analysis has shown that the interaction of laser pulses with a ferromagnetic nanodisk leads to change in the direction of its magnetization. This process is accompanied by magnetization oscillations with duration from units to tens of nanoseconds. As it follows from the obtained results, the main cause of magnetization switching is the reduction of magnetic anisotropy energy at heating of the structure by laser. The field of the inverse Faraday effect can lead to an increase in frequency and amplitude of this oscillations.

Key words: magnetization oscillations, ferromagnetic nanoparticles, magnetooptical inverse Faraday effect

INTRODUCTION

An important practical application of single-domain ferromagnetic nanoparticles is the development of non-volatile magnetic memory. The speed of such memory depends on the duration of magnetization reversal. It's necessary to use single-domain nanoparticles with a large value of the coercive force \( H_c \) in order to increase the storage density. However, modern writing/reading systems using external magnetic field aren't capable to switch of the magnetization of nanoparticles with a large \( H_c \) value. The perspective way of the local decrease

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of the $H_c$ value is heating by laser. Moreover, the interaction of laser with a ferromagnetic particle leads to the creation of additional magnetic field induced by the magnetooptical inverse Faraday effect in the case of circularly polarized radiation. If a magnetic nanoparticle is included in a structure ferromagnetic / nonmagnetic metal / ferromagnetic, then in this structure the spin-polarized current is induced by photon pressure [1]. This current influences on magnetization of the particle by the Slonczewski-Berger mechanism of the spin transfer torque [2]. In this case the stable magnetization oscillations in this structure may be excited. This effect can be used for development of microwave nanogenerators. However, the main problem here is the request of large current density.

Recent experimental investigations have shown that it is possible to switch locally magnetization in magnetic thin films by nano- and picoseconds laser pulses. Depending on conditions the reason of such magnetization reversal includes various factors. It is the decrease of the coercive force due to heating of the sample, the influence of the magnetooptical inverse Faraday effect and the influence of spin-polarized current. However, the transient process and magnetization oscillations during the moment of switching is not completely studied.

The purpose of this work is to clarify the role of the inverse Faraday effect in switching process and magnetization oscillations in a ferromagnetic single-domain particle of hexagonal cobalt under the influence of nanosecond laser pulses at zero magnetic field.

**MODEL**

We consider a magnetic nanoparticle of hexagonal cobalt in the disk (nanodisk) with following parameters: the saturation magnetization at zero temperature $M_0 = 1.432\cdot10^6$ A/m, the Curie temperature $T_C = 1394$ K, the Gilbert damping parameter $\alpha = 0.02$. The aspect ratio of the disk $\varepsilon = L/D$, where the diameter $D$ is ranging from 10 to 18 nm, the height $L$ is ranging from 5 to 20 nm. The disk of such size has a single-domain state. In the chosen coordinate system the $z$ axis is perpendicular to the plane of the nanodisk. The nanodisk is irradiated by laser beam with power of 5 – 100 MW/cm$^2$ and duration of 0.1 – 2 ns.

The dependence of saturation magnetization from temperature $T$ is approximated by expression $M(T)=M_0[1 – (T/T_C)^2]^{1/2}$. We use the Landau-Lifshitz-Gilbert equation for description of magnetization dynamics:

$$\frac{d\mathbf{m}}{d\tau} = -[\mathbf{m} \times \mathbf{h}] - \alpha [\mathbf{m} \times [\mathbf{m} \times \mathbf{h}]]$$

Where $\mathbf{m} = M/M(T)$, $|\mathbf{m}| = 1$ is the unit vector of magnetization $\mathbf{M}$, $\mathbf{h} = \mathbf{H}/M_0$ is the effective field, $\tau = \gamma M_0 t/(1+\alpha^2)$, $t$ is the time, $\gamma$ is the gyromagnetic factor. The effective field $\mathbf{h}$ includes the field of magnetic crystallographicanisot-
ropy $h_a$, the demagnetization field $h_d$, the field of the inverse Faraday effect $h_{mo}$ and the field of thermal fluctuation $h_T$.

**RESULTS AND DISCUSSION**

The influence of the inverse Faraday effect is the most significant for thin and thick disk, when the [0001] crystallographic direction is parallel to the planes of the disk.

**Thindisk.** Let’s consider a thin nanodisk with height of 5 nm, diameter of 18 nm. If this disk is heated from 300 to 610 K by a linearly polarized laser pulse with peak intensity $I_{1m} = 95$ MW/cm$^2$ and duration of 0.1 ns, its magnetization is switched from the $x$-direction to the $y$-direction (fig. 1a). This switching is accompanied by magnetization oscillation with average frequency of 8.5 GHz. If laser beam has left circularly polarization, the magnetization vector deviates towards the negative direction of the $z$ axis and rotates around this axis during the moment of action of a laser pulse. Then it moves to the position parallel to the $y$ axis (fig. 1b).

**Thickdisk.** The thick nanodisk is characterized by height of 20 nm and diameter of 10 nm. A laser pulse with peak intensity $I_{1m} = 60$ MW/cm$^2$ and duration of 0.15 ns heats this disk from $T_0 = 300$ K to $T_1 = 590$ K. For such a disk at temperature $T_0$ the steady magnetic state is parallel to the $x$ axis, while at temperature $T_1$ it is parallel to the $z$ axis.

If the laser has linearly polarization, the inverse Faraday effect is absent. In this case after heating the disk by laser the magnetization is switched from the $x$ direction to the positive or negative direction of the $z$ axis with equal

![Fig. 1](image-url)
probability due to thermal fluctuations (fig. 1c). The frequency of accompanied magnetization oscillation is ranging from 3 to 10 GHz.

If the laser has right circularly polarization, the magnetization is switched only to the positive direction of the z axis. In the case of the left circularly polarization, the magnetization is switched only to the negative direction of the z axis (fig. 1d). Thus, in this thick disk for any polarization of laser beam the magnetization is switched from the planar state to the one of perpendicular states, but the specific direction depends on the laser polarization.

CONCLUSIONS

It is shown the process of magnetization switching of cobalt single-domain nanoparticles in the disk form under the influence of laser nanosecond-pulses is accompanied by magnetization oscillations. The frequencies and duration of these oscillations for different thickness of the disk and crystallographic orientation are defined. The influence of the magnetooptical inverse Faraday effect on the switching and oscillation of magnetization has been investigated.

Two cases have been considered when the inverse Faraday effect has essential influence: thin and thick disks with the [0001] crystallographic direction in the plane of the disk. For the thin disk the influence of inverse Faraday effect leads to the deviation of the magnetization vector along the axis of the disk only during the moment of action of a laser pulse. For the thick disk the direction of laser polarization (right circularly or left circularly) determines the direction of magnetization switching: along the positive or negative direction of the z axis.

REFERENCES

MAGNETIC NANOPARTICLES COMBINED WITH NATURAL PROTEIN FIBRES

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ABSTRACT

Human hair and sheep wool are the natural protein fibres of complex structure, composed of $\alpha$-keratin chains are analyzed as basic components for the fabrication of nanomaterials. After carrying out some successful experiments in which we demonstrate that silver nanoparticles can be immobilized on the surface and inside hair and wool fibers [1, 2], we attempted to use another type of metal-containing nanoparticles and unite in one composite material such properties as superparamagnetism of iron oxide and nonmagnetism of natural protein fiber.

The hair fibers, immersed in a reductant solution in order to break their surface disulfide groups, were placed in a $\alpha$-Fe$_2$O$_3$ – nanoparticle suspension while synthesis. After some time, the fiber surface took on a brown tinge. Hematite-containing nanoparticles were found to penetrate not only into the hair cuticle but also into melanin granules inside the fibre volume. Electron magnetic resonance data (Varian Spectrometer, 9.1 GHz) indicates that the nanoparticles produced in the matrix are superparamagnetic at room temperature. This interesting finding suggests that such a carrier can be associated with a magnetic bubble. The observed line width and effective g-factor are comparable to those reported for superparamagnetic iron oxide nanoparticles in a nonmagnetic matrix.

Key words: nanocomposite, magnetic nanoparticles, natural fibers.

INTRODUCTION

Functional metal oxide nanocrystals have been extensively investigated in the recent decade for their outstanding new properties suitable for a broad spectrum of downstream applications. Iron oxide is one of the most widely investigated nanomaterials for both biological and industrial applications. Iron oxides (Fe$_2$O$_3$) have four phases: $\alpha$-Fe$_2$O$_3$ (hematite); $\beta$-Fe$_2$O$_3$; $\gamma$-Fe$_2$O$_3$ (maghemite); $\varepsilon$-Fe$_2$O$_3$. Magnetic nanocrystals of $\gamma$-Fe$_2$O$_3$ have been applied in information storage, magnetic refrigeration, bioprocessing, controlled drug delivery, and ferrofluids, while $\alpha$-Fe$_2$O$_3$ is environmentally friendly and of great interest for potential applications as a gas sensor, lithiumion battery and pigment.

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The immobilization of metal-containing nanoparticles on microcarriers of various compositions is a rapidly growing area of nanomaterials research. The advantages of spheroidal microgranules as carriers for nanoparticles are well-known [3-5]. In contrast, essentially the only one dimensional (1D) carriers described in the literature are carbon nanotubes, with various nanoparticles attached to their surface. Proteins form linear structure, such as hair, wool and silk and in contrast to carbon nanotubes, such raw materials are readily available and sufficiently well studied. Wool is among the most important subjects of research for textile manufactures.

A very limited number of studies have been concerned with the fabrication of nanoparticles inside or on the surface of hairs or wool fibres. They mainly addressed the accumulation of toxic metal ions in hair, the poisoning of the human organism with such ions, and techniques for identifying them.

A human hair and sheep wool are composite protein fibers of natural origin consisting mainly of water-insoluble α-keratin comprising hydrophobic amino acid residues (phenylalanine, isoleucine, valine, methionine, alanine) and, correspondingly, numerous functional groups including S- and N-containing ones.

The surface layer of a hair, cuticle, contains the highest amount of cystine and consists of planar horny cells of amorphous keratin applied onto one another in a tile pattern and containing four layers with different contents of disulfide bonds: epicuticle on the very surface, which is a ~ 5 nm thick hydrophobic membrane; mechanically most stable α-layer; exocuticle connected to the α-layer; endocuticle with a low cystine content (3 %). The hydrophobicity of the surface layer, in particular, the epicuticle is caused by the presence of an outer β-layer (2.4 nm) of covalently bonded lipid, presumably, 18-methylarachidonic acid (18-MEA).

The natural color of the hair is caused by the granules of the pigment melanin present in its cortical layer. Melanin is insoluble in water but is rather readily soluble in alkali or concentrated acids and consists of conjugated polymers with S- and N-containing groups. Melanin is deposited as granules, each being a structurised body forming spheres 70 – 500 nm in diameter. The destruction of melanin occurs supposedly as separation of the disc-like granules into layers under the action of an oxidant (which preferably interacts with melanin rather than with the hair keratin) accompanied by elimination of oligomer residues. The ability of melanin to reduce a solution of silver nitrate to silver metal (Masson–Fontana stain) due to the presence of unpaired electrons is also known from medical sources.

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

For binding of the obtained nanoparticles to ligands within biofibers, the hair and wool were pretreated with a solution of a reducing agent (such
as NaBH₄) to activate the disulfide ligands on their surface, then washed with water to remove NaBH₄, and placed into solutions of nanoparticles for a week.

Hematite nanoparticles were prepared by coprecipitating Fe²⁺ and Fe³⁺ ions in aqueous ammonia solution. To 200 mL of water containing ferric chloride and chlorous chloride in molar ratio 1:1, was dropped 1.5 M NH₄OH solution under room atmosphere while the solution was stirred rapidly. The resulting precipitate was stirred for 2 h. After triple washes with water and ethanol the precipitates were re-suspended in water. The magnetic nanoparticles were isolated from the solution by a magnet bar. The fibers were placed into the reaction solution directly at the beginning of the experiment.

While the experiment, the solution color gradually changed from black to brown as a result of absence of an inert atmosphere in the reactor and the surface of the fibres also became brown.

**RESULTS AND DISCUSSION**

The samples treated in the nanoparticle suspension during the reaction were examined by transmission electron microscopy (TEM) on LEO 912 AB microscope. Cross-sectional TEM specimens were prepared using a Reichert-Jung ultramicrotome. It follows from the TEM micrograph in Figure 1 and Figure 2 that the nanoparticles are formed not only in the cuticle of the fibre, but locally in the volume of melanin granules. The particles are less than 10 nm. Electron diffraction patterns of agglomerates correspond to α-Fe₂O₃.

Thus, treatment of the hair with a reducing agent resulted in partial cleavage of cystine disulfide S–S bonds on the hair surface or (partially) in the hair bulk, some of cystine being converted to cysteine containing thiol groups S–H. These groups are known to be efficiently coordinated by Fe-containing nanoparticles to form strong bonds.

![Fig. 1 – Presence of Fe-containing nanoparticles in the cuticle of the hair (on the left: the fiber before the experiment; on the right: the fiber after the experiment)](image-url)
As for the melanine granules, we can suppose that the coordination of Fe-nanoparticles inside them occur apparently in the way of their passing through the micro and nanopores in the fibrillar structure of the protein after the treatment of a hair with a reducing agent (the cuticle flakes are partly opened). The S- and N-containing functional groups of melanin coordinate the nanoparticles thus stabilizing them and preventing them from agglomeration.

The samples also have been investigated by a method of an electronic magnetic resonance with use of the computerized spectrometer “Varian” (working frequency of 9.1 GHz). Measurements were spent at room temperature. The sample fastened on the quartz holder thus that it was possible to spend measurements at its various orientations concerning an external magnetic field. Besides, EMR spectrum in the conditions have been written down, allowing to find out a hysteresis of microwave absorption and residual magnetization of the sample [6]. As the hysteresis hasn't been found out, particles are superparamagnetic at room temperature.

EMR spectrum for two orientations of the magnetic field (a field perpendicularly and in parallel hair) are shown on Figure 3a. Values for width of a line (970/910 \( \pm / \| \)) and the effective g-factor (1.9/2.1 \( \pm / \| \)) are close to the data received for superparamagnetic nanoparticles of Fe-oxides inside not magnetic matrix [7, 8].

Value change of g-factor at turn of the sample can be explained as follows. The magnetic field operating on nanoparticles in hair, is the sum of two contributions: fields of a magnet of a spectrometer and a field caused by magnetization of the sample. In the elementary model of infinitely long homogeneously magnetized cylinder (Fig. 3b) in a case when hair is parallel to an external field, intensity in it is the same, as intensity of a field of magnet \( H_0 \) in absence of the sample. In the cylinder the magnetic field induction increases by size \( \mu_0 M \), where M—magnetization of the cylinder. In a case when an external
field of perpendicularly axis of the cylinder, increase in a magnetic field in the cylinder for the account magnetization twice is less (Fig. 3b). As the resonant field registered in experiment, is the electromagnet field (equal $\mu_0 H_0$), in the second case will shift EMR spectrum to the right concerning a spectrum for parallel orientation of the sample (Fig. 3a).

![Fig. 3](image_url)

**Fig. 3**—a. EMR spectrum of the samples for two orientations of the magnetic field; b. Diagram illustrating the difference in values of the magnetic field inside the hair with nanoparticles in two orientations: (A) – the external field is parallel hair removal, (B) – the external field perpendicular to the hair (M magnetization, H – is the magnetic field, B – induction of a magnetic field)

For the investigated samples the size of shift in terms of intensity of a magnetic field is equal 0.03 T (in terms of an induction). It is 10 times less, than magnetization of a magnetite (0.6 T) or magemite (0.47 T). It is necessary to consider, however, that magnetization is a dipolar magnetic moment on volume unit, and nanoparticles occupy only insignificant part of hair. For a magnetization estimation of nanoparticles it is necessary to increase 0.03 T by a volume fraction of nanoparticles in hair.

The increase in width of EMR line approximately on 10 % at turn of the sample from parallel to perpendicular orientation is caused, basically, heterogeneity of the field caused by magnetization of the sample which smoothly decreases from the center to edge of the sample. Thus, nanoparticles in the center of hair and on its edges are in various fields (at the same current of an electromagnet of a spectrometer), and their resonant fields are displaced rather each other. It leads non-uniform widening total of EMR spectrum.

**CONCLUSIONS**

The present results demonstrate that the polyfunctional properties of hair and wool fibers can be successfully used to immobilize metal-containing nanoparticles with various compositions and physicochemical proper-
ties (such as hematite and silver nanoparticles) on the surface and in the bulk of the fibres.

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DEVELOPMENT METHODS LABELED TECHNETIUM-99M MAGNETICALLY NANOCOLLOIDS FOR MEDICAL DIAGNOSIS


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ABSTRACT

The opportunity of drawing of a radioactive label $^{99m}$Tc on a surface nanoparticles of iron Fe$_2$C, covered by a carbon environment, and also particles Fe$_2$C (IDA), modified arenediazoniumtosylates is investigated. It is shown, that on not modified particles about 11.2 % $^{99m}$Tc from its entered quantity are adsorbed. Thus the size of atomic adsorption does not exceed 0.736·10$^{-9}$ g-at/g $^{99m}$Tc on 1 g Fe$_2$C. On the modified particles Fe@C (IDA) physical adsorption is not observed. At their chemical interaction with $^{99m}$Tc at presence of reducing agent of tin (II) output labeled a product increases more than in 1.5 times and makes 21.3 % from the general entered activity radionuclide. For achievement of higher output carrying out of the researches connected with selection of optimum concentration and conditions of preparation of a reducer or selection of other more effective reducer is necessary.

Key words: nanoparticles of iron Fe@C, particles Fe@C (IDA), modified aryldiazoniumtosylates, nanocolloid labeled technetium-99m

INTRODUCTION

Last years significant strengthening interest to use radioactive nanocolloidin medicine [1] all over the world is marked. They have found wide application for labeled autoleykotsity with the purpose of diagnostics of inflammatory processes, revelations of "sentry" lymph nodes at oncological sick, lymphoscintigraphy and other areas [2]. The most simple method of reception labeled nanocolloid with the set sizes and properties is immobilisation $^{99m}$Tc on a surface nanomaterials. For a basis of such materials in work have been chosen nanoparticles the iron, (Fe@C) covered by carbon. The technology of their reception has been developed in Institute of physics of metals URO the Russian Academy of Science. The general view of a particle is shown in a photo (fig. 1).

