

## The Effect of Diameter and Thermal Treatment on Magnetic Properties of $\text{Co}_{1-x}\text{Zn}_x$ Alloy Nanowires

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Nanowire arrays of the alloy,  $\text{Co}_{1-x}\text{Zn}_x$  ( $0 \leq x \leq 0.2$ ), with 20 and 35 nm diameters have been fabricated by the electrochemical deposition method into pores of anodized aluminum oxide (AAO) templates. Samples with different composition could be obtained by adjusting the concentration ratio of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  in the solution of the electrolyte. The structure and magnetic properties were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and alternating gradient force magnetometer (AGFM). It is found that the magnetic properties of the arrays are critically dependent on the compositions and diameter and thermal treatments. We found that the optimized composition for  $\text{Co}_{1-x}\text{Zn}_x$  nanowire is around  $\text{Co}_{90}\text{Zn}_{10}$  with 20 nm diameter annealed at 575 °C in which the coercivity ( $H_c = 2120$  Oe) and squareness ( $M_r/M_s = 0.98$ ) have their maximum values consistently.

**Keywords:** Nanowire, AAO Template, Magnetic Property, Thermal Treatment.

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### 1. INTRODUCTION

There are many different types of nanowires that promising us to used them in near future to link of tiny pieces in very small circuits [1]. Electrodepositing the magnetic metal wires with nanoscale into the porous anodic aluminum oxide (AAO) templates have been utilized previously by many groups to prepare the one-dimensional nanostructure [1–3]. Anodic alumina oxide (AAO) template has been widely used to prepare nanowire arrays because of its self-organized, tunable pore dimensions over a wide range of diameters and lengths, good mechanical strength and thermal stability. AAO template fabricated in process of Anodize in optimal condition. In this work, we synthesis  $\text{Co}_{1-x}\text{Zn}_x$  nonowires with 20 and 35 nm diameter and effect of annealing on magnetic properties of nanowires investigated.

### 2. EXPERIMENTAL

Porous anodic aluminum oxide template were fabricated by two step anodize process [7]. For this purpose aluminum foil with high purity (99.999) and thickness of 0.3 mm were prepared. After annealed at 450 °C for about 20 min in Ar-He to remove the oxide layer on surface of aluminum sample were used NaOH solution for 5 minutes then a mirror surface was achieved by electro-polishing in a 1:4 solution of  $\text{H}_2\text{ClO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  at voltage of 20 V at room temperature. With use of electro-polish process to decrease roughness of Al surface. The first anodizing was performed according to table 1 in 0.3 M acids. The formation of pours in this process is completely randomized so created templates have not a suitable ordering. So after the first anodize

the oxide layer created during first anodize was removed within a chemical process in solution of 0.5 M phosphoric acid and 0.2 M chromic acid at temperature of 70 °C. To achieve a relatively regular structure with hexagonal arrangement sample again in a similar condition with first anodize, re-anodized the samples. The thick aluminum oxide in the bottom of pores is an insulator barrier to fill them by electrodeposition of metals.

**Table 1** – condition of fabricated of AAO

Acid	Sulfuric	oxalic
Duration of 1 <sup>st</sup> anodize (h)	7	15
Duration of chemical removing (h)	10	15
Duration of 2 <sup>nd</sup> anodize (h)	5.0	1
Voltage(v)	20	40
Temperature (°C)	1	14-15

Immediately after the second anodization the thickness of oxide layer in bottom of holes decrease. Perfumed anodize at low voltages the perfect solution to decrease thickness of barrier layer [8] so voltage step to step reduced to 8 V. After preparation of template by AC electrochemical deposition method for 3 min with a frequency of 200 HZ and peak to peak voltage of 30 V  $\text{Co}_{1-x}\text{Zn}_x$  ( $x = 0, 0.01, 0.05, 0.1, 0.15, 0.2$ ) nanowires alloy fabricated in AAO template. For electro deposition of sample was used Cobalt Sulfate ( $\text{CoSO}_4$ ) and Zinc sulfate ( $\text{ZnSO}_4$ ).

In order to check for annealing effects on  $\text{Co}_{1-x}\text{Zn}_x$  nanowire arrays, all the samples are annealed at different temperatures 200, 300, 400, 450, 500, 550 and 575 °C, respectively in Ar atmosphere. The magnetic properties of sample with draw the hysteresis loop by

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AGFM were studied. The fine structure of nanowires by resolving of AAO in NaOH 1M solution by SEM was studied.

