Immersion Lithography with Using of Photostimulated Etching of Germanium Chalcogenide Films

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The new effect of photo-stimulated dissolution of as-evaporated and annealed Ge-based chalcogenide glass (ChG) films was investigated. The etching rate increases with the illumination intensity, and its spectral dependence is correlated with absorption in the film at the absorption edge. The high-frequency diffraction gratings on germanium ChG - more environmentally acceptable compounds than traditionally used arsenic chalcogenides, were recorded by method of interference immersion photolithography with photoinduced etching.

Keywords: Chalcogenide Glasses