As have shown researches on experimental animals, nanopowders Fe@C are not toxic and, basically, can be used as carriers $^{99m}$Tc if the problem of drawing of it radionuclide on their surface will be solved.

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The choice nanoparticles on the basis of iron is caused also by that they, possessing magnetic properties, can be simultaneously used as radiopaque agents for carrying out of a magnet -resonant tomography. All this opens ample opportunities for their application in two parallel kinds of diagnostics with the subsequent reception of the information not only on topography of the center of an inflammation, but also its functional condition.

For giving iron-carbon to particles lipophilic properties and increase of their stability in a solution in colloid to the form, on faculty of organic chemistry TPU the technique of preliminary drawing on a surface of these particles of organic radicals - aryldiazoniumtosylates has been developed, which are capable to react spontaneously with carbonaceous surfaces with allocation of nitrogen and covalent prishivkoyfossil (fragments benzildimethylenaminouksusnaya acids - IDA) to a carbon environment. It was supposed, that connection $^{99m}$Tc to such modified particles will occur by formation of complexes to the sewn radicals, instead of by physical adsorption for a case of a pure carbon surface. The general scheme of synthesis of particles Fe@C (IDA) and their subsequent interaction with $^{99m}$Tc is shown on Figure 2.

From the point of view of reception of high activity of a preparation, the degree of filling of a surface nanoparticles radicals IDA should be whenever possible maximal since it, on the one hand, will raise probability of their interaction with $^{99m}$Tc, and with another, - will allow to lower the general concentration nanoparticles in an entered diagnostic doze.

Experimental studying of process of interaction $^{99m}$Tc with particles Fe@C (IDA) was spent under the following program. At the first stage adsorption $^{99m}$Tc on not modified particles Fe@C with the purpose of their quantitative definition sorption capacities on radionuclide and stability of received connection was investigated. These data were necessary for the subsequent comparison with similar parameters of the modified particles.
Fig. 2—The scheme of synthesis of particles Fe@C (IDA) and their interactions with $^{99m}$Tc

At the second stage conditions of introduction of a radioactive label $^{99m}$Tc in structure of organic radicals on a surface Fe@C (IDA) with the subsequent estimation of an output labeled product were fulfilled.

**EXPERIMENTAL RESULTS AND THEIR DISCUSSION**

For reception of an initial preparation $^{99m}$Tc (eluate) in the form of a solution of sodium pertechnetate, $^{99m}$Tc it was used chromatographic the generator «$^{99m}$Tc-GT-TOM» manufactures of scientific research institute of nuclear physics TPU.

Quantitative estimation of efficiency of sedimentation $^{99m}$Tc on a carbon surface of not modified particles Fe@C spent a method of direct mixing of water suspension of a powder (10 mg to 1 ml of water) about 4 ml eluate from the generator having the general activity on $^{99m}$Tc $A = 1,268$ GBq. Preliminary from initialeluate $^{99m}$Tc 3 tests in volume 5 µl for carrying out of radiometric measurements of their activity by means of the single-channel peak analyzer Strahlungsmessgerat 20 046 which have been adjusted on energy scale-quantums 0,140 MeV($^{99m}$Tc) have been selected. After intensive hashing a mix
and it incubated during 5 mines the branch of particles from a water phase has been lead. With this purpose the bottle with suspension has been placed above a constant magnet. After sedimentation of particles the deposit Fe@C has been washed out by the distilled water, and from the received washing waters selection of 3 tests in volume 5 µl also has been made. By results of measurement activities tests initial eluate ($A_{\text{source}}$) and washing waters ($A_1$), after their normalization on time, calculation of quantity reacted with particles $^{99m}$Tc (in %) with use of a parity has been lead:

$$\beta = \frac{A_{\text{source}} \cdot 4 - A_1 \cdot V_1}{A_{\text{source}} \cdot 4} \cdot 100 \quad (1)$$

Where 4 – volume of the entered preparation $^{99m}$Tc, ml; $V_1$ - total amount of washing waters, ml.

Calculations have shown, that on particles 11,2 % $^{99m}$Tc from its general entered quantity Fe@C are adsorbed.

It is known, that between size of activity $A$ and quantity of radioactive atoms $N$ the parity is carried out: $A = \lambda N$. From here, proceeding from activity eluate $A = 1,268$ GBq, the total of atoms $^{99}$Tc, entered in initial mix $N = 3,97 \cdot 10^{13}$ at. has been certain., and also the size of its atomic adsorption on investigated particles is found:

$$G = \frac{3,97 \cdot 10^{13} \cdot 0,112}{0,01N_a} = 0,736 \cdot 10^{-9} \text{ g-at}^{99}$\text{Tc}\text{in1 gFe@C} \quad (2)$$

Where $N_a = 6,02 \cdot 10^{23}$ – Avogadro's number.

Further similar experiment has been lead with the modified powder Fe@C (IDA). Here too to 1 ml of suspension 4 ml eluate $^{99m}$Tc have been added. After hashing and incubated mixes during 5 mines sedimentation of particles has been lead to a field of a constant magnet. Unlike not modified Fe@C, particles Fe@C (IDA) long enough were in a suspension that confirms presence at them lipophilic properties alongside with display of ability to colloid formation. The calculations lead by subsequent, have shown, that adsorption $^{99m}$Tc on a surface Fe@C (IDA) is not observed. From here has been drawn a conclusion, that as a result of the lead updating nanoparticles Fe@Caryl Diazoniumtosylates, they have lost ability to physical adsorption $^{99m}$Tc on the surface. The reason of it, most likely, is blocking of an initial graphitic environment by organic radicals that testifies to their high concentration on a surface. This fact is extremely important from the point of view of the subsequent introduction $^{99m}$Tc in structure of such radicals not in the form of physically adsorbed ions, in summary chemisorption which is steadier.
As is known, $^{99m}$Tc, present in initial eluate from the generator, has the maximum degree of oxidation (VII). In this chemical form it does not show-complexing properties. Therefore for "linkage" $^{99m}$Tc with organic radicals it was necessary to lead preliminary its restoration up to lower valent condition. As such reducing agents formalin, an ant acid and tin (II) chloride dihydrate (SnCl$_2$·2H$_2$O) have been tested. Last from them is the classical reducer widely used in medicine, in particular, for manufacturing of standard sets (lyophilized) for the generator technetium-99m [3]. Thus process of introduction of an isotope label $^{99m}$Tc in structure of substances can be characterized approximately the scheme:

\[
^{99m}\text{TcO}_4^+ + \text{Sn(II)}L \xrightarrow{\text{Subst./H}_2\text{O}} ^{99m}\text{Tc} - \text{Sn} - L + \text{Sn(IV)}L
\]

Where $L$ - the substance which is exposed labeled.

As a result of such reaction, except for expected target products [$^{99m}$Tc-Sn-L] or [$^{99m}$Tc-L], the complex $^{99m}$Tc with tin, and also radiochemical impurity in the form of not reacted ions initial $^{99m}$Tc (VII) and its restored ions can be formed.

![Fig. 3 – The Initial preparation $^{99m}$Tc](image)

Check of restoring abilities of formalin and ant acid spent by their direct introduction in quantity on 10 µl to the bottles containing on 1 ml initial eluate $^{99m}$Tc. After hashing mixes and incubated during 5 mines from the received solutions selected tests for removal radiochromatogrammon installation «Гаммаскан-01А». Simultaneously as the sample of comparison selected test from an initial preparation. Expected result, in case of restoration $^{99m}$Tc, occurrence on chromatograms additional peak in the field of a line of start unlike peak $^{99m}$Tc (VII) initial preparation located in the end chromatograms. On the basis of the lead researches has been drawn a conclusion, that restoration $^{99m}$Tc in these environments does not occur.
The positive result has been received at use as reducer \(\text{SnCl}_2\cdot 2\text{H}_2\text{O}\). Radiochromatogramm of an initial preparation \(^{99m}\text{Tc}\) and a preparation with tin (II) are presented on Figure 3 and Figure 4, accordingly.

![Fig. 4– A preparation \(^{99m}\text{Tc}\) with tin (II)](image)

Comparison presented chromatograms shows, that at mixing eluate with tin (II) basic peak on chromatogram (fig. 4) is displaced in area of 2 sm (Rf = 0,1), that speaks about formation restored \(^{99m}\text{Tc}\) (presumably \(^{99m}\text{Tc}\) (IV)) or its complex with Sn which as it is established in work [4], can be presented by the formula: \((-\text{O-TcO-O-SnCl}_2\text{-O-TcO-})_n\), where \(n = 2, 3, \ldots\) - the number depending from pH of a solution.

The subsequent introduction of a label \(^{99m}\text{Tc}\) to structure Fe@C (IDA) at presence of tin (II) spent by a following technique. With the modified substance (6,8 mg in 1 ml of water) have entered into a bottle 100 µl (0,7 mg) SnCl₂ and 4 ml of a solution preparation \(^{99m}\text{Tc}\). After incubated during 5 mines of a particle have besieged on a magnet. Behind that have made selection of a water phase and have washed out a deposit water. Have preliminary lead sampling (3 tests on 5 µl) from an initial solution of a preparation, and after - from washing waters for measurement of activity \(^{99m}\text{Tc}\) and the subsequent carrying out of calculations of an output labeled product. From these results it has been found, that at chemical interaction Fe@C (IDA) with \(^{99m}\text{Tc}\) at presence of tin (II) size of absorption radionuclide has increased up to 21,3 % from the general entered activity, that in 1,52 times it is more, than at not modified Fe@C.

**CONCLUSIONS**

On the basis of the received results, it is possible to draw following conclusions.

The basic lack of not modified particles Fe@C as the carrier of a radioactive label \(^{99m}\text{Tc}\) is them not high enough adsorption capacity on radionuclide, that can limit their use at carrying out scale-scintigraphic of researches where the quantity of entered substance should be minimal. Besides physical adsorp-
tion does not provide reliable linkage $^{99m}$Tc on a surface of particles, and, hence, there is a danger of uncontrollable hit radionuclide in case of its desorption in critical bodies. In this plan the modified particles Fe@C (IDA) with chemisorbed $^{99m}$Tc, possessing lipophilic properties and propensity to colloid formation in a water solution are more preferable. The subsequent development of works in this direction is connected with selection of optimum concentration and conditions of preparation of a reducer or selection of other more effective reducer which would provide an output labeled a product at a level of 90 - 95%.

REFERENCES


EXACT GROUND STATES FOR QUASI 1D SYSTEMS WITH HUBBARD INTERACTION

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ABSTRACT

Using a positive semidefinite operator technique we deduced exact ground states for a modified diamond chain described by a non-integrable Hubbard model with on-site repulsion. Our results are valid for arbitrary length of the chain and strength of the Hubbard interaction. For the analyzed quasi 1D chain structure we found that two flat bands are present in the bare band structure of the system, both for zero and for a fixed value of magnetic field. We obtained ground states of nonmagnetic and ferromagnetic insulator type and studied their physical properties.

Keywords: Strongly interacting systems, Hubbard model, nanowires, ferromagnetism

INTRODUCTION

The investigations of nanostructure objects with itinerant electrons are one of the most quickly progressing fields in the modern material science. These systems present a drastic change of physical properties under given conditions, e.g. fixed external magnetic field or given site-selective gate potential[1, 2]. In this frame we investigate below electron systems where the interaction between the electrons is the well-known Hubbard on-site term. Our goal is to find exact ground-state wave functions for arbitrary strength of the interaction, thus we do not use perturbation theory or any other approximations. It is worth to mention that the full exact solution of the Hubbard model is still unknown for dimensions larger than 1. In the paper [1] a new method was developed and applied for the diamond Hubbard chain. In this paper we used the same method to a similar, but modified system.

THE STUDIED SYSTEM

Figure 1. shows the modified Hubbard diamond chain we analyzed. The sites of the chain for the cell defined at the site i are denoted by \( i + r_s \), where \( s = 1, 2, 3 \) is the sublattice index. The Bravais vector of the lattice is \( a \), horizontal in the figure. \( N_C \) is the number of unit cells, \( N \) is the number of electrons, \( N_S \) is the number of sites, and one has \( N_S = 4N_C \).

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\[ \hat{H} = \sum_{\sigma} \sum_{i=1}^{N_c} \left[ t e^{i\delta/2} \left( c_{i+r_1,\sigma}^\dagger c_{i,\sigma} + c_{i+a,\sigma}^\dagger c_{i+r_2,\sigma} + c_{i+r_2,\sigma}^\dagger c_{i+a,\sigma} + c_{i,\sigma}^\dagger c_{i+r_2,\sigma} \right) \\
+ t_3 c_{i+r_3,\sigma}^\dagger c_{i,\sigma} + t_\perp c_{i+r_1,\sigma}^\dagger c_{i+r_2,\sigma} + t_\parallel c_{i+a,\sigma}^\dagger c_{i,\sigma} + H.c. \right. \\
\left. + \epsilon_0 n_{i,\sigma} + \epsilon_1 n_{i+r_1,\sigma} + \epsilon_2 n_{i+r_2,\sigma} + \epsilon_3 n_{i+r_3,\sigma} \right] + U \hat{U} \]

The operator \( c_{i,\sigma}^\dagger \) creates an electron with spin \( \sigma \) in at site \( i \), \( n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma} \) is the particle number operator, while \( \hat{U} = \sum_{i=1}^{N_c} n_{i,\uparrow} n_{i,\downarrow} \) the operator of the on-site Coulomb repulsion, \( U>0 \). The movements of the electrons are described by the hopping matrix elements \( t, t_\parallel, t_\perp \) and \( t_3 \).

The first one characterize the nearest-neighbor hoppings (except for sites \( i+r_3 \)) while \( t_\parallel \) and \( t_\perp \) the second nearest neighbor terms parallel and perpendicular to \( a \), respectively. The last hopping term \( t_3 \) refers to movements along the external leg, and the epsilons are one-site one particle potentials. The system is placed in an external magnetic field perpendicular to the plane of the chain and described by the Peierls phase factor delta. During the calculations arbitrary but fixed \( N \) and periodic boundary conditions are taken into account along the chain. One notes that the presence of the external legs into the system allows the use of external site selective gate potentials in order to modify and easily manipulate the potential \( T_3 \) and therefore the physical behavior of the system.

**ABOUT THE METHOD**

First we calculate the non-interacting band-structure of the system. For this we have to write the Hamiltonian without the \( U \hat{U} \) term into the \( k \)-space.
by Fourier transformation. Then, by diagonalizing the obtained expression we derive an algebraic equation with four unknowns – as we have four sites in the primitive cell – and the solutions of this equation as a function of \( k \) gives the four bands of the bare band structure. We obtained that the lowest two bands are always flat.

To find the GS of the interacting system, we use the method of positive semidefinite operators. A Hermitian operator is called positive semidefinite if its spectrum is nonnegative, i.e. its lowest eigenvalue is zero or positive. Therefore if \( H_+ \) is a positive semidefinite Hamiltonian and we have an eigenvector of \( H_+ \) with zero eigenvalue, then this vector belongs to the ground-state (GS) subspace of \( H_+ \). Suppose that we manage to write the Hamiltonian of the interacting system in the form

\[
H = H_+ + C
\]  

where \( H_+ \) is positive semidefinite and \( C \) is a constant which depends on the parameters of the Hamiltonian. Now if \( \left| \Psi_g \right> \) is the most general element of the kernel of \( H_+ \), then \( \left| \Psi_g \right> \) is the GS vector of \( H \) and the corresponding GS energy is \( C \). Thus in our method we transform the Hamiltonian into the form (1) and calculate the kernel of \( H_+ \).

On this line we managed to transform the Hamiltonian into the form

\[
\hat{H} = \sum_{\sigma} \sum_{i=1}^{N} (A_{i,\sigma}^{\dagger} A_{i,\sigma} + B_{i,\sigma}^{\dagger} B_{i,\sigma}) + U\hat{U} - K\hat{N}
\]  

where the terms \( A \) and \( B \) are block operators which represent a linear combination of fermionic operators defined on a finite domain of the system. One can easily see that the terms in the bracket are positive semidefinite. On the other hand, the Hubbard-term is positive semidefinite, and presents its smallest possible zero eigenvalue if there are no doubly occupied sites in the system. Furthermore, \( C = -K\hat{N} \), where \( \hat{N} \) is the operator of total particle number of the system.

**THE OBTAINED GROUND STATE**

We obtained the GS wave vector in the form

\[
\left| \Psi_{gs} \right> = \prod_i \hat{G}_{i,\sigma_i}^{\dagger} \left| 0 \right>
\]  

where \( \left| 0 \right> \) is the vacuum state. We consider the \( \hat{G}_{i,\sigma}^{\dagger} \) operators as the most general linear combination of creation operators with acting on each lat-
tice site of the system. Furthermore, one takes into consideration that the lowest energy value must be provided by a state without doubly occupied sites. We found the following two families of $\hat{G}_{i,\sigma}^{\dagger}$ operators at $\delta = 0$:

$$
D_{i+a,\sigma}^{\dagger} = \frac{t}{t_\perp} c_{i+r_1,\sigma}^{\dagger} - c_{i+a,\sigma}^{\dagger} + \frac{t_3}{t_\perp} c_{i+a+r_3,\sigma}^{\dagger} + \frac{t}{t_\perp} c_{i+a+r_2,\sigma}^{\dagger}
$$

$$
E_{i,\sigma}^{\dagger} = c_{i+r_1,\sigma}^{\dagger} - c_{i+r_2,\sigma}^{\dagger}
$$

A similar expression is obtained for $\delta = \pi / 2$. So we have two sets of operators, namely $D_{i,\sigma_i}^{\dagger}$ and $E_{i,\sigma_i}^{\dagger}$ which can appear in the GS vectors, each with $N_C$ terms for both up and down spins. Every vector from the kernel of the transformed Hamiltonian can be written as a product of these operators. The number of the operators in the product specifies the number of electrons in the system. The most general GS vector is obtained as a linear combination of these vectors. As $D_{i,\sigma_i}^{\dagger}$ and $E_{i,\sigma_i}^{\dagger}$ have no common lattice-points for different $i$ (except for $D_{i,\sigma_i}^{\dagger}$ and $E_{i+1,\sigma_i}^{\dagger}$), the spin indices $\sigma_i$ of them for different cells are usually independent. For the same cell, the $D_{i,\sigma_i}^{\dagger}$ and $E_{i,\sigma_i}^{\dagger}$ operators must have the same spin index in order to avoid the double occupancy. Physically this means that the solution is globally a non-magnetic phase up to the electron number $N < 2N_C - 1$. For the case when in the same cell both operators D and E are present, the cell itself is ferromagnetic and behaves as a ferromagnetic cluster. However, different cells are magnetically not correlated. This is the reason why the system globally is non-magnetic if $N < 2N_C - 1$. At $N = 2N_C - 1$ or $N = 2N_C$ the D and E operators touch each other, the connectivity condition is satisfied and the system becomes ferromagnetic.