3. RESULTS AND DISCUSSION

By electropolish of Al samples the height of roughness decrease from 250 nm to 3 nm. AFM image of the surface before and after of electropolish was shown in Fig. 1. The mirror-like surface is suitable to fabricate of highly ordered porous anodic aluminum oxide.

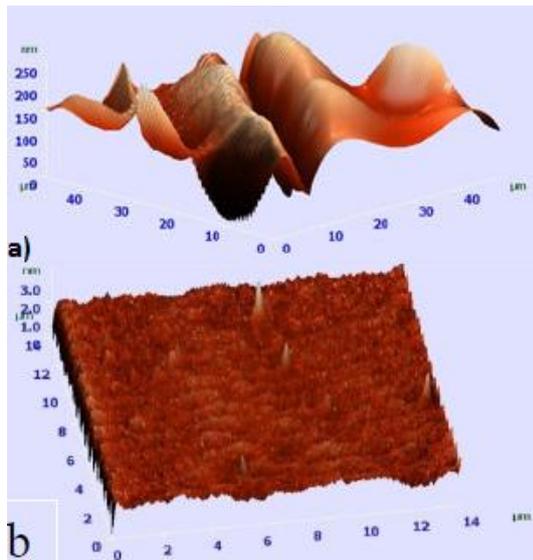


Fig. 1 – AFM of Surface of the Al foil (a) before and (b) after the electropolish

To improve the ordering of the surface side of the anodic porous alumina, two-step anodization is effectively adopted. After the removal of the oxide, an array of highly ordered dimples was formed on the Al, and these dimples can act as initiation sites for the hole development in the second anodization. The AFM view of surface for anodization with acid sulfuric after remove the oxide layer in first anodization was shown in Fig. 2. SEM image of AAO template after second anodization in sulfuric was seen in Fig. 3.

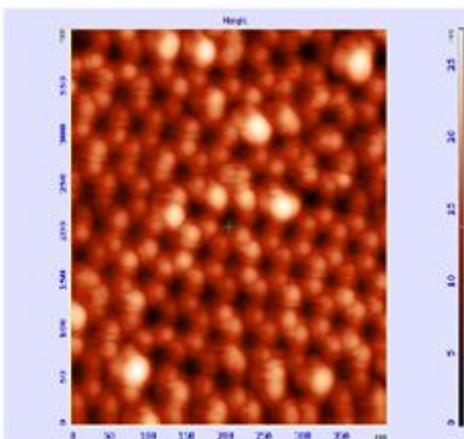


Fig. 2 – SEM AFM image of Surface of the AAO after remove the oxide layer in first anodization in sulfuric acid

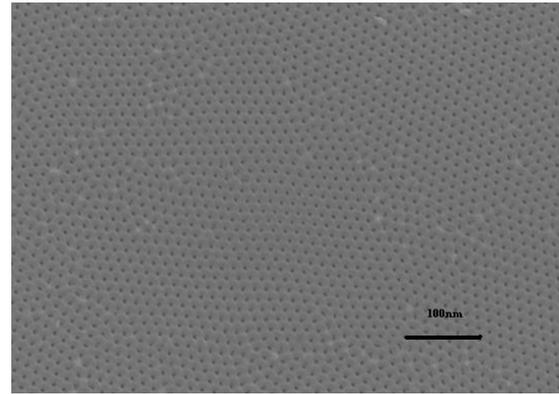


Fig. 3 – SEM image of surface of AAO after 2nd anodization in sulfuric acid

SEM image of synthesized nanowires with diameter of 20 and 35 nm are shown in Fig. 4.



Fig. 4 – a) SEM image of nanowires with 35 nm diameters and 2.1 mm length and (b) with 20 nm diameter and 2.5 mm length

The coercivity and squareness of the samples are shown in Fig. 5. It can be seen coercivity of nanowires with 20 and 35 nm diameter by addition of impurities zinc in the electrolyte of electro deposition. The coercivity decreases because Zinc atoms replaces to cobalt atoms and reduce magnetic properties. The regular increase coercivity with decreasing diameter was shown with Comparison two curves with 20 and 35 nm.