We also calculated the mean value of the long range hopping function

$$
\langle \Psi_{gs} | \hat{c}_{1+r_1+r_3,\sigma}^{\dagger} \hat{c}_{1+r_1,\sigma} + H.c. | \Psi_{gs} \rangle
$$

as a function of $r$, more precisely the logarithm of the absolute value of this function. We obtained that this is close to a straight curve, which means that the long range hopping function is exponentially decreasing. Thus we can conclude that the ground state electrons are localized, although not exactly to one lattice point. Therefore the GS is an insulator, albeit not a band insulator.
**SUMMARY**

An itinerant diamond chain with external link is analyzed in the presence of a perpendicular external magnetic field in the frame of a non-integrable Hubbard model. For this chain exact ground states are deduced by a method using positive semidefinite operator properties. The ground states turn out to be nonmagnetic and ferromagnetic in character being localized in the thermodynamic limit.

**Acknowledgements**

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**REFERENCES**

SATURATION MAGNETIZATION AND PHASE COMPOSITION OF SYNTHESIZED MAGNETIC NANOPARTICLES

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ABSTRACT

The organisms of different animals, including human beings contain magnetite nanoparticles. Creation of synthetic analogues of this biomineral is of great importance for solving of wide range of scientific problems. We describe here the creation and investigation of synthetic magnetic nanoparticles. Four samples of magnetic nanoparticles were synthesized by the method of co-precipitation of iron salts at ambient temperature with and without ultrasonic treatment. The characterization of synthesized magnetic nanoparticles was performed by Nuclear Gamma Resonance (NGR) and magnetometry. It was shown, that application of ultrasonic treatment during the synthesis of magnetic nanoparticles leads to formation of superparamagnetic nanoparticles. In our opinion it takes place due to formation of single superparamagnetic nanoparticles during the covering procedure. If covering procedure takes place in the absence of ultrasonic treatment, aggregation of uncovered nanoparticles happened and formation of aggregated magnetite nanoparticles, covered by silica occurs.

Key words: magnetic nanoparticles, superparamagnetic properties

INTRODUCTION

Research of properties of biogenic magnetite and its synthetic analogues is of great importance for solution of a wide range of mineralogical, medico-biological and material science problems. Biogenic magnetite is the most intriguing biomineral. It is believed, that biogenic magnetite serve for realization of a wide range of biological functions, including realization of the animals’ orientation in the space [1] and play an important role in the brain functioning. Magnetite is ferrimagnetic at ambient temperature. Biogenic magnetite is nearly perfect single crystals without defects and dislocations [2]. The size of such crystals is usually in a range from 10 to 200 nm and they are tending to be rather pure iron oxides. It is known, that biogenic magnetite has unique magnetic properties [3]. In our laboratory by means of magnetic resonance the room-temperature macroscopic quantum oscillations in nanobiomagnetite of brain tissues have been discovered. When the microwave power exceeds a critical

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value, the coherent signals are appearing on the contour of the resonance lines. The increase of the power leads to increasing the quantity of the coherent signals, which characterize the quantum oscillations in the nanoscale particles. The resonance characteristics of such nanobiomagnetite differ essentially from other materials, namely, no one from other known natural or synthetic materials shows room-temperature macroscopic quantum oscillations.

During last two decades many different methods of magnetic nanoparticles synthesis were developed [4]. Among them: microemulsions, sol–gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection and electrospray syntheses. But the most widespread, simplest and most efficient method for magnetic nanoparticles synthesis is the method of iron salts co-precipitation, although huge variety of reaction parameters have an influence upon the properties of obtained nanoparticles (phase composition, size, magnetic characteristics etc.). Among them pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), iron salts concentration ratio. It is very important to study the influence of these parameters upon the characteristics of synthesized magnetic nanoparticles.

Many factors can define magnetic properties of synthesized magnetic nanoparticles; among them one can mention chemical composition of the nanoparticles, crystal lattice type, degree of crystal lattice imperfection, size and shape of the particles, interaction of nanoparticles with surrounding matrix and adjacent particles [5]. By changing of the size, shape, composition and structure of nanoparticles, one could in some degree manage magnetic characteristics of such materials. It is very difficult to control all these factors during the synthesis of nanoparticles with roughly same size and chemical composition, that’s why the properties of single-type materials could vary greatly.

We report here the method of magnetic nanoparticles preparation and investigation of their magnetic properties by the methods of magnetometry and NGR.

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

All chemicals and solvents used were of analytical grade and used without further purification. The water was the reagent-grade. All solutions were freshly prepared. All samples were synthesized by the co-precipitation method. *Sample M1* was synthesized by co-precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 1M iron (II) sulfate solution by 1M NH₄OH (reaction time is 40 min). The obtained nanoparticles were covered by 4% (3-aminopropyl) triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents. *Sample M2* was synthesized by co-
precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 2M iron (II) sulfate solution by 1M NH₄OH (reaction time is 14 min). The obtained nanoparticles were covered by 4% (3-aminopropyl)triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents. *Sample M3* was synthesized by co-precipitation of 4.0 ml of 2M iron (III) chloride solution and 1 ml of 1M iron (II) sulfate solution by 1M NH₄OH (reaction time is 26 min). The obtained nanoparticles were covered by 4% (3-aminopropyl)triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents.

*Sample Mag50* was synthesized by co-precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 2M iron (II) sulfate solution by 1M NH₄OH. Obtained magnetite was coated with silica via tetraethoxysilane hydrolyzation in alcohol-water-ammonia mixture. Thereto, 100 ml of ethanol, 2 ml of concentrated NH₄OH were added to the reaction mixture at slow mechanical stirring. After that, 3 ml of tetraethoxysilane (TEOS, 98% (v/v)) were added drop-by-drop to the reaction mixture. The hydrolysis of TEOS was carried out for 20 hours under normal conditions. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents.

The properties of synthesized magnetic nanoparticles were analyzed by the methods of NGR and magnetometry.

**RESULTS AND DISCUSSION**

Saturation magnetization of obtained nanoparticles was approximately 10 A·m²/kg for samples *M1, M3* and 55 A·m²/kg for samples *M2, Mag50*. Differences of magnetic properties of synthesized nanoparticles one could attribute to different chemical composition of the nanoparticles.

The room-temperature NGR-spectra of the samples *M1, M2* and *M3* that were synthesized under ultrasonic treatment include superparamagnetic component (quadrupole doublets) with parameters that are characteristic for high-spin iron (II) ions in octahedral coordination. Change of isomer shifts for resonance doublets of these samples were 0,33 – 0,43 mm/s, and for quadrupole splitting – 0,58 – 0,72 mm/s. The relative areas of superparamagnetic doublets (or iron (III) concentration) for these samples were ~ 60, 7, and 7%, correspondingly. If one proceed from the assumption about equality of resonance adsorption coefficients for iron ions of different valences of all phases, than the ratio of resonance components areas would display the ratio of iron concentrations in each phase. Appearance of superparamagnetic component, probably, caused by ultrasonic treatment of nanoparticles and formation of single super-
paramagnetic nanoparticles during the covering procedure. *Figure 1* presents the room-temperature NGR-spectrum of sample *M1*.

![Room-temperature NGR-spectrum of sample M1.](image)

*Magnetic components of NGR-spectra of these samples are presented by several Zeeman sextets that are results of resonance absorption in structures of several phases of iron oxides and hydroxides – maghemite, hematite and hydrogoethite. Samples composition is very different. For example, goethite content is varying from several to 80 percent. Presence of oxidized magnetic phases (maghemite, hematite), probably, caused by oxidation of magnetite nanoparticles by atmospheric oxygen due to prolongation of reaction time and increasing of reaction temperature.*

NGR-spectrum of sample *Mag50*, consists of six sextets. Two sextets with total area of 41 % are attributed to strongly oxidized magnetite and four sextets – to hydrogoethite. Ratio of concentrations of iron (III) ions in tetrahedral (A) and octahedral (B) positions of magnetite structure to iron (II) and iron (III) ions in octahedral positions based on the areas ratio of corresponding sextets is \(\sim 2.14\). This ratio denotes the nonstoichiometry of magnetite composition due to oxidation of iron in octahedral positions. Using this ratio one could determine the number of vacancies in octahedral sublattice and write the magnetite formula. Four sextets of iron (III) in goethite spectrum are related to watering of its structure and formation of four non-equivalent positions of resonance ions.

Thus, the change of concentration ratio Fe (II)/Fe (III) greatly affect the obtained phase ratio in magnetic nanoparticles and, correspondingly, saturation magnetization of the sample. For instance, samples *M2* and *Mag50* with saturation magnetization approximately 55 A·m²/kg contain mainly maghemite and magnetite, correspondingly. Samples *M1* and *M3* with saturation magnetization approximately 10 A·m²/kg contain mainly hematite and hydrogoethite. Increase
of temperature of covering reaction result in total oxidation of magnetite and formation of maghemite and other iron oxides (samples $M1$, $M2$ and $M3$), whereas covering at ambient temperature leads to formation of magnetite (sample $Mag50$). Ultrasonication during the covering procedure brings to formation of superparamagnetic phases (“small” particles), while covering without ultrasonication leads to formation of ferrimagnetic phases (“large” particles).

**CONCLUSIONS**

Ultrasonic treatment of the magnetic nanoparticles during the covering by silica leads to formation of single superparamagnetic nanoparticles. Covering of magnetic nanoparticles in the absence of ultrasonic treatment leads to aggregation of uncovered nanoparticles and formation of aggregated magnetic nanoparticles.

**REFERENCES**

DETERMINATION OF THE OPTIMAL CONDITIONS OF THE SYNTHESIS OF MANGANESE TUNGESTATE NANO-PATES

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ABSTRACT

In this study, an orthogonal array design (OAD), OA9, was employed as a statistical experimental method for the controllable, simple and fast synthesis of manganese tungestate nano-plates in flower-like clusters. Ultrafine manganese tungestate clusters were synthesized by a precipitation method involving the addition of manganese ion solution to the tungestate reagent. The effects of reaction conditions, i.e., manganese and tungestate concentrations, flow rate of reagent addition and temperature, on the diameter of the synthesized manganese tungestate nano-plates were investigated. The effects of these factors on the width of the manganese tungestate nano-plates were quantitatively evaluated by the analysis of variance (ANOVA). The results showed that manganese tungestate nano-plates can be synthesized by controlling the manganese and tungestate concentration and flow rate. Finally, the optimum conditions for the synthesis of manganese tungestate nano-plates by this simple and fast method were proposed. The results of ANOVA showed that 0.005 mol/L manganese ion concentration, 0.01 mol/L tungestate ion concentration, 10 mL/min flow rate for the addition of the manganese reagent to the tungestate solution and 30 °C temperature are the optimum conditions for producing manganese tungestate nano-plates with 50 ± 6 nm width.

INTRODUCTION

There has been an increasing amount of interest in the synthesis of inorganic structures with nanoscale dimensions MnWO₄ is a complex compound which has bulk electrical conductivity, relatively low melting point and novel magnetic property [1]. MnWO₄ is highly sensitive to change in humidity [2] and having great potential to be used as high sensitivity humidity sensors [3,4], which are important for many industrial applications such as meteorology, medicine, food production, agriculture and the domestic environment [2]. It displays photoluminescence with two main bands at 421 and 438nm [5]. In addition, it has been reported that MnWO₄ showed attractive

Various methods have been used to synthesis MnWO₄, including hydrothermal [6], solvothermal route [2], spray pyrolysis [1], cyclic microwave-assisted spray synthesis [1], precipitation synthesis [7,8], template synthesis [9] and solid state metathetic [10]. The purpose of this work was to produce
MnWO4 nanoplates with flower-like clusters, using precipitation method, which is fast, simple and cost effective method.

**EXPERIMENTAL**

Analytical-grade Mn chloride and sodium tungstate were used as received from Merk. The MnWO4 particles were prepared by adding Mn$^{2+}$ solution, at various concentrations and different flow rates, to the tungstate solution under vigorous stirring and various temperatures. After precipitation, the formed MnWO4 was filtered and washed with distilled water three times. The product was then washed with ethanol and dried at 70ºC for 2 h. To optimize experimental parameters for the synthesis MnWO4 particles, an experimental design approach was followed. The variables (Mn concentration, tungstate concentration, flow rate of addition of Manganese reagent to the tungstate solution, and temperature) were as shown in Table 1. All samples were characterized by scanning electron microscopic (SEM) and energy-dispersive analysis by x-rays (EDAX). SEMs were recorded using on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a Sputter Coater model SCD005 made by BAL-TEC (Switzerland).

<table>
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<tr>
<th>Experiment Number</th>
<th>Mn$^{2+}$ Concentration (M)</th>
<th>WO$_4^{2-}$ Concentration (M)</th>
<th>Mn$^{2+}$ Feed flow rate (ml/min)</th>
<th>Temperature (ºC)</th>
<th>Diameter of MnWO$_4$ particles (nm)</th>
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</table>

**RESULTS AND DISCUSSION**

Mixing the solutions of the anion and cation of an insoluble inorganic salt such as MnWO4 is a commonly used technology for synthesis many of water insoluble inorganic materials [11]. The control of particle size and shape is a complex process requiring a fundamental comprehension of the interactions of reagents. The purpose of this study was to determine how the various parameters affect the diameter of MnWO4 nano-plates in flower-like clusters. The factors included in this study were Mn$^{2+}$ and WO$_4^{2-}$ solution concentrations, flow rate for
addition of Mn\(^{2+}\) solution to the WO\(_4^{2-}\) solution, and the temperature of the solution. Factors and levels tested are reported in Table 1.

The generated nano-plates clusters were characterized by X-ray powder diffraction and EDAX spectrum for the evaluation of their composition and purity. Figure 1 shows the XRD pattern of the obtained manganese tungstate nano-plates. All the diffraction peaks in the figure can be indexed to be in agreement with the hydrated structure of manganese tungstate (Moolooite) from PC-APD, Diffraction software.

![XRD pattern](image)

**Fig. 1** – XRD pattern of the MnWO\(_4\) nano-plates clusters prepared by precipitation method

*Figure 2* shows the SEM images for four samples of MnWO\(_4\) obtained by this method. Also, data obtained by results of the experiments are given in Table 1. The FTIR spectra (Fig. 3) of MnWO\(_4\) with huebnerite structure show the inorganic modes in the range 556–983 cm\(^{-1}\) of the low wavenumber side at 912.30, 874.27, 810.16, 749.26, 652.15, 576.22 and 504.34 cm\(^{-1}\). The vibrations are in accordance with those of other researchers [5, 12]. These bands are assigned to be the internal stretching modes of \(\nu_3\)(Au) and \(\nu_3\)(Eu) transitions [5].

*Fig. 3* shows the photoluminescence (PL) spectra of the present research. By using a 290 nm excitation wavelength, PL spectra show electronic transition within (WO\(_4\))\(^{2-}\) anion molecular complex, associated with the intrinsic emission. It can be excited either in the excitonic absorption band or in the recombination process [15], resulting from the huebnerite-structured products.
Fig. 2 – SEM images of MnWO$_4$ nano-plates clusters obtained at different runs by precipitation method: (a) run 1, (b) run 2, (c) run 4, and (d) run 7

Fig. 3 – PL spectra (292 nm excitation wavelength) of MnWO$_4$ nano-plates clusters prepared with precipitation method
The emissions are blue spectra at 415–423 nm. Although the products were produced using different conditions. The results are in accordance with those detected by other researchers [5, 13].

CONCLUSIONS

In summary, a simple, fast and controllable method for the synthesis of manganese tungstate nano-plates in flower-like clusters in aqueous media was explored. An OAD method was employed for the optimization of the reaction conditions. Some experimental parameters, such as manganese ion concentration, tungstate concentration and flow rate were found to play significant roles in determining the particle size of the manganese tungstate nano-plates. The experiments proved that by using this method, the prediction of the optimum synthesis conditions of manganese tungstate nano-plates can be successfully performed.

REFERENCES

STRUCTURE AND THE MAGNETORESISTIVE PROPERTIES OF THE NANOPARTICLES

$\text{Pr}_{0.6}\text{Sr}_{0.3}\text{Mn}_{1.1}\text{O}_3+\Delta$

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ABSTRACT

Using sol-gel nanotechnology and synthesizing annealings at different temperatures, were obtained and investigated the single-phase nanoparticles $\text{Pr}_{0.6}\text{Sr}_{0.3}\text{Mn}_{1.1}\text{O}_3+\Delta$. Research was conducted both on the powder models and the pressings, preliminarily molded by the usual anisotropic extrusion ($P=0.2$ GPa), and then by high hydrostatic pressure ($P=1$ GPa). The parameter $a$ the pseudocubic perovskite structure of single-phase models increased with an increase in the temperature of synthesis from $550^\circ\text{C}$ to $900^\circ\text{C}$. According to BET decreased the specific surface area and the size of nanoparticles increased. Two forms of the particles being increased with the temperature are characteristic according to the data of the SEM. The reason for two sizes of nanoparticles is the mechanism of perovskitoformation, according to which the forming of perovskite phase occurs on the basis of two most thermostable oxides of praseodymium and strontium with the predominant diffusion of manganese ions. From the temperature dependences resistivity of the nanoparticles, synthesized at different temperatures, follows conclusion about the predominance of the semiconductor nature of tunnel type conductivity on the interparticle contacts. The analysis of the temperature dependences of $4\pi N_{\text{ac}}$ of nanoparticles, testifies about the presence of phase transition the ferromagnetic-paramagnetic. Changes in the quantity $\text{FM}$ are connected with an increase in the portion of magnetic (intra-partial) and the decrease of the magnetodisordered (near-surface) portion with an increase in the size of nanoparticles.

Key words: sol-gel nanotechnology, nanoparticle, rare-earth manganites.

INTRODUCTION

The most urgent actual contemporary trends in physics and the condensed state technique includes studies of the multifunctional nanostructure rare-earth manganites (REM) with debatable nature of the unique interrelation of transport and magnetic properties. This interrelation is manifested in the colos-
sal magnetoresistive (MR) effect near the phase transitions the metal-dielectric $T_{mi}$ and ferro-paramagnetic $T_c$ or in low-temperature region ($T=77$ K) [1-3]. Special attention deserve obtained by promising nanotechnologies [4-6] nanoparticles RE manganites with superstoichiometric manganese, which, being dissolved in the form nanostructural clusters, increases MR effect [7, 8]. The establishment of laws governing the effect of temperature of synthesis and size of nanoparticles on the structure and the functional properties of such rare-earth manganites is of interest.

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

In the work, using sol-gel nanotechnology and synthesizing annealing at different temperatures (at first with 550, then with 600-900 °C), were obtained and investigated the single-phase nanoparticles of $\text{Pr}_{0.6}\text{Sr}_{0.3}\text{Mn}_{1.1}\text{O}_{3+\delta}$. Research was conducted both on the powder models and the pressings, preliminarily molded by the usual anisotropic extrusion (P=0.2 GPa), and then by high hydrostatic pressure (P=1 GPa).

Studies are executed with the aid of the wide arsenal of the methods: 1) X-ray diffraction in Cu Ka–radiation - for determining of phase structure, parameter of perovskite lattice ($a$) and size of the regions of coherent scattering ($d_r$); 2) low-temperature adsorption (BET) - for determining specific surface area ($S_{sp}$) of powders with the conversion to size ($d_s$) of nanoparticles; 3) thermogravimetric - for determining the change in the oxygen content with the annealing from the relative loss of mass ($\Delta m/m_0$); 4) electronic scanning microscopy (SEM) on the Japanese microscope - for determining of microstructure and size of nanoparticles ($d_m$); 5) four-contact resistive at a constant current - for determining resistivity ($\rho$) in the interval 77-400 K; 6) measurements of the temperature dependence of the relative and absolute differential magnetic susceptibility ($\chi_{ac}$ and $4\pi N\chi_{ac}$) of $\nu=600$ Hz, $H=0.1$ Oe - for determining the temperature of magnetic phase transition $T_c(T_N)$ and quantity of ferromagnetic phase (FM); 7) magnetoresistive $\text{MR}=\Delta\rho/\rho$ (%) with $H=0$ and 5 kOe in the interval 77-400 K.

**RESULTS AND DISCUSSION**

The size of the regions of coherent scattering ($d_r$), connected with the size of nanoparticles, increased with an increase in the temperature of synthesis from 550 °C to 900 °C according to X-ray structural data. The parameter $a$ of the pseudo-cubic (or the weak-distorted orthorhombic) perovskite structure of single-phase samples in this case increased (Fig. 1) from $a=3.853$ Å (550 °C) to 3.858 Å (800 °C) as a result of the decrease of oxygen content and respectively increase in the concentration of the large ions Mn$^{3+}$ ($r=0.785$ Å) in comparison with Mn$^{4+}$ ($r=0.67$ Å) [9]. Such changes confirmed an increase in the relative loss of the mass $\Delta m/m_0$ (See Table 1).
Noteworthy a sharp increase in background and intensity of diffusion scattering for \( t_{\text{syn}t}=800^\circ C \) (Fig. 2). This increase in the intensity is possibly connected with the nanostructured clusterization of that caused by orthorhombic distortion [5].

According to BET decreased \( S_{\text{sp}} \) from 26.7±0.35 m\(^2\)/g (550 °C) to 18.7±0.19 m\(^2\)/g (700 °C) and 4.6±0.19 m\(^2\)/g (900°C), and the size of nanoparticles increased from 35.8 nm to 51.2 and 208.1 nm, respectively. The density of pressings (γ), molded by usual (γ\(_1\)) and high isostatic (γ\(_2\)) pressure, increased (Fig. 1, Table 1), respectively from γ\(_1\)=2.80 g/cm\(^3\) and γ\(_2\)=3.155 g/cm\(^3\) (550°C) to 3.18 g/cm\(^3\) and 3.34 g/cm\(^3\) (700°C) and 3.58 g/cm\(^3\) and 3.84 g/cm\(^3\) (900°C). Interparticle porosity decreased in this case.

According to data of the scanning electron microscopy (Fig. 3) for the nanoparticles are characteristic two forms of the particles with the sizes being increased with the temperature: \( d_1=5 \text{ nm} \) and \( d_2=100 \text{ nm} \) (550 °C), 10 and 70 nm (600 °C), 50 and 80 nm (700 °C), 100 and 400 nm (800 °C), 150 and 500 nm (900 °C).

Table 1 – Specific surface (\( S_{\text{sp}} \)), size nanoparticles (d), perovskite structure parameters (a), hydrostatic density (γ) and relative loss of the mass (\( \frac{\Delta m}{m_0} \)) \( \text{Pr}_{0.6}\text{Sr}_{0.3}\text{Mn}_{1.1}\text{O}_{3.8} \).

<table>
<thead>
<tr>
<th>( t_{\text{ann}} ) °C</th>
<th>BET ( S_{\text{sp}}, \text{m}^2/\text{g} )</th>
<th>d, nm (SEM)</th>
<th>a, Å</th>
<th>Density, g/cm(^3) ( \gamma_1 )</th>
<th>Density, g/cm(^3) ( \gamma_2 )</th>
<th>( \frac{\Delta m}{m_0} ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>26.7±0.35</td>
<td>35.8</td>
<td>5</td>
<td>100</td>
<td>3.853</td>
<td>2.803</td>
</tr>
<tr>
<td>550+600</td>
<td>23.5±0.55</td>
<td>40.7</td>
<td>10</td>
<td>70</td>
<td>3.856</td>
<td>2.898</td>
</tr>
<tr>
<td>550+700</td>
<td>18.7±0.19</td>
<td>51.2</td>
<td>50</td>
<td>70</td>
<td>3.8585</td>
<td>3.182</td>
</tr>
<tr>
<td>550+800</td>
<td>9.5±0.21</td>
<td>100.8</td>
<td>100</td>
<td>200</td>
<td>3.8583</td>
<td>3.378</td>
</tr>
<tr>
<td>550+900</td>
<td>4.6±0.19</td>
<td>208.1</td>
<td>150</td>
<td>500 (λ=1000)</td>
<td>3.862</td>
<td>3.582</td>
</tr>
</tbody>
</table>
The reason for two sizes of nanoparticles is the mechanism of perovskitoformation, according to which the forming of perovskite phase occurs on the basis of two most thermostable oxides of praseodymium and strontium with the predominant diffusion of manganese ions.

From the temperature dependences of resistivity (Fig. 4a) and absolute differential magnetic susceptibility (Fig. 4b) of the nanoparticles, synthesized at different temperatures, follows conclusion about the predominance of the semiconductor nature of tunnel type conductivity on the interparticle contacts.

Fig. 2 – X-ray diffraction pattern of the nanoparticles of Pr$_{0.6}$Sr$_{0.3}$Mn$_{1.1}$O$_{3\delta}$ at different temperatures

Fig. 3 – Size and form of nanoparticles with different $t_{\text{suit}}$ according to the data of SEM
With an increase in $t_{\text{sint}}$ from 550 °C to 700 °C $\rho$ (with 77 K) it decreases from 1800 $\Omega\cdot\text{cm}$ to 300 $\Omega\cdot\text{cm}$, and then it increases to 600 $\Omega\cdot\text{cm}$ (900 °C) as a result of a change in the contribution of different mechanisms of electrical conductivity (n- and p- of the type of jump and tunnel). About this testify the bends on $\rho(T)$ near 250 K.

![Temperature dependence of resistivity](image1)

![Temperature dependence of absolute differential magnetic susceptibility](image2)

**Fig. 4** – Temperature dependences of resistivity (a) and absolute differential magnetic susceptibility (b) of Pr$_{0.6}$Sr$_{0.3}$Mn$_{1.1}$O$_{3+\delta}$

This was also confirmed by the decrease of activation energy calculated by equation [10]:

$$\rho = \frac{kT}{ne^2D} \exp \left( \frac{E_a}{kT} \right),$$

where $D = a^2\cdot v$ is diffusion factor ($e$ and $n$ is change and its concentration, respectively).

The analysis of the temperature dependences of $4\pi\chi_{ac}$ (Fig. 4b) of the nanoparticles, synthesized at different temperatures, testifies about the presence of phase transition ferromagnetic-paramagnetic. The temperature of the peak $T_c$ of this transition increase from 250 K (550 °C) to 280 K (700 °C) with further reduction to 270 K (900 °C). This it correlates with the changes $\rho$. Is observed an increase in the quantity of ferromagnetic phase (FM) with $T_c$ from 12% (550 °C) to 18% (700 °C) and 24% (900 °C). With 77 K these changes less: from 5% (550 °C) to 8% (700 °C) and 14% (900 °C). Such changes in the quantity FM are connected with an increase in the portion of magnetic (intra-partial) and the decrease of the magnetodisordered (near-surface) portion with an increase in the size of nanoparticles with an increase in $t_{\text{sint}}$. Since RE manganites are of interest in connection with the manifestation in them MR effect on Fig. 5 they are given temperature dependences with H=5kOe for the nanoparticles, synthesized with different $t_{\text{sint}}$. 
The weakly MR effect in interval of 250-300 K, i.e. near the phase transitions of $T_c(T_N)$ is observed only for $t_{\text{int}}=800$ and 900 °C. With an increase in the temperature of measurement this MR the effect substantially increase. Value this MR of the effect, measured with 77 K, monotonically decreases from 14.8% (550 °C) to 13% (700 °C) and 12.5% (900 °C) with an increase in $t_{\text{int}}$ and size of nanoparticles. This is connected with a change in the interparticle contacts, whose width and extent depend on the size of nanoparticles.

REFERENCES

LIFETIME OF THE PRECESSION MODE OF A NANOPARTICLE MAGNETIC MOMENT IN A ROTATING MAGNETIC FIELD

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ABSTRACT

The influence of the rotating magnetic field on the thermal stability of the precession modes of the nanoparticle magnetic moment is studied analytically and numerically. The analytical results are obtained within the Fokker-Planck formalism, while the numerical ones are determined by the simulation of the stochastic Landau-Lifshitz equation. We numerically calculated the lifetime for both uniform and nonuniform precession modes, derived the expression for this time in the case of small amplitudes of the rotating field, and investigated in detail its frequency dependence.

Key words: magnetic moment, rotating magnetic field, stochastic Landau-Lifshitz equation, Fokker-Plank equation, lifetime.

INTRODUCTION

Recently ferromagnetic nanoparticles and their ensembles attract attention due to high potential of their application. In particular, two equilibrium states of the uniaxial particle magnetic moment can be utilize as a binary bit. This offers great opportunities to use such objects in modern data-storage and data-processing devices [1, 2]. One of the important issues, which stimulates the study of the magnetic moment dynamics, is the performance of such devices. It was the main motivation of many studies [3-9], where several alternative ways of switching the magnetic moment were proposed. Among them, the magnetic field that is rotated in the plane perpendicular to the nanoparticle easy axis deserves a special attention because of small switching time [9]. However, dynamics of the magnetic moment driven by such field is complex and may be nonlinear for the defined field parameters [5, 9]. That is why its study in the case of nonzero temperature is a difficult problem. But at the same time, it is promising enough in regard to identifying the new remarkable effects, such as thermal enhancement of magnetization [6], or resonant suppression of the magnetic moment stability described in the present work.

MODEL AND BASIC EQUATIONS

We suppose that the nanoparticle magnetization is characterized by vector

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\( \mathbf{m} \) which magnitude is constant \((| \mathbf{m} | = m = \text{const})\), but whose direction fluctuates under the action of thermal bath. The above assumption corresponds to the model of coherent rotation \([10]\). Only the uniaxial magnetocrystalline anisotropy defined by the anisotropy field \( H_a \) is taking into account because of the spherical shape of the particles. The \( \mathbf{m} \) dynamics is described by the sto-chastic Landau-Lifshitz equation which can be written in dimensionless form as

\[
\frac{d \mathbf{m}}{dt} = -\mathbf{m} \times (\mathbf{\tilde{H}} + \mathbf{\tilde{n}}) - \lambda \mathbf{m} \times (\mathbf{m} \times \mathbf{\tilde{H}}),
\]

where \( \mathbf{m} = m/\mathbf{m} \), \( t = \omega_r t \) is the dimensionless time, \( \omega_r = \gamma H_a \) is the Larmor frequency, \( \gamma (> 0) \) is the gyromagnetic ratio, \( \mathbf{\tilde{H}} = \partial \mathbf{\tilde{W}} / \partial \mathbf{m} \) is the dimensionless effective magnetic field representing the deterministic action on \( \mathbf{m} \), \( \mathbf{\tilde{n}} \) is the dimensionless effective magnetic field representing the random action on \( \mathbf{m} \), \( \mathbf{\tilde{W}} = W / m H_a \) is the dimensionless magnetic energy of the particle \((W \text{ is the magnetic energy})\), \( \lambda (> 0) \) is the damping parameter. Also we imply that the \( oz \)-axis of the laboratory Cartesian coordinate system is parallel to the nanoparticle easy axis. In this case the rotating field can be defined by the expression \( \mathbf{\tilde{h}} = e_x h \cos(\mathbf{\tilde{\omega}} t) + e_y h \rho \sin(\mathbf{\tilde{\omega}} t) \), where \( \mathbf{\tilde{\omega}} = \omega / \omega_r \) is the dimensionless field frequency, \( \mathbf{\tilde{h}} = h / H_a \) is the dimensionless field amplitude \((h \text{ and } \omega \text{ are the amplitude and the frequency of the field, respectively})\), \( e_x, e_y \) are the Cartesian unit vectors, \( \rho = \pm 1 \) for the counterclockwise and clockwise field polarization, respectively. And finally, the dimensionless magnetic energy can be expressed as \( \mathbf{\tilde{W}} = 0.5 \sin^2 \theta - \mathbf{\tilde{h}} \sin \theta \cos \psi \), where \( \theta \) is the polar angle of \( \mathbf{m} \), \( \psi = \phi - \rho \omega t \), \( \phi \) is the azimuthal angle of \( \mathbf{m} \).

From the other hand, the statistical properties of the magnetic moment can be described using the conditional probability density \( P = P(\theta, \psi, \tilde{t} | \theta', \psi', \tilde{t}') \), \( \tilde{t} \geq \tilde{t}' \) \([11]\) which obeys the forward Fokker-Plank equation

\[
\frac{\partial^2 P}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2 P}{\partial \psi^2} - \frac{2a}{\lambda} \frac{\partial}{\partial \theta} \left[ \cot \theta + \frac{2a}{\lambda} u(\theta, \psi) \right] P - 2a \frac{\partial}{\partial \psi} \left[ v(\theta, \psi) - \rho \mathbf{\tilde{\omega}} \right] P = \frac{2a}{\lambda} \frac{\partial P}{\partial \tilde{t}}, \quad (2)
\]

and backward Fokker-Plank equation

\[
\frac{\partial^2 P}{\partial \theta'^2} + \frac{1}{\sin^2 \theta'} \frac{\partial^2 P}{\partial \psi'^2} + \left[ \cot \theta' + \frac{2a}{\lambda} u(\theta', \psi') \right] \frac{\partial P}{\partial \theta'} + 2a \frac{\partial}{\partial \psi'} \left[ v(\theta', \psi') - \rho \mathbf{\tilde{\omega}} \right] \frac{\partial P}{\partial \tilde{t}'} = \frac{2a}{\lambda} \frac{\partial P}{\partial \tilde{t}'} \cdot (3)
\]

Here
\begin{equation}
\begin{aligned}
    u(\theta, \psi) &= -\lambda \sin \theta \cos \phi + \tilde{h}(\lambda \cos \theta \cos \psi - \sin \psi), \\
    v(\theta, \psi) &= \cos \theta - \tilde{h} \frac{\cos \theta \cos \psi + \lambda \sin \psi}{\sin \theta}, \\
\end{aligned}
\end{equation}

\begin{equation}
a = mH_d/2k_B T, \ k_B \text{ is the Boltzmann constant, } T \text{ is the temperature.}
\end{equation}

Based on the equation (2) one can transform the Landau-Lifshitz equation (1) into a system of two stochastic differential equations which are more suitable for the numerical simulation

\begin{equation}
\begin{aligned}
    \dot{\theta} &= u(\theta, \psi) + \frac{\lambda}{2a} \cot \theta + \sqrt{\frac{\lambda}{a}} \eta_\theta(t), \\
    \dot{\psi} &= v(\theta, \psi) - \rho \tilde{\omega} + \sqrt{\frac{\lambda}{a}} \sin \theta \eta_\psi(t),
\end{aligned}
\end{equation}

where the values of \( \eta_\theta(\tau) \) and \( \eta_\psi(\tau) \) denote two independent Gaussian white noises with zero mean and correlation function \( \langle \eta_i(\tilde{t})\eta_j(\tilde{t}') \rangle = 2\Delta \delta_\tau \delta(\tilde{t} - \tilde{t}') \), \( i, j = \theta, \psi, \Delta = \lambda k_B T/\gamma m \) is the random field intensity, \( \delta_{ij} \) is the Cronecer symbol, \( \tilde{\delta}(\cdot) \) is the Dirac \( \delta \) function.

**RESULTS AND DISCUSSION**

The main characteristic of thermal stability is the lifetime \( \tilde{T} = \tilde{T}(\theta', \psi') \), i.e., the time during which the magnetic moment stays in a given precession mode. The average value of this time was calculated using the mean first passage time method [12]. When the initial state of \( \mathbf{\mu} \) is along the \( oz \)-axis the lifetime within this approach can be written as follows

\begin{equation}
\tilde{T} = \int \frac{2\pi}{0} d\theta_0 \int \frac{2\pi}{0} d\psi_0 \int \frac{2\pi}{0} d\theta \int \frac{2\pi}{0} d\psi P(\theta, \psi, \tau | \theta', \psi', 0),
\end{equation}

where \( \tau = \tilde{t} - \tilde{t}' \), \( \theta_0 \) is the angle of the cone surface placed well beyond the separatrix of the corresponding deterministic system. Reaching of this surface by the magnetic moment actually denotes the completion of the switching process. In the present study we assume that \( \theta_0 = 0.8\pi \).