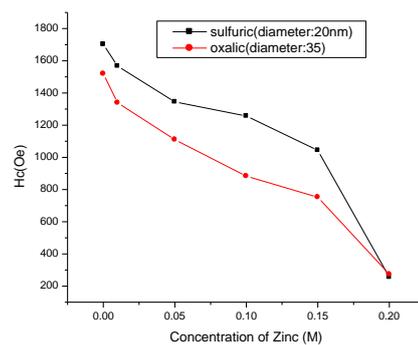
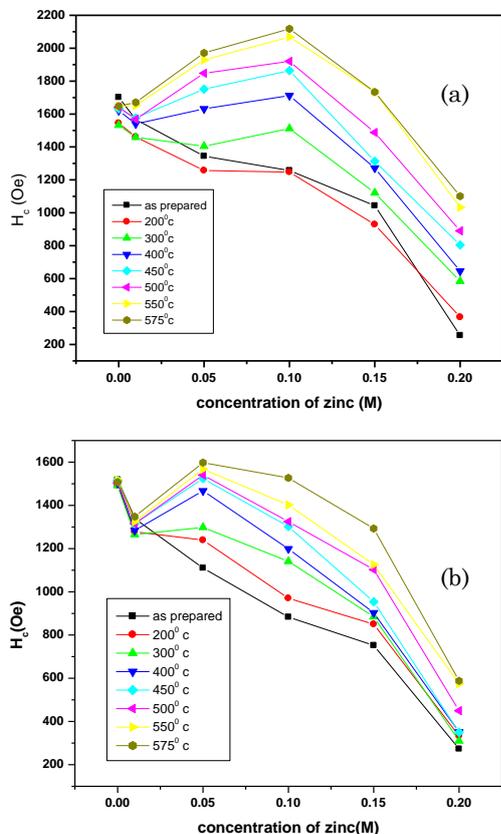


Fig. 5 – Coercivity of nanowires with diameters of 20 and 35 nm

Coersivity field of nanowires with diameters of 20 nm and 35 nm when increase zinc in electrolyte of electro deposition, decrease from 1711 Oe to 260 Oe and from 1500 to 270 Oe respectively. The effect of annealing temperature of samples with diameter of 20 and 35 nm on coersivity was examined in Fig. 6. It is supposed the loss of tension in annealing process is the reasons to improve the coersivity. The most coersivity

( $H_c = 2120$  Oe) related to sample with 10 percentage ( $x = 1$ ) of zinc in electrodeposition electrolyte with diameter of 20 nm. Fig. 7 is shown squareness of samples before and after the annealing. The most change in both diameters is related to the sample with  $x = 5$  after annealing in  $575^\circ\text{C}$ .



**Fig. 6** – The coercivity of  $\text{Co}_{1-x}\text{Zn}_x$  nanowires with diameter of (a) 20 nm and (b) 35 nm as a function of percentage of Zn and annealing temperature

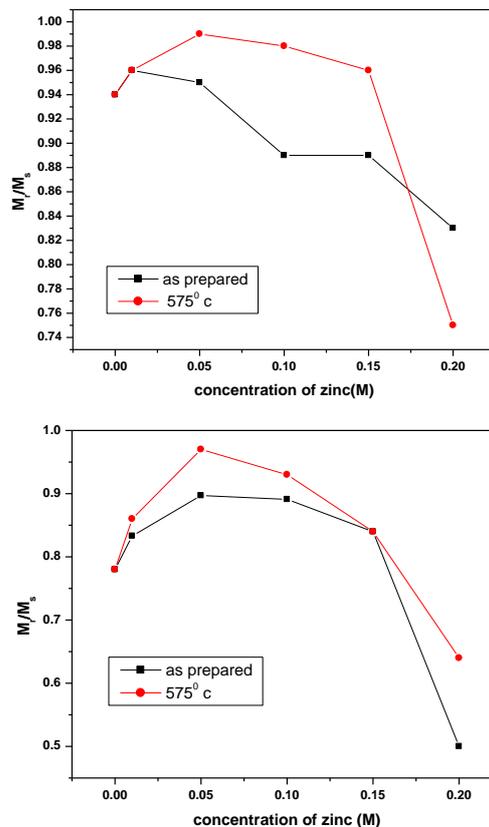
#### 4. CONCLUSIONS

In this paper the nanowires of  $\text{Co}_{1-x}\text{Zn}_x$  with 20 and 35 nm fabricated by electrodeposition method and coercivity field decrease by increasing of Zinc but annealing in  $575^\circ\text{C}$  causes the magnetic properties of nanowires clearly increase. The highest coercivity and squareness

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after annealing related to  $\text{Co}_{90}\text{Zn}_{10}$  ( $H_c = 2120$  Oe) and  $\text{Co}_{95}\text{Zn}_5$  ( $\text{sq} \approx 1$ ), respectively.



**Fig. 7** – Squareness of nanowires with (a) 20 nm and (b) 35 nm diameter to concentration of zinc (M) before and after annealing in  $575^\circ\text{C}$

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