Using the backward Fokker-Planck equation (3) and lifetime definition (5), the frequency dependence of the lifetime for the uniform precessional mode was obtained in the case of \( h \rho \ll 1 \)

\begin{equation}
\tilde{T} = \frac{e^a}{\lambda} \sqrt{\frac{\pi}{a}} \left[ 1 - \frac{ah^2}{(1 - \rho \tilde{\omega})^2 + \lambda^2 + ah^2} \right] \left[ 1 - \frac{\rho ah^2}{\tilde{\omega}(\lambda^2 + \tilde{\omega}^2)/(1 + 2\tilde{\omega}^2) + \rho ah^2} \right].
\end{equation}

Depending on the direction of the field rotation \( \tilde{T}(\tilde{\omega}) \) displays different behavior. If this direction coincides with the direction of the natural precession of the magnetic moment, then this dependence exhibits a resonance minimum.
This suggests about the resonance suppression of thermal stability of the magnetic moment by the rotating field. In other case, when these directions are opposite, the frequency dependence of the lifetime has a weak maximum. Asymptotic analysis of equation (6) shows that the lifetime does not depend on the direction of the field rotation and its value at small frequencies can be much less than at large ones.

Obtained analytical results are confirmed by the numerical simulations based on the solution of system (4) (see Fig. 1a). In addition, simulations let us to reveal a number of unexpected features of the lifetime of the nonuniform mode. Particularly, lifetime is practically the same as it would be expected for the uniform mode. Indeed, the long dashed curve in Fig. 1b ($h = 0.1$) covers the uniform mode only. At the same time, the short dashed curve in Fig. 1b ($h = 0.18$) covers both the uniform and nonuniform modes. This result is not obvious, because at zero temperature the time-dependences of the precession angle are different enough for these modes. It can be concluded that since the character of precession mode does not define the lifetime of this mode, the distance to the separatrix which for a given set of parameters separates one stable precession mode from the other affects this time strongly. Another feature of $\hat{T}(\tilde{\omega})$ is the dependence of the minimum location on the field amplitude that is purely nonlinear effect.

**CONCLUSIONS**

The thermal stability of the uniaxial nanoparticle magnetic moment was investigated in the term of the lifetime of the precession mode. The lifetime was studied both numerically and analytically within the mean first passage time approach. The exact analytical expression for the uniform mode lifetime in the case of small rotating field amplitude was obtained. When the direction of the field polarization coincides with the direction of the magnetic moment natural precession, the resonance suppression of thermal stability of the magnetic
moment by the rotating field was revealed. The numerical calculation of the frequency dependence of the lifetime for different field amplitudes confirmed the analytical predictions and in addition showed a number of features of the nonuniform mode.

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REFERENCES

Thin films
MAGNETIC PROPERTIES OF Fe/Cu MULTILAYERS PREPARED USING PULSED-CURRENT ELECTRODEPOSITION

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ABSTRACT

[Fe (tFe) nm/Cu (tCu) nm]N multilayer films were prepared using pulsed-current electrodeposition method. The role of the pulsed-current electrodeposition on microstructure and magnetic properties was investigated. The microstructure of the multilayer films is dependent on the thicknesses of both the Fe and Cu layers. The saturation magnetization of the multilayers strongly correlated with the crystalline structure of Fe at the interface of Fe and Cu layers.

Key words: pulsed-current electrodeposition, Fe/Cu, multilayers, saturation magnetization, microstructure

INTRODUCTION

Interest in artificially tailored nanostructures has greatly surged in recent times because of their novel magnetic properties and potential technological applications [1]. One of the excellent examples of artificially tailored nanostructure is Fe/Cu, which is composed of mutually insoluble metals such as iron and copper. In spite of its complex structure, Fe can be combined with Cu to prepare multilayers of fcc-Cu and bcc-Fe [2-4]. Extensive studies have been done on the crystalline structure and magnetization properties of the multilayers of Fe/Cu prepared by physical methods such as sputtering [5, 6], molecular beam epitaxy [7], and e-beam evaporation [8]. However, these methods require an ultra-high vacuum to control their film thicknesses. In contrast, the electrochemical method employs the liquid phase, which is relatively simple, inexpensive, and efficient for growing multilayers at the atomic level.

Pulse electrodeposition offers an easy adjustment of the current and time required in finding appropriate electrodeposition conditions. It also offers direct control over the composition and thickness, which can be achieved by adjusting the quantity of the pulsed-current through the electrolyte. Also, the

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thickness and composition of the multilayer containing the layers of Fe and Cu can be conveniently controlled by changing pulse amplitude and width [9].

Earlier, we reported findings on the chemical compositions and magnetoresistance of compositionally modulated Fe-Cu-Ni alloys [9], and Fe-Ni [10] and Fe-Cu [11] multilayers and alloys.

In this study, we re-examine the relationship between saturation magnetization and the microstructure of the Fe/Cu multilayers. The saturation magnetization of the multilayer strongly correlated with the crystalline structure of Fe at the interface of Fe and Cu layers.

**EXPERIMENTAL PROCEDURES**

Fe/Cu multilayers were electrodeposited in a 250 cc glass beaker from a single sulphate electrolyte using pulsed-current electrodeposition, which utilized two electrodes. The pulsed-current (potential) was supplied and controlled by a programmable micro-computer and a digital current source as shown in [12].

The solution was composed of FeSO$_4$.6H$_2$O (25.01 gm/litre), CuSO$_4$.5H$_2$O (2.5 gm/litre), and NaCl (2.5 gm/litre). Ammonium hydroxide (NH$_4$OH) was used as a complexing agent because it improves the quality of the deposit [13]. The pH was maintained at 3.5 and it was controlled by the addition of sulphuric acid (H$_2$SO$_4$). The total composition of the solution was 0.1 mol/litre. The solution was prepared in double distilled water. The temperature of the bath was maintained at room temperature. Further details are available in [11] and [14]. The distance between the cathode and anode was maintained at 2 cm. The current density was changed from 0.2 to 20 mA/cm$^2$. Metal ions were collected at the cathode. Ferromagnetic Fe and non-magnetic Cu were alternately deposited to form very fine layered films. After deposition, the films were cleaned with double distilled water, dried, and immediately wrapped in paraffin paper.

The saturation magnetization of the Fe/Cu multilayers was measured in the range of ± 21 kOe, using a vibrating sample magnetometer. The microstructure was analyzed with CuK$_\alpha$ radiation using an X-Ray diffractometer. The lattice spacing, d, was calculated from the diffraction curve using Bragg’s law as:

$$2d \sin \theta_B = n\lambda$$

where $n$ is the integer, $\lambda$ is the wavelength of the X-rays, and $\theta_B$ is the Bragg’s angle.

The multilayer periodicity was determined using a composition of Fe and Cu in the film, and the composition was estimated using micro-balance and energy dispersive X-ray analysis.

**RESULTS AND DISCUSSIONS**

Fig.1a shows pulsed-current waves with different widths and intervals
and (Fig 1b) the corresponding multilayer structures. The composition of each layer of Fe and Cu in (Fig 1b) corresponds to the height of the pulse wave whereas the thickness corresponds to the pulse width, which is also a deposition time in (Fig 1a). The beauty of this process is that by controlling both the pulse amplitude and widths one can produce various combinations of multilayers and alloys on an atomic scale via a single electrolyte [12].

Fig. 2 shows the saturation magnetization of [Fe 1 nm/Cu (tCu)]120 and [Fe 3 nm/Cu (tCu)]40 multilayers as the Cu layer thickness, tCu, is changed from 0.5 to 2 nm. The total Ms tended to decrease when tCu is increased. However, decrease in magnetization for tFe= 1 nm is different from when tFe= 3 nm, and the gap between the two widens with the increase of tCu, i.e., the decrease of Ms with tFe= 1 nm is sharper than when tFe= 3 nm. Furthermore, Ms tends to decrease when subject to heat treatment.

The reasons for the decrease in magnetization with the change in thickness of Cu layer are likely due to a change-over of fcc-Fe from the bcc-Fe crystalline structures [14]. The reasons for further decrease in magnetization due to heat treatment are likely due to the inter-diffusions of Fe and Cu atoms at the interface [15] [16].
The details about how the lattice constant changes with the layer thickness are given in Fig. 3 and Fig. 4. It should be noted that total Fe content in the multilayers is always kept constant.

Fig. 3 shows the dependence of Cu layer thickness on the lattice constant of Fe, $a_{Fe}$, which increases as the Cu layer thickness, $t_{Cu}$, of [Fe 1 nm /Cu ($t_{Cu}$)]$_{120}$ multilayer is changed from 1 to 3 nm. The inset shows the X-ray diffraction curves. A sharp diffraction peak of [Fe 1 nm /Cu ($t_{Cu}$)]$_{120}$ corresponding to bcc-Fe (110) is indicated by long dashed lines. When the fcc-Cu<111> layer thickness is increased, the peak shifts towards the lower side, and also results in a decrease in the diffraction peak height and an increase in the diffraction width, a sign of significant change in the crystalline structure of bcc-Fe (110) [15]. The broad peak of Fe (110) is believed to be originated from the intermixing of atoms of Fe and Cu in the interface as the thickness of Cu is increased [14].

Fig. 4 shows the Fe layer thickness dependence on lattice spacing. The lattice spacing of [Fe ($t_{Fe}$) nm/Cu 1 nm]$_{N}$ multilayers, where $N$ is varied from 120 to 40, increases as the thickness of the Fe layer in the multilayer is increased from 1 to 3 nm. The lattice spacing is lower than the bulk value of $d_{110}Fe$ for $t_{Fe}$<1 nm, followed by an increase that approaches the bulk value of $d_{110}Fe+d_{111}Cu$ for $t_{Fe}$ = 3 nm. These multilayers display a combination of properties whose atomic structures and properties vary strongly with the individual layer thickness of Fe and Cu, indicating how the electronic structure might be engineered to enhance saturation magnetization [17].
CONCLUSIONS

We have observed unusual changes in the atomic structures of the Fe/Cu multilayers depending on the layer thickness of Fe and Cu. The change in the electronic properties of Fe is believed to arise from the intermixing of atoms at the interface between Fe and Cu layers. The thickness dependence of the magnetization shows that the decrease in magnetization is caused by changes in the crystalline structures from bcc-Fe to fcc-Fe, which is consistent with the results of X-ray diffraction. Research on the Fe/Cu multilayer is growing rapidly and has many technological applications including in the biomedical sectors.

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Preparation and Characterization of Thin Films Derived from Polyelectrolyte-Surfactant Complexes based on Cationic Polymer – JR-400 and Anionic Surfactant – Sodium Dodecylbenzenesulfonate

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ABSTRACT

Thin films derived from polyelectrolyte-surfactant complexes on the basis of cationic polymer – JR-400 and anionic surfactant – sodium salt of dodecylbenzenesulfonate (SDBS) were isolated from the equimolar mixture of aqueous solutions of polyelectrolyte and surfactant. Characteristic bands of functional groups of JR-400 and SDBS involved into complexation reaction were identified from FTIR spectra. Elemental composition and morphology of thin layers of polyelectrolyte-surfactant complexes deposited on SiO₂ surface were evaluated by SEM and AFM. The height of polyelectrolyte-surfactant complexes evaluated from AFM and SURFUS data is in good agreement and arranged between 10 and 50 nm. The XRD analysis of thin films revealed that polyelectrolyte-surfactant complexes have amorphous structure with a broad halo near 2θ. Contact angle measurements show that the glass surface treated by polyelectrolyte-surfactant complexes is more hydrophobic than that of untreated glass surface due to replacement of surfactant brushes on air. Thin films of polyelectrolyte-surfactant complexes may be perspective materials as antifogging materials.

Key words: cationic polyelectrolye, anionic surfactant, polycomplexes, solubility, structure, morphology, thin films, coating

INTRODUCTION

Polyelectrolyte-surfactant complexes (PSCs) attract much attention from fundamental and applied points of view. PSCs based on biopolymers – DNA and/or proteins and lipids play a crucial role in biological systems to model the structure and function of biological membranes in living cells [1,2]. Applied aspects of PSCs cover bio-, and nanotechnology, medicine, food science etc. Self-assembled polyelectrolyte-surfactant complexes in the solid state and as nanoparticles have been reviewed by Thunemann [3]. Usually interaction of
polyelectrolytes and surfactants leads to formation of insoluble stoichiometric polycomplexes that restrict their wide researches in solution. However discovery of PSCs which are soluble in organic solvents considerably intensified interest in this area [4]. Authors [5] reported on organosoluble, in particular in chloroform, PSCs assembled from the pairs DNA-cationic surfactant, poly(l-lysine)-anionic surfactant [6] and cationic polyelectrolyte-anionic surfactant [7]. They were studied in chloroform by viscometry, turbidimetry, $1H$ NMR, isothermal diffusion, flow birefringence, and dynamic light scattering techniques [8, 9]. Solubility of the PSCs in low-polarity solvents increased in the order chloroform > chlorobenzene > benzene. Only few reports are available from literature on organosoluble PSCs, inverted micells, formed from poly(amidoamine) dendrimers [10] and hyperbranched poly(ethyleneimine) [11] and fatty acids. It has been reported that stoichiometric polyelectrolyte–surfactant complexes precipitated from aqueous solution can be further dissolved in some organic solvents and form a bottle-brush arrangement where the head groups of amphiphiles are electrostatically attached to the polyelectrolyte backbone and the solvation of the hydrophobic tails contributes to the stability of the complexes [12]. Concerning the PSCs formed between N,N,N-trimethylammonium derivatized hydroxyethyl cellulose JR-400 and anionic surfactants literature survey [13] shows their adsorption onto solid surfaces. Information on isolation of PSCs based on JR-400 and anionic surfactants from aqueous solution and their further dissolution in organic solvents to our knowledge is lacking. The present paper is devoted to ethanol solution behavior and thin films morphology of PSCs derived from cationic polyelectrolyte JR-400 and anionic surfactant – sodium salt of dodecylbenzenesulphonate.

**EXPERIMENTAL PART**

**Materials**

Cationic polymer JR-400 – N,N,N-trimethylammonium derivatized hydroxyethyl cellulose – with molecular weight $M=1\cdot10^5$–$3\cdot10^6$ and anionic surfactant – sodium salt of dodecylbenzenesulphonic acid (SDDBS) purchased from Polysciences.Inc. were used without additional purification.

**PREPARATION OF PSCs**

40 mg of JR-400 dissolved in 100 mL of distilled water. 10 mL aliquot was titrated by aqueous solution of SDDBS with concentration 1 mM. Inflection point of conductimetric titration curve that is equal to 11 mL was taken as optimal amount of SDDBS that is necessary for full precipitation of JR-400. Thus it was found that to precipitate 40 mg of JR-400 it is needed 68 mg of SDDBS. Due to difficulties in selection of repeating monomer unit for JR-400 in further experiments the mass ratio of $[m_{SDDBS}]/[m_{JR-400}] = 5/3$ was used for PSCs preparation protocol.
For preparation of PSCs as precipitate an aqueous solution of SDDBS was dropwisely added to aqueous solution of JR-400 during 2 h under stirring. After, the precipitate was decanted by distilled and deionized water several times and finally it centrifuged at 10^4 rpm.

White precipitate was then dried in air at room temperature and in vacuum oven at 40 °C till the constant mass. The yield of PSCs glass powder was equal to 66.7%. The chemical composition of solid sample performed by energy dispersive X-ray (EDX) attached to SEM indicated on the absence of counterions (Na^+ and Cl^-) that release into aqueous solution in the course of complexation reaction. Additionally the absence of chloride ions in supernatant was confirmed by titration with AgNO_3. The solubility of PSCs was checked in various organic solvents (*Table 1*).

**Methods**

Viscosity of PSCs in ethanol was measured on Ubbelohde viscometer at 25±0,1 °C. The dynamic light scattering (DLS) measurements were performed on a commercial goniometer equipped with a ALV 6000 correlator (ALV, Langen, Germany) with a He-Ne laser (Polytech, Waldbronn, Germany) at a wavelength of λ=633 nm in quartz cells (Hellma, Germany). DLS measurements were performed in the angle of 90° with an ALV6000 multibit autocorrelator.
Table 1 – Solubility of JR400/DDBSNa in various organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>–</td>
</tr>
<tr>
<td>Ethanol</td>
<td>+</td>
</tr>
<tr>
<td>DMF</td>
<td>+</td>
</tr>
<tr>
<td>DMSO</td>
<td>+</td>
</tr>
<tr>
<td>Toluene</td>
<td>–</td>
</tr>
<tr>
<td>Ethanol:Toluene (3:1 vol/vol)</td>
<td>+</td>
</tr>
<tr>
<td>Ethanol:Toluene (1:1 vol/vol)</td>
<td>+</td>
</tr>
<tr>
<td>Ethanol:Toluene (1:3 vol/vol)</td>
<td>emulsion</td>
</tr>
<tr>
<td>Ethanol:Water (1:4 vol/vol)</td>
<td>+</td>
</tr>
</tbody>
</table>

*) + soluble; – insoluble

The inverse Laplace transformation using the REPES method [14] of constrained regularization (a part of the GENDIST program), which is similar in many respects to the inversion routine CONTIN, was used for analysis of time autocorrelation functions. The average hydrodynamic radius $R_h$ was calculated from the diffusion coefficient $D$ using the Stokes-Einstein equation. At least 10 measurements were made of the sample to check repeatability. The experimental error of the $R_h$ determination was typically 2.5% for all measurements. The sample with concentration 5 mg·mL$^{-1}$ was filtered by 0.45 µm filter (Milllex, Millipore) before use.

SEM measurements were carried out on scanning electron microscope JEOL, JSM5800 (Japan). FTIR spectra were recorded on a Alpha-P (Burker). AFM measurements were made with the help of NT-MDT (Russia). 5 or 10 mg·mL$^{-1}$ ethanol solution of PSCs was deposited onto silicon surface SURF by microsyringe and the morphology of PSCs was studied. XRD spectrum of PSCs was recorded on X’Pert MPD PRO (PANalytical). Conductimetric titration was carried out on the pH/conductivity meter "Mettler Toledo MFC 227" (Switzerland) at room temperature. Separation of PSCs precipitate from solution was carried out on preparative centrifuge “Eppendorf” (Germany) at 10$^4$ rpm and room temperature.

RESULTS AND DISCUSSION

The PSCs preparation protocol includes the following stages: 1) mixing of aqueous solutions of JR-400 and SDDBS; 2) formation of hydrophobic micellar polyelectrolyte-surfactant complexes (PSCs); 3) aggregation of micelles and precipitation; 4) thoroughly washing of precipitate by distilled and deionized water; 5) drying of precipitate and 6) dissolution of PSCs in ethanol. Fig.2 shows the dependence of the reduced viscosity on PSCs concentration in ethanol. It is seen that in pure ethanol PSCs behave polyelectrolyte character, e.g. the reduced viscosity increases with dilution. This is probably connected with existing of some uncompensated with SDDBS cationic sites of JR-400. In pure
ethanol PSCs can be represented as expanded chains. In the presence of 0.05 or 0.1 N KBr the polyelectrolyte effect disappears and PSCs solution behave as nonionic polymer. Earlier [15] the polyelectrolyte character of PSCs based on poly-N,N-dimethyl-N-benzylolxethylmethacryloylammonium chloride and sodium dodecylsulfate (or sodium salts of alkylsulfonic acids RSO₃Na, where R = C₁₆−C₁₈) was observed in chloroform and methanol. Dependence of the reduced viscosity of JR-400/DDBSNa on the composition of ethanol-water mixture passes through maximum at ethanol-water mixture 3:2 vol/vol. Appearance of well defined maximum may be explained by expanding of PSCs chains as a result of solvation of hydrophobic groups by ethanol and hydrophilic ones by water. Sharp decrease of the reduced viscosity in enriched by water mixture may be due to poor quality of water with respect to hydrophobic tails of surfactant. Light scattering results show on appearance of 4 peaks that correspond to 2.4 nm (1.2%), 29.3 nm (1.07%), 417 nm (7.13%) and 2600 nm (90.5%) (Fig.3). In our mind the peak 1 is probably responsible for the single PSCs chains; the peak 2 reflects the micelles or PSCs coils. The peaks 3 and 4 may represent big aggregates of PSCs. It should be mentioned that PSCs solution was filtrated through filter with diameter of pores 450 nm while the hydrodynamic radius of agglomerated particles is 2600 nm. It means that aggregation of PSCs particles takes place after filtration. However big particles or aggregates scattering more light are not so representative than that of small particles.

Ethanol solution of PSCs with concentrations of 5 or 10 mg·mL⁻¹ was deposited onto SiO₂ surface and the elemental composition of thin films were evaluated by SEM-EDX.

Pure SURF contains Si and O originating from SiO₂. Appearance of S on the deposited PSCs films confirms the presence of SO₃⁻ groups in the composition of the PSCs. FTIR spectra of PSCs also contain the characteristic bands of
SO$_2$ scissoring, symmetric stretching vibrations of O=S=O and S=O at $\nu$ = 578, 1031, and 1061 cm$^{-1}$ together with functional groups of JR-400 and SDBS.

Morphology of thin layers of PSCs deposited on SiO$_2$ surface was evaluated by AFM and Sarfus (high-resolution optical microscope) (Fig. 4). The height of PSCs aggregates evaluated from AFM and Sarfus data is in good agreement and arranged between 10 and 50 nm.

![Fig.4 – AFM (left) and Sarfus (right) pictures of PSCs deposited on SiO$_2$ surface.](image)

Equivalent diameter distribution of PSCs particles derived from Sarfus is depicted on Fig. 5.

![Fig.5 – Diameter distribution of 78 particles of PSCs deposited on solid surface](image)

Mean diameter of PSCs particles is 239±169 nm and is broadly distributed. Approximately 13 particles have average diameter of 30 nm, 14 particles – 230 nm. Mean diameter of 23 particles is about 320 nm. These data are less comparable with light scattering results may be due to adsorption of PSCs particles on charged surface.

XRD pattern of PSCs shows a broad halo at $\Theta=20^\circ$ that is specific for amorphous structure (Fig. 6). Analogous XRD picture was also characteristic for hydrophobically modified polyampholytes.
The wettability of glass surface was also checked. As seen from Table 2, the glass surface treated by 5 and 10 mg·mL$^{-1}$ PSCs solutions is more hydrophobic than that of untreated ones suggesting the potential applicability of PSCs as antifogging coating. Upon increasing of the PSCs concentration the contact angle increases (Table 2).

<table>
<thead>
<tr>
<th>No. samples</th>
<th>Concentration of PSCs, mg·mL$^{-1}$</th>
<th>Thickness of film, mm</th>
<th>$\alpha$, $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.2</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>&lt;10</td>
<td>0.2</td>
<td>90</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Solid polyelectrolyte-surfactant complexes precipitated from aqueous solution of interacting components were dissolved in ethanol and deposited on solid surface of SiO$_2$. The height of deposited thin films determined by AFM and SARFUS is in good agreement and arranged between 10 and 50 nm. Contact angle measurements reveal that thin films of polyelectrolyte-surfactant complexes deposited on glass surface may be useful as antifogging coatings.

**Acknowledgements**

The authors are thankful to Dr. Nicolas Medard from Research & Development NANOLANE (France) for Sarfus experiments.
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INVESTIGATION OF THE EPITAXIAL GROWTH OF AIIIBV-N HETEROSTRUCTURES FOR SOLAR CELL APPLICATIONS

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ABSTRACT

The In_{1-y}Ga_{y}As_{1-x}N_{x} alloy semiconductor alloys, so called diluted nitrides (AIIIBV-N), have been extensively studied recently. Unusual properties of these materials such as a huge and negative band gap bowing coefficient and a large conduction band offset come mainly from a large size and electronegativity difference between N and As atoms. These features make AIIIBV-N alloys very promising for applications in 1.3 – 1.55 μm lasers and very efficient multijunction solar cells. On the other hand the small amount of nitrogen strongly deteriorates the material quality of diluted nitrides. So, a lot of research efforts are focused on understanding the reasons of the generated defects and optimisation the growth methods (mainly MBE and MOVPE technologies). This work presents the influence of the growth parameters on the properties of undoped GaAsN/GaAs and multiple quantum well (MQW) InGaAsN/GaAs heterostructures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The structural and optical properties of the mentioned structures were examined using high resolution X-Ray diffraction HRXRD, contactless electroreflectance spectroscopy CER (T = 300 K), secondary ion mass spectrometry (SIMS). The influence of the growth temperature and the nitrogen source concentration in a gas phase on the composition and material quality of both GaAsN epilayers and InGaAsN quantum wells is presented and discussed.

Key words: diluted nitrides, APMOVPE epitaxy, MQW InGaAsN/GaAs, HRXRD, CER, SIMS

INTRODUCTION

The InGaAsN/GaAs heterostructures proposed in 1996 by Kondow et al. [1] have been successfully used in telecom laser constructions on GaAs substrate. Additionally, the InGaAsN with a bandgap of 1 eV are lattice

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matched to both GaAs and Ge for the nitrogen and indium contents of around 3% and 9%, respectively. These features make this semiconductor an ideal candidate for high-efficiency multijunction solar cells (MJSCs) based on the Ge/InGaAsN/GaAs/InGaP structure [2]. The growth technology of the GaAsN alloy-based diluted nitrides is very difficult because of the large miscibility gap between GaAs and GaN. The incorporation of more than 3% of nitrogen into GaAs crystalline structure drastically deteriorates the optical quality of GaAsN epilayers [3]. They contain a lot of the point defects (vacancies, antisites, interstitials) and impurities (oxygen, carbon, hydrogen). The main efforts of the investigators have been made to understand physics of these alloys, to optimize the growth conditions and improve their structural and optical quality in order to application in high-performance optoelectronic devices.

This work presents the epitaxial growth of undoped GaAsN layers and multiple quantum well (MQW) - $3 \times \text{InGaAsN/GaAs}$ - structures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The main growth parameters such as the growth temperature, the hydrogen flow rate through the bubbler with the organic nitrogen source and the molar ratio of the gallium to indium in the gas phase were changed to achieve the high material quality and alloy composition suitable for application in MJSCs. The properties of the obtained structures were examined using HRXRD, CER and SIMS methods while the most of the growth characteristics were estimated based on HRXRD measurements.

**EXPERIMENTAL AND MEASUREMENT DETAILS**

The investigated heterostructures were grown by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE) with AIX200 R&D AIXTRON horizontal reactor on (100)-oriented semi-insulating SI GaAs and Si-doped n-type GaAs substrates. Trimethylgallium (TMGa), trimethylaluminium (TMAl), tertiarybutylhydrazine (TBHy) and arsine (AsH$_3$: 10% mixture in H$_2$) were used as the growth precursors. High purity hydrogen was employed as a carrier gas. The following growth parameters were changed: the growth temperature $T_g=566 \div 585$ °C, the hydrogen flow rate through the saturator with TBHy - $V_{H2/TBHy}=1100 \div 3000$ ml/ min, the ratio of the gallium to indium source concentration in the gas phase III$_{Ga}/$III$_{In}=4.8$ and 6.9. Stable parameters during all runs were: the arsine flow rate $V_{AsH3}=50$ ml/ min (for GaAsN and InGaAsN) and 300 ml/ min (for GaAs), the total flow of the hydrogen carrier gas $V_{H2tot}=9.6$ l/ min, the organic source temperatures: $T_{TMGa}=-10$ °C, $T_{TMAl}=18$ °C, $T_{TMIn}=20$ °C, $T_{TBHy}=30$ °C.

Two types of samples were investigated:

1. Undoped GaAs$_{1-x}$N$_x$/GaAs heterostructures consisted of 450 nm thick GaAs buffer and $\sim$180 nm thick GaAs$_{1-x}$N$_x$ (samples: N41, N42, N44, N47, N48, N54).
2. Undoped MQW structure consisted of 450 nm thick GaAs buffer and \(3 \times \ln_y \Ga_{1-x} \As_{1-y} \N_x / \GaAs\) MQW region capped by 40 \(\pm\) 50 nm thick GaAs (samples: NI43, NI45, NI46, NI49, NI51, NI53).

Structural properties of the obtained heterostructures were studied by high resolution X-Ray diffraction (HRXRD). The modification and improvement of the simulation programme of the HRXRD Philips equipment was performed for determination of the structural quality of diluted nitrides. The rocking curves allow the evaluation of the thickness and composition of the AIIIBV-N epilayers. The reciprocal space maps give additional information about the presence of the structural defects and the relaxation state. Optical properties were analysed using contactless electroreflectance (CER) modulation spectroscopy. The reflectivity from the investigated sample is modulated by external electric field. This is a very useful, nondestructive method, very sensitive at room temperature described in [4]. SIMS measurements performed using a Cameca Magnetic Sector instrument and sputtering with Cs Gun allowed to obtain the composition depth profiles of investigated structures.

**RESULTS AND DISCUSSION**

The investigations were concentrated on determination of the influence of the technological parameters on efficiency of nitrogen incorporation into GaAs and InGaAs alloys and properties of the obtained \(\GaAs_{1-x} \N_x / \GaAs\) and MQW \(3 \times \ln \GaAs \N_x / \GaAs\) heterostructures. *Fig. 1a* shows symmetric (004) scans of \(\GaAs_{1-x} \N_x\) films with different nitrogen contents (x=0.55, 0.65, 1.5 %).

![Rocking curve for the (004) reflection of GaAs\textsubscript{1-x}N\textsubscript{x} with different nitrogen content](image)

**Fig. 1** – a) Rocking curve for the (004) reflection of \(\GaAs_{1-x} \N_x\) with different nitrogen content; b) CER spectra of \(\GaAs_{1-x} \N_x\) grown on n-type and SI GaAs substrate

For higher values of nitrogen the \(\GaAs_{1-x} \N_x\) reflex shifts to the higher diffraction angles indicating that the lattice constant normal to the surface decreases. Additionally, some deterioration of the structural quality is visible by lowering of the reflex intensity and its broadening. *Fig. 1b* presents two CER spectra (performed at 300 K) of \(\GaAs_{1-x} \N_x\) (x=1.95 %) grown on n-type and SI GaAs substrates. Based on the transition related to GaAs\textsubscript{1-x}N\textsubscript{x} epilayer the band
gap energy of this material can be determined what allows the evaluation of the nitrogen content using band-anticrossing BAC model. Some difference between the GaAs$_{1-x}$N$_x$ composition grown on Si-doped and undoped SI substrates were observed for both CER and HRXRD measurements.

Fig. 2 presents the nitrogen content ($x$ parameter) in GaAs$_{1-x}$N$_x$ epilayers grown at $T_g$=566 °C as a function of the hydrogen flow rate through the saturator with TBHy - $V_{H2/TBHy}$. The growth temperature of 566 °C determined from our earlier results [5] guarantees the efficient nitrogen incorporation without degradation of the structural quality. The GaAs$_{1-x}$N$_x$ composition was estimated from the rocking curves and CER spectra (BAC model). The divergence of the nitrogen composition estimated using CER and HRXRD methods are probably connected with the presence of interstitials defects and strains in GaAs$_{1-x}$N$_x$ films. The most efficient nitrogen incorporation occurs in the range of $V_{H2/TBHy}$=1500 ÷ 2500 ml/ min, above 2500 ml/ min the saturation of the nitrogen content is observed. The lowest value of the GaAs$_{1-x}$N$_x$ band gap of 1.12 eV was determined from CER spectra for the sample N54 ($x$=2.26 %).

In the case of MQW structures the main efforts were focused on optimization the growth parameters to get the In$_y$Ga$_{1-y}$As$_{1-x}$N$_x$ alloy with the band gap near 1 eV and lattice matched to GaAs. At first step we investigated the influence of the growth temperature $T_g$ on the quantum well composition and the structural and optical quality of the MQW region. The growth parameters were as follows: $T_g$=566, 575, 585 °C; $V_{H2/TBHy}$=1500 ml/ min; $III_{Ga}/III_{In}$=4.8. The symmetric (004) HRXRD scans for the MQW structures grown at 566 °C (NI43) and 585 °C (NI46) are presented in figure 3a. It seems that the interface quality is better for the sample NI46 grown at 585 °C. The nitrogen and indium contents in In$_y$Ga$_{1-y}$As$_{1-x}$N$_x$ quantum wells were determined by comparison of the measurement and simulations curves. The results shown in fig. 3b indicate that the nitrogen content decreases from 0.75 % to 0.4 % - enhanced N desorption from the surface [6] - while the indium content is constant (~11 %) with increasing $T_g$. 

![Graph](image-url)
The CER spectra of the investigated MQW structures grown on n-type (black line) and undoped (red line) GaAs substrates are presented in fig. 4. The quantum well (QW) transitions appear below the band gap of GaAs (1.43 eV). In the case of the structure grown at 566 °C (sample NI43) the QW transitions are nearly invisible what indicates the poor optical quality. This is connected with decreasing the rate of the surface reactions (the migration length of the atoms also decreases), the insufficient arsine decomposition and more efficient incorporation of impurities at low growth temperatures.

MQW structures grown at higher temperatures (samples NI45, NI46) exhibit the strong and distinct QW transitions and the energy of ground state (GS) can be determined. Based on the obtained results we decided to increase the nitrogen content in In$_{y}$Ga$_{1-y}$As$_{1-x}$N$_{x}$ by increasing the III$_{Ga}$/III$_{In}$ ratio. Due to the weaker In-N bond strength (7.70 eV/atom) in comparison with the Ga-N (9.12 eV/atom) bond [7] the nitrogen incorporation in InGaAs alloys decreas-

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**Fig. 3** – a) The symmetric (004) HRXRD scans for the MQW structures grown at 566 °C (sample NI43) and 585 °C (sample NI46); b) the nitrogen content in In$_{y}$Ga$_{1-y}$As$_{1-x}$N$_{x}$ quantum wells as a function of the growth temperature $T_g$.

**Fig. 4** – CER spectra of the MQW structures grown at 566 °C (sample NI43), 575 °C (sample NI43) and 585 °C (sample NI46). Black and red line corresponds to the n-type and undoped SI GaAs substrate, respectively.
es with increasing the indium content. Our first experimental results and HRXRD measurements showed that by increasing the \( \text{III}_{\text{Ga}}/\text{III}_{\text{In}} \) ratio from 4.8 to 6.9 we increased the nitrogen content from 0.5 % to 1.3 % for the MQW structure grown at 575 °C.

SIMS measurements were carried out to get information about the atom distribution inside the investigated structures. The SIMS profiles of GaAs\(_{1-x}N_x\)/GaAs (sample N54) and MQW (sample) heterostructures are presented in Fig. 5.

![SIMS profiles](image)

**Fig. 5** – SIMS profiles of heterostructures: a – GaAsN/GaAs (sample N54); b – MQW (sample NI51).

The nitrogen concentration in GaAs\(_{1-x}N_x\) (Fig. 5a) is about 3 % which is higher than the \( x \) value determined from HRXRD (\( x=1.4 \) %) and CER spectra (\( x=2.26 \) %). SIMS measurements give information about the total N concentration inside the sputtered material while the HRXRD corresponds to the substitutional N concentration hence such a large discrepancy between the nitrogen contents estimated from these two methods. In the case of the MQW structure the composition of the InGaAsN quantum wells is more difficult to evaluate. The SIMS profile of the sample NI51 grown at 575 °C (Fig. 5b) shows some difference between the III-group and V-group atoms position what can be connected with the interdiffusion process at the InGaAsN/GaAs interface.

**CONCLUSIONS**

This work presents the optimization of the epitaxial growth of undoped GaAsN layers and multiple quantum well (MQW) - 3 × In GaAsN/GaAs - structures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The optimal growth parameters for GaAsN with the band gap near 1 eV are: \( T_g=566 \) °C, \( V_{\text{H}_2}/V_{\text{TB}}=2500 \) ml/min. In the case of MQW structures the low growth temperature drastically deteriorates their optical quality, so the higher values of \( T_g \) are required. In order to increase the nitrogen content in
In$_y$Ga$_{1-y}$As$_{1-x}$N$_x$ wells grown at higher temperatures the III$_{Ga}$/III$_{In}$ ratio was increased. First experimental results confirmed this decision.

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HIGH-TEMPERATURE SURFACE DIFFUSION OF COPPER ON THE (112) FACE OF TUNGSTEN UNDER CONDITION OF FILM-LAYER GROWTH OF ADSORBED FILM

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ABSTRACT
The phase state of the epitaxial Cu film on W(112) face has been investigated by the method of the contact difference of potentials under condition of film-layer growth. We have determined desorption heat, critical temperature and critical coverage experimentally. The phase diagram has been plotted as well as the temperature dependence of heat of a two-dimensional phase transition “liquid – gas” has been obtained. An exponent of order parameter has been found.

Key words: phase transition, desorption, surface diffusion.

INTRODUCTION
Intensive development of many of today's trends in technology serves as an incentive to study the processes in ultrathin (monolayer) films. Such films are known to cause strong changes in different surface properties. The influence of surface phase transitions on the properties is of particular both theoretical and practical interest [1]. The establishment of equilibrium between the coexisting phases is indispensable in the study of the phase state of the heterogeneous adsorbed film. However, phase transitions can occur in the adsorption systems that are very far from equilibrium, but those in which dynamic processes are stationary.

The methods of equilibrium statistical physics are used in the study of equilibrium and weakly nonequilibrium phase transitions. Such phenomena as nonergodicity of statistical ensemble, the emergence of hierarchical structures, structural relaxation etc can be observed in the case of strongly non-equilibrium condensed matter. Such systems can be studied on the basis of synergetic pattern that represents the evolution of the mutually agreed hydrodynamic modes that parameterize the system [2].

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METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

In the paper, we used the method of the contact difference of potentials to investigate phase transformations in adsorbed layers (adlayers) of copper on the W(112) face and desorption processes that occur in stationary conditions.

The changes of local values of work function are caused by redistribution of copper adatoms due to their desorption and surface diffusion. Metal-on-metal systems are widely used practically. The W(112) face presents particular physical interest due to its strongly anisotropic structure. The face consists of closely packed parallel rows of tungsten atoms, separated by furrows of atomic depth. This structure determines the important features in the lateral atom interaction, symmetry of two-dimensional adsorbate lattice [3], as well as in the nature of surface diffusion [4]. The aim of our work was to study of desorption characteristics and phase state of copper monolayers on the W(112) face under condition of film-layer growth in wide temperature range. Such data may be valuable to create surfaces with desired properties and management of surface processes. Surface diffusion of copper on the W(112) face at low temperatures has been investigated in our paper [5]. High-temperature diffusion is often accompanied by adatom desorption. For example, in [6-8] it was shown that diffusion coefficients of such adsorbates as strontium and barium in the second monolayer on the (112), (110) faces of tungsten and molybdenum still remain low at temperatures beginning of desorption. Therefore it is impossible to obtain the coverage distributions formed by diffusion in second monolayer, since the adatoms are desorbed before they manage to move a distance greater than the spatial resolution of the experimental method used (1 micron). A completely different situation occurs in the case of diffusion of copper. Different authors have shown that the diffusion growth of copper films on tungsten takes place first layerwise, in other words the Stranski-Krastanov mechanism is implemented. And it is typical both for atomically smooth (110) [9] and atomic anisotropic (112) [5] faces. Desorption is carried out layerwise within the first three monolayers. Copper forms strong bonds with the tungsten. The bonds of adatoms in the second monolayer are weakened by lower layer of copper, and the third geometric monolayer is transitional [10]. Here mutual attraction of the copper atoms becomes very significant for the diffusion of individual atoms on the background of low levels of potential barriers [5]. The adatoms form two-dimensional lattice gas from physical monolayer under desorption, so two-dimensional condensed phases of copper are absent [10]. But film of copper remains heterogeneous in the third monolayer even at temperatures of intensive desorption (there are islands of condensed phase in the background of the lattice gas). It is known that the phase state strongly affects the diffusion characteristics of the adatoms [4], which clearly manifests in the formation of diffusion concentration profiles [5]. We have used this fact to study phase transitions...
under conditions where the rate of desorption and diffusion in two different phases are very different.

**RESULTS AND DISCUSSION**

The zone of heterogeneity on the concentration profiles formed by the diffusion process is allocated by a high concentration gradient due to the strong differences in the values of diffusion coefficients in the two phases. Herewith desorption occurs predominantly from the gas phase. The zone separates the film into two parts. One part is formed by two-dimensional gas and the second – by two-dimensional condensed phase. Desorption is controlled by diffusion of copper in the field of heterogeneous state of the adsorbed film, i.e. by the rate of arrival of material in a zone of intense desorption. We have performed a series of experiments at different temperatures. The obtained information allowed to plot a phase diagram for two-dimensional system “gas – condensed phase”, to find the concentration dependence of the heat of desorption, to determine the critical temperature and the critical coverage, to calculate the enthalpy of evaporation of two-dimensional condensed phase and to estimate the value of the exponent of the order parameter.

**CONCLUSIONS**

If an adsorbate is easily desorbed from the gas phase at diffusion temperatures and desorption from the condensed phase can be neglected, a dynamic equilibrium between the liquid and gas phases is established, which is controlled by the diffusion process. In this case, concentration profile will move with constant velocity toward higher concentrations without changing its shape over time. This allows us to accurately define the concentrations at which phase transitions occur at given temperatures, and to find the critical parameters of the adsorbed film.

**Acknowledgements**

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**REFERENCES**

MTJ PROPERTIES MODIFICATION

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ABSTRACT

The electrophysical properties changing of MTJ-structures Fe/MgO/Fe have been investigated. The detected changes of properties are concerned with changes occurring in insulating barrier. It can be conditioned by diffusion in insulator. The zone with the negative differential resistance, similar to a tunnel diode, is found out on a volt-ampere characteristic. It is supposed, that it can be due to formation of excitons in the modified MgO layer.

Key words: MTJ, Fe/MgO/Fe, diffusion, TMR, spin polarization, excitons.

INTRODUCTION

The MTJ-structures fabricated by various methods in the conditions of a high vacuum (~10^-8 Torr) [1,2] are traditionally investigated. MBE and EBE-technology allow to grown up epitaxial film structures Fe/MgO/Fe on monocrystal substrates. Advantage of such structures is their crystallographic orientation set by a surface of a substrate, allowing to provide high values of spin polarisation coefficients (up to 70 % and more) and TMR more than 150 % at room temperatures [3]. Such parametres are well consistent with existing theoretical works in this area [4], but demand not only precision techniques, but also especially pure materials.

In manufacture of microelectronic elements and microchips materials with the parameters strongly differing from ideal, both on a composition, and on structure are widely used. For instance, polycrystalline corundum and glass-ceramics are used as substrates for chips. They, as is known, have polycrystalline structure, correspondingly, with large (up to 10 microns for polycrystalline corundum) and small (up to 0.5 microns for glassceramics) crystal grains. The morphology of carefully prepared surface of such substrates appears quite suitable for production of multilayer film structures Fe/MgO/Fe. Such structures will have fine-crystalline structure with corresponding orientation of a magnetic moment within grains of a film [5]. Unlike the films which have been grown up on monocrystal substrates, their total magnetic moment without a magnetic field will not have the clearly defined orientation. Depending on a relation between the typical crystal grains sizes and MTJ dimensions such situation can

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be valid within all MTJ. In such structures it is possible to expect the elec-
physicoal properties differing from characteristic for MTJ with epitaxial films on
monocrystals. For this the size of a fabricated MTJ should considerably exceed
the characteristic size of domains. For fine-crystalline structures it is possible to
consider, that the size of the domain of an order of magnitude of grain.

At manufacturing of MTJ-structures by traditional processing techniques
presence of impurities makes the negative effect on their electrophysical prop-
erties. In [6] one of possible mechanisms of influence of impurities on a spin-
dependent tunneling in a ferromagnetic-oxide-ferromagnetic systems is viewed.
Presence of impurities can lead to change as quantities, and sign of TMR. Thus,
by means of the insertion of impurities in MTJ structure it is possible to expect a
new properties for use in spin electronic devices of new type.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Film evaporation of MTJ-structures was done in installation VUP-5m by
means of an elektron-beam evaporation (EVE) of corresponding substances on
substrates from pyroceram CT52-1. Such substrates, as is known, widely use
for manufacturing of electronic microcircuits. Substrates with dimensions
20x20 mm before sputtering were subjected to chemical treatment. An evapo-
ration mask was imposed on a substrate effective area before sputtering of each
film. Typical volt-ampere characteristic of MTJ-structures Fe (30nm)/MgO (3
nm)/Fe (20 nm)/Cr (25 nm) with interlayer resistance of 1.8 kOhm has semi-
conductor character of conductance.

RESULTS AND DISCUSSION

After measuring degradation of electrical properties of MTJ-structures
was observed. With time interlayer electroresistance of tunneling junction de-
creased practically to 0 (Fig. 1).

On the assumption of an ex-
ponential view of the curve, what is typical for diffusion depend-
ence, it is possible to suggest, that degradation occurred as a result of
conductive impurities diffusion. The estimation of an average
diffusion coefficient through layer
MgO with thickness $d = 3 \cdot 10^{-9}$ m gives the value $D \approx 3 \cdot 10^{-19}$ cm$^2$/s.
It more than ten orders exceeds a volume diffusion coefficient of
metals in MgO [7].

Carbon presence is the non-

Fig. 1 – Degradation of properties MTJ with
time
technique of film evaporation in installation VUP-5m. Therefore further for inhibition of degradation processes of MTJ special attention devote to flattening of interfaces and magnification of a MgO film thickness from 2 nanometers to 7-8 nanometers. 

Fig. 2 show VA-characteristics of MTJ Fe (30 nm)/MgO (7 nm) / Fe (80 nm) against a junction voltage within 0 – 3 – 0 V.

![VA_characteristics_of_MTJ](image1)

**Fig. 2** – VA-characteristics of MTJ

On an initial section of a direct branch 0 – 3 V a curve has nonlinearity (Fig. 2a). It is typical for semiconductors. At voltage rise electrodiffusion processes can become more active. Impurity atoms, in particular, carbon, move from one interface metal - dielectric to other dielectric-metal. Impurity presence forms in a dielectric additional energy levels which provide occurrence of excitons in band-gap: couple of an electron-hole. Thus, as a result of impurity exhaustion at one interface and concentration at another the structure with energy bands as in a tunnel p-n junction is formed. It is exhibited by occurrence of a section with the negative differential resistance on a decaying section of Volt-ampere characteristic at voltage reduction (fig. 2a). At repeated measuring of Volt-ampere characteristic of the same MTJ the negative differential resistance is already observed both at voltage increasing and at reduction (Fig. 2b).

![Dependence_of_signal_amplitude_U_mV_on_MTJ](image2)

**Fig. 3** – Dependence of signal amplitude U (mV) on MTJ versus magnitude of a magnetic field at a various mode of magnetic fixing of the ferromagnetic layer and a thickness MgO: a)7 nanometers b) 3 nanometers.
Magnitude of a magnetic field influence on properties of the obtained structures. Results of investigations of MTJ properties in linearly changing magnetic field are presented on Fig. 3.

Regarding, that voltage drop on MTJ is proportional to change to its resistance in variable magnetic field, the tunnel magnetoresistance TMR for a curve at fig.4a can be defined as

\[
TMR = \frac{U_{ap} - U_p}{U_p} \cdot 100\% = 10.5\%,
\]

An average coefficient of spin polarization for this system it will be defined as

\[
P \simeq 1/\sqrt{\frac{2}{TMR}} + 1 \simeq 31\%
\]

**CONCLUSIONS**

It is shown possibility of MTJ obtaining at sputtering of thin-film structure on fine-crystalline substrates. Stability of MTJ properties achieved by increasing of a thickness of an insulating barrier and interface smoothing between Fe and MgO layers. The increasing of a thickness of a insulating barrier and change of its electrophysical properties leads to decreasing TMR of MTJ. Control of a transmittance and conductance of potential barrier of MTJ can be carried out by means of amount and type of an implanted impurity. In MTJ-structure with impurities in a barrier layer at potential supply is possibility of energy structure formation as in a \( p-n \) junction with Volt-ampere characteristic, similar to a tunnel diode. It can be due to formation of excitons in the modified MgO barrier. The results will be useful at making spintronic oscillator devices of new type.

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**REFERENCES**

ELECTRICAL AND OPTICAL PROPERTIES OF ZnO:AL FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION (CVD)

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ABSTRACT

In this paper we will prepared thin films from transparent conductive oxide (TCO) ZnO pure, and doped for Various concentration of aluminum Al(4,8%) using technique chemical vapor deposition (CVD) at different substrates temperatures (400,450,500°C). on glass substrates. The films were characterized by X-ray diffraction and UV spectrometer, pure ZnO films and (ZnO: Al) shows, a polycrystalline structure of the hexagonal Wurtzite Type, the diagnostics show preferred peaks for the growth of the crystal grains in the directions (002). The optical measurements have shown that the absorption edge is shifted towards the shortwave lengths which mean that the energy gap increases with the increase of Aluminum concentration in ZnO, and then we noticed the transmittance increases with increasing the substrate temperature and doping percentage with aluminum and the highest value was observed at 500°C and (8%) doping. The electric conductivity of ZnO films doped with aluminum increases with the percentage of doping until the doping percentage of (4%) , then starts to decrease with the increase in doping percentages at substrate temperatures (450°C and 500°C), also an increase in the concentration of charge carriers and Hall Effect mobility was observed at doping (4%) , while it decreased at (8%) doping, as well as we can see from the seem image, the smoothly surface was obtained in case of 4% doping Al.

Key words: thin film, chemical vaporous deposition, ZnO, ZnO: Al, doping, energy gap

INTRODUCTION

Zinc Oxide is an II–VI wide band gap semiconductor with a large band gap of about 3.3 eV is one of the most potential materials for being used as a TCO because of it’s good electrical and optical properties, abundance in nature, absence of toxicity [1,2] and the ability to deposit these films at relatively low temperatures [3]. The oxygen vacancies and/or zinc interstitials correspond to the n-type conductivity of the ZnO films. The resistivity of these films can be further lowered by doping them with group III elements like B, Al, Ga or In. Among all these elements, Al is considered to be a good dopant for opto-

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electronic applications like solar cells due to the high transmittance that Al-doped ZnO films exhibit. ZnO: Al is fabricated by RF magnetron sputtering [4, 5], sol–gel process [3], pulsed laser deposition [5], spray pyrolysis [6] and chemical vapor deposition [7], etc. Among them, chemical vapor deposition that used in this paper, The process of deposition and producing homogeneous films is not a simple process but requires a number of tests including the selection of the precursor material, the temperature of substrates, the evaporation temperature and the flow rate of the carrier gasses in addition to the location of the sample in the deposition chamber. All these factors have a direct effect on the type of the required prepared film that and on its physical properties. In this study we observed a number of observations concerning the films. In some instance the films did not grow over the substrates or they only partly covered them. In other instances we observed that the films were formed as stripes. These cases took place at temperatures less than 450°C. While at this temperature and above, we found that the films status was enhanced significantly concerning the rate of growth and homogeneity while the optimal temperature degree in this study was found to be 500°C as the optical, and electrical properties of the films.

**METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

In order to prepare pure ZnO films using chemical vapors deposition (CVD) techniques on glass and substrates the deposition material used was pure zinc acetate hydrous Zn(Ch₃COO)₂·2H₂O) with 98% purity. After preparing the substrates, they were placed and adjusted in the deposition unit while the temperature degrees were varied between (400-500°C) in order to ensure optimum film properties. The pressurized air flow was also adjusted to the best flow rate which was found to be 2 L/min to produce the best samples as .The rate of airflow is related to the uniformity of the deposited film and it must be adjusted to prevent the formation of colored strips on the glass substrates that can interfere with visional and microscopic inspection. Various temperature degrees were tested when heating the deposition material and it was found that the temperature of (340°C -350°C) is the appropriate temperature degree range. Deposition time was kept constant at (20 minutes) for the both the pure and doped samples in order to determine the combination of optimal duration with temperature degree that produces the best results of zinc oxide deposition and the samples were left afterwards to cool. The first choice of doping material was to use chloride aluminum hydrous as a doping material but it was not possible to produce a doped film in any of the varied deposition conditions. The reasons were attributed to the weak or lack reaction ability between the Zn and hydrous aluminum. This led us to seek a different material which was aluminum nitrate hydrous with a purity of (98.5%). After using this compound, aluminum doped ZnO films were successfully produced with good homogeneity.
The various weight percentages of this used material were between (4,8%) that were added to the weight percentages of zinc acetate. The following equations show how ZnO is produced.

\[ \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{ZnO} + \text{CO}_2 + \text{CH}_3 + \text{steam} \]  

The following equation used to get the lattice constant [3],

\[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 +hk + k^2}{a^2} + \frac{L^2}{C^2} \right) ; \]  

where \( a, c = \) lattice constant, \( \text{hkL} = \) miller indices.

The crystalline structure was analyzed by X-ray diffractometer (DROT-20 \( \nu \) Cu-\( k_\beta \)) in the range 2\( \theta \) of 30 – 80, the surface morphology of the films was analyzed using a scanning electron microscope model (REM - 106) before and after annealing. The optical transmittance was measured using a ENGLAND (1000SERIES\( \nu \)CECIL 1021) spectrophotometer in the wavelength range from 300 to 1000 nm.

**RESULTS AND DISCUSSION**

X-ray diffraction studies of the structure of the material were carried out on an automated DRON-4-07 (Bourevestnik », www.bourevestnik.spb.ru). Automation system using a DRON-4-07 is based on a microprocessor controller that provides control of the goniometer GUR-9 and data transmission in digital form on a PC.

**Table 1– Lattice parameter of ZnO**

<table>
<thead>
<tr>
<th>No</th>
<th>2( \theta ) Degree</th>
<th>h k L</th>
<th>( d_{hkl} ), E</th>
<th>a ,( \mu )</th>
<th>c ,( \mu )</th>
<th>Result standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>31.72</td>
<td>1 0 0</td>
<td>2.816</td>
<td>3.24</td>
<td>5.17</td>
<td>a=3.249</td>
</tr>
<tr>
<td></td>
<td>34.76</td>
<td>0 0 2</td>
<td>2.56</td>
<td>2.603</td>
<td>c=5.206</td>
<td></td>
</tr>
</tbody>
</table>
and found the following results. The films exhibit a dominant peak corresponding to the (002) plane of ZnO, and other peaks corresponding to (100), (101), and indicating the polycrystalline nature of the films. It is seen from the figure that the relative intensity of the (002) peak decrease with increasing Al dopant concentration. The decrease in peak intensity indicates an improvement in the crystalline of the films. Besides, a slight shift was observed in the peaks in the direction of the lesser angles which may be attributed to the small increase in the bond. These result were confirmed with those obtained from the Joint committee of powder diffraction standards JCPDS for the ZnO.

Microscope test process has been done after finishing from depositing ZnO thin film on glass substrate by (CVD).

It can be easily seen that the grains are tightly packed. And we can see that the smoothly surface was obtained in case of Al doping in 4%. Fig. 4 show the absorption spectra as a function of the wavelength of the pure ZnO films and the ZnO films doped with (4, 8%) aluminum. From these fig-

![Fig. 2—X-ray diffraction patterns of ZnO](image)

![Fig. 3—Seem image of thin film ZnO, a— pure, b – 4% doping Al, c – 8% doping](image)
ures, we can see the transmission decreased with decrease wavelength, also we can see two regions are obvious: The first was the region wave length energy larger than the energy gap (Eg>3eV) which equals to (λ < 400 nm) as during this region, the absorption increase sharply therefore shows that the ZnO: Al can be used as UV protection films. The second region lies within the wavelengths range of (400 < λ < 1000nm) in which the energy of the incident photon is low and the (ZnO:Al) film is transparent to this range and the absorption is lowest. We can see from the figure (4) that the increase in the percentage of aluminum added to the ZnO leads to the shift in the absorption towards the short wavelengths, a shift that is termed (Burstein-Moss) shift.

This type of shift leads to an increase in the optical energy gap, also we can see the decrease of wavelength, as its value very high at the wave length which is located with in optical spectrum and infra – red radiation, which indicates that these films have large energy gap to allow most of the visible light to pass as shown in figure, also the results show that the transmittance is higher than 80 % in all thin films.

The optical energy gap (E_{opt}) is defined as the lowest energy required for the electron to travel from the peak of the coordinate band to the peak of conductivity band and can be calculated directly using the electron traveling formula as follows:

$$\alpha(h\nu) = A(h\nu - E_{opt})^{1/2}$$  \hspace{1cm} (3)

And can be rewritten as follows

$$(\alpha h\nu)^2 = A^2(h\nu - E_{opt})$$  \hspace{1cm} (4)

And when $(\alpha h\nu)^2 =0$, then $E_{opt} = h\nu$

The relationship between $(\alpha h\nu)^2$ and $(h\nu)$ can be plotted as a curve and the extended part of the curve intersects with the photon energy axis at $(\alpha h\nu)^2 =0$ and from it we determine the energy gap of direct allowed traveling as shown in fig. 5, as shows the energy gaps for pure ZnO and doped with a(}

![Fig. 4 – Transmittance spectra as a function of wave length for Zno samples deposited at various temperatures(400,450,500 C°)](image_url)
4.8%) aluminum. An obvious increase is observed for the values of the energy gap with the increase in the concentration of aluminum and is in accord with previous studies (4,5) within various preparation techniques, this increase is explained by the proposition that the ZnO:Al films are semiconductors in which the Fermi level lies in the conducive band which means that the levels at the bottom of the conductivity band are occupied by electrons and the shielding of electronic traveling to these levels is termed the Burstein-Moss effect.

For these films, $E_{\text{opt}}$ is determined from the intersection of the straight lines of the curve with the energy axis at (hv), and $E_{\text{opt}}$ was found to be (3.25, 3.4, 3.65) eV. Fig. 6 shows the change in the electric conductivity of pure ZnO films doped with aluminum at (4.8%) at substrate temperatures of (400, 450, and 500°C). It is shown that the electric conductivity increases with the increase in the temperature of the substrate and reaches its highest level at a substrate temperature of 500°C. The reason attributed to this increase in conductivity with the increase in the substrate temperature is the improvement of crystal structure and then increase in the crystal grains which leads to a decrease in the scattering of the charge carriers at the edges of the grains and in turn increases the mobility of the carriers and conductivity. And then the effect of doping on the electric conductivity was determined at various doping percentages and it was shown in fig (6) that doping had a significant effect of the electric conductivity of ZnO doped with aluminum. At ($T= 400 \text{ C}^0$) the electric conductivity is low in general when compared with the substrate temperatures of (450, and 500C$^0$).
At (450 and 500 C°) the electric conductivity increased when the doping with aluminum increased until 5% were after that percentage of doping the electric conductivity decreased. The increase in electric conductivity of films doped with an average percentage of aluminum is due to the atoms of triple metals like aluminum that interacts with him film in various was and the aluminum atoms compensate the Zn locations in the Al_m lattice acting as donors as shown in the following formula:

\[ Al^{3+} \rightarrow Al^{2+} + e; \]  

(5)

Al^{2+} occupies the locations in the ZnO lattice and (e) the free electrons that participate in electric conductivity

CONCLUSIONS

From the X-ray diffraction we found, the effects of different aluminum concentrations on the structural properties, electrical resistivity and optical transparency of the films were studied. The films exhibit a dominant peak corresponding to the (002) plane of ZnO, and other peaks corresponding to (100), (101), and indicating the polycrystalline nature of the films. It is seen from the figure that the relative intensity of the (002) peak decrease with increasing Al dopant concentration. The decrease in peak intensity indicates an improvement in the crystalline of the films. The seem morphology shows the grains are tightly packed, and we can see that the smoothly surface was obtained in case of Al doping in 4%, from the optical properties we can see the transmission increases with the increase in concentration of doping aluminum, the highest transmission is observed at (8%) doping, also the results show that the transmittance is higher than 80 % in all thin films. The value of the band gap is enhanced from 3.25eV(un doped ZnO thin film) to 3.65 in case of doping with 8%. The increase in the band gap can be explained by the Burstein – Moss effect. ZnO films show good electric conductivity at (450 and 500C°) and was found to be (9.740741 (Ω cm)^{-1} and (14.34615(Ω cm))^{-1}, and then the electric conductivity of The ZnO films doped with aluminum increases with the increase in temperature and the highest was was and (14.34615(Ω cm)^{-1} at 500C°.

REFERENCES

ABSTRACT
This paper presents experimental results of the investigation of strain resistive properties of Cu and Co films with thickness of 20 nm, 40 nm and Cu(30)/Co(30)/S film system. Thin films were analyzed in deformation range from 0 to 6 percents. With help of atomic force microscopy the moment of fracture formation was determined. According to obtained results the conclusions were made that up to 2 percents of deformation ratio ($\varepsilon_l$) the samples preserve their structural integrity. For thin films Cu(20) and Co(20) fracture occurs at $\varepsilon_l \geq 6$ percents. For thicker samples the moment of transition from quasielastic to plastic deformation differs and film destruction is observed at $\varepsilon_l \leq 4$ percents. The study of Cu(30)/Co(30)/S system showed that in spite of sample’s thickness raise the deformation ratio of film destruction didn’t decrease as for one layer films.

Key words: strain gauge, plastic deformation, atomic force microscopy, strain sensitivity coefficient, thin film

INTRODUCTION
Due to unique mechanical, physical and optical properties film materials are widely used as base for sensors. Multilayer film systems detectors have definite advantages over semiconductor ones, for example, under high temperature they possess more stable characteristics. Therefore, the study of film properties, such as electro physical properties, remains very important problem. The most common and promising systems for developing strain gauge are systems on the basis of Cu, Co, Cr and Fe. Strain resistive properties of these films and systems built on their basis are investigated well enough under deformation in the range from 0 to 2 %, i.e. elastic, quasielastic and partly under plastic deformation. The mechanism of deformation in range over 2 % for thin films is not well studied yet. So the aim of this work was to investigate how electro physical properties and structure of Co, Cu films and systems on their basis changes in the deformation range from 4 to 6 %. [1]

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS
While carrying out the work Cu and Co films with thickness of $\approx 20$ nm,
40 nm and Cu(30)/Co(30)/S film system were investigated. Samples were built by thermal evaporation method in VUP-5M unit. Since the resistance of obtained films was about tens of ohms the contacts had to be done low-impedance to decrease their influence on strain resistive properties of samples. Therefore, polystyrene tapes with thickness $\approx 0.4$ mm were used as substrate. They have smoothly polished surface and good elastic properties. The only disadvantage of these tapes is low temperature resistance, but in this case samples were not heated up. On the polystyrene surface the copper contacts with thickness of $\approx 70$ nm were formed by vacuum evaporation method. To reduce the influence of contacts on strain resistive properties of the films polystyrene tapes were attached to aluminum plates in the way that only copper film and small area near its junction with contacts was under deformation. After obtaining the sample it was left for 3 hours in vacuum to stabilize the phase structural processes. Then deformation curves were traced dynamically. Each cycle “strain – relaxation” was followed by increasing of deformation range from 1 up to 4 – 6 % [2, 3].

For correct interpretation of results it is extremely important to control the structural integrity of the film during deformation. For this purpose atomic force microscopy (AFM) is used [4]. This is convenient method to explore the topology of surfaces. AFM – portraits were obtained in topology mode and surface profile mode.

**RESULTS AND DISCUSSION**

*Figure 1* shows the examples of deformation dependencies for Cu (21) (a) and Cu (20) (b) films. In first case cycles “strain – relaxation” were traced up to 4 % of deformation ($\varepsilon_i$), in second – up to 6 %.

![Fig. 1 – “Strain” curves for Cu (21) (a) and Cu (20) (b) films under deformation of 4 % and 6 % respectively.](image-url)
As we can see from the charts, the resistance doesn’t increase rapidly till 2 % and the dependency of ΔR/R on \( \varepsilon \) has linear behavior that indicates the elastic and quasielastic deformation in this area. With further increase of \( \varepsilon \) the transition to plastic deformation proceeds that in its turn causes the growth of coefficient of strain sensitivity (CS). For deformations higher then 4 % the

\[ \text{Fig. 2} \quad \text{AFM – portraits for} \quad \varepsilon = 0 \%, \quad 2 \% \quad \text{and} \quad 4 \% \quad \text{in profile mode respectively:} \quad \text{Cu(20)} \ (a, b, c), \ \text{Co(20)} (d, e, f), \ \text{Cu(30)/Co(30)/S} \ (g, k, l). \]
rapid growth of film resistance and CS occurs that indicates the fracture of copper. Similar results were obtained for Co films and for Cu(30)/Co(30)/S system.

Figure 2 presents some AFM – portraits of Cu, Co films and Cu(30)/Co(30)/S system in profile mode for different values of $H_l$.

The analysis of AFM experimental data indicates that for deformation values less than 2 percents the depth of micro fractures in all samples changes insignificantly (approximately on 1 nm). At $a_l = 4\%$ the changes have more effect, e.g. for Cu(20) – 4 nm and for Cu(30)/Co(30)/S – 3 nm. Further increase of deformation value leads to film destruction.

CONCLUSIONS

During the research deformation curves were traced for copper and cobalt films with thickness of $\approx 20 \text{ nm}$, 40 nm and for system on their basis at $a_l$ up to $4 - 6 \%$. At $a_l \approx 6 \%$ the fracture of samples with thickness of 20 nm occurs that is indicated by the rapid growth of film resistance and its CS. For samples with thickness of 40 nm the destruction appears at lower deformation ratio ($\approx 4 \%$). But the system Cu(30)/Co(30)/S has good strain resistive properties like 20 nm film in spite of big total thickness. The structural integrity of the samples was controlled with AFM help. The portraits that were taken in profile mode prove the intensive appearance of fractures only at high deformation ratio.

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MAGNETIC AND MAGNETO-RESISTANCE PROPERTIES OF SPIN-VALVES BASED ON Co AND Cu OR Au FILM SYSTEMS

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ABSTRACT

The construction of module for automation measurement of magnetoresistance (MR) and coercitivity force ($B_c$) in spin-valve structures based on Co and Cu or Au film systems was proposed. The peculiarities of dependences of MR and $B_c$ from angle $\alpha$ between substrate plane and direction of external magnetic field induction were studied. The abrupt changes of MR and $B_c$ in the range $\alpha=70-90^\circ$ were determined. The dependence character of MR from $\alpha$ describes as a level of solution of atoms of bottom ferromagnetic layer Co(3 nm) or Co(20 nm) in layer Cu(6 nm) as long as atoms Co(3 nm) have a practically full solution but Co(20 nm) – only limited solution. In this case magnetization of magnet layers of Co(20) and solid solution (s. s.) – [Cu, Co(3)] and layers of Co(20-x)+s.s. – [Cu, Co(x)] realize in different ways. This fact is cause of increase or decrease of MR.

Key words: spin-valve, induction of magnetic field, coercitivity, angle between induction and substrate plane.

INTRODUCTION

Giant magnetoresistance (GMR) was detailed studied based on different film systems (Fe/Cr, Co/Cu, Co/Au, Co/Ag, Co/Ru, Ni/Cu etc.). The investigation of GMR effect in spin-valve structures is the most important researcher’s interest [1-3]. The angle of direction of applied external magnetic field has the most significant influence on magnetoresistance properties of thin film systems. There are two geometries of applied magnetic field: FIP (lines of magnetic induction are parallel to film plane) and FPP (lines of induction are perpendicular to sample).

On the basis of theoretical conception the research of the dependence MR and coercitivity from angle between substrate plane and direction of applied external magnetic field was the aim of the work.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

The studied samples were spin-valve structures and were prepared by thermal vacuum evaporation method under the pressure of residual atmosphere $10^{-7}$ Pa. Deposition was provided by electron beam evaporation on single-crystalline silicon substrate with dioxide silicon surface layer. The layer thick-
ness was controlled by quartz resonator method. MR measure at temperature 300 K using updating complex. Working methodic was described in work [4].

The automated measurement module was developed for research magnetoresistance in spin-valve structures subject to angle of external magnetic field direction with minimal changing step 1°. The system controlled with using software that was developed within graphical programming environment Lab-VIEW 2010 SP1. Structural scheme of developed complex showed in fig. 1. Hardware module mounts between limb of magnet (fig. 1 pos. 1) and consists of console (pos. 4), contact holder (pos. 3), sample holder (pos. 2) and stepper motor (pos. 5) that controlled with DAQ NI USB 6008 (pos. 6). Gold contact pins have minimal resistance and round tip that couldn’t destroy thin film. Contact probes mount in special way that allows changing geometry of current flow without changing spin-valve position in sample holder.

![Fig. 1](image)

**Fig. 1** – Scheme of developed hardware complex with mechanism for sample rotation (a) and image of contacts holder (b): 1 – limb magnet; 2 – sample; 3 – contacts holder; 4 – console of rotation mechanism; 5 – stepper motor; 6 – DAQ NI USB 6008

The possibility of automated MR measurement in thin film systems in the frame of different geometries of applied external magnetic field direction was the principle feature of developed system. The possibility of sample rotation during measurement realized in the system in the angle range of ±180° with minimal step 1°.

**RESULTS AND DISCUSSION**

The magnetoresistance properties were researched on the basis of spin-valve systems with CIP geometry of current flowing:
Au(1)/Co(3)/Au(6)/Co(20)/SiO₂/Si (spin-valve №1);
Au(1)/Co(3)/Cu(6)/Co(20)/SiO₂/Si (spin-valve №2);
Au(1)/Co(20)/Au(6)/Co(3)/SiO₂/Si (spin-valve №3) and
Au(1)/Co(20)/Cu(6)/Co(3)/SiO₂/Si (spin-valve №4),

where the layer thickness showed in the brackets. The peculiarity of studied spin-valve systems is the difference of nonmagnetic intermediate layer material (Cu or Au) and also thicknesses of magnetic layers Co.

The typical dependences of MR from magnetic induction with different angles \( \alpha \) between substrate plane and induction direction in samples with CIP geometry current flowing showed in the fig. 2.

The most interesting peculiarities are MR value not depend from angle \( \alpha \) in the range of \( \alpha=0^\circ-70^\circ \). In the range of \( 70^\circ-90^\circ \) MR jump decrease in case of spin-valves Au(1)/Co(20)/Au(6)/Co(3), Au(1)/Co(3)/Au(6)/Co(20) and Au(1)/Co(3)/Cu(6)/Co(20) or vice versa jump increase in case of spin-valve Au(1)/Co(20)/Cu(6)/Co(3). This fact illustrated in the chart dependences of MR and \( B_c \) from magnetic field value at different angles sample orientation relative to the substrate plane (fig. 2 and 3a). The coercitivity force (fig. 3b) also practically did not depend from angle \( \alpha \) in the range of \( \alpha=0^\circ-70^\circ \), but in the range of \( \alpha=70^\circ-90^\circ \) jump increased in the case of all type of spin-valve systems. This fact could be interpreted by anisotropy of Co layers in the substrate plane.

Spin-valve (1) and (2) had “standard” structure in which fixed ferromagnetic layer Co(20) was hard layer and layer Co(3) was soft. The upper soft layer become to magnetized under the smaller value of magnetic induction in compare
with hard layer Co(20). The jump changes were in the range of angles $\alpha=70^\circ-90^\circ$. It could be connected with magnetized both layers Co(3) and Co(20). Layer changing in case of spin-valves (2) and (3) did not change the character of the dependence MR and $B_c$ from angle $\alpha$. Otherwise there was jump dependence in case of spin-valve (4). The peculiarity of this spin-valve was the interface between bottom layer Co(3) and non magnetic Cu(6). In this case the solid solution with absolutely solution and granule elements was obtained [5]. Magnetization of solid solution led to “anomaly” dependence MR from $\alpha$. In the case of nonmagnetic layer Au(6) the solid solution with limited solution was obtained [5] that had not influence on magnetization Co(3).

**Fig. 3** – Dependences of MR (a) and coercitivity force (b) from angle of external magnetic field direction

**CONCLUSIONS**

The research of MR and coercitivity force in four spin-valve systems based on Co and Cu or Au was provided in the dependence from angle $\alpha$ between substrate plane and external magnetic field direction. The fact of jump changes of MR and $B_c$ in the range of $\alpha=70^\circ-90^\circ$ was established. The dependences had a similar character in the case of three systems. The anomaly jump change was observed when atoms Co(3) diffused into Cu(6).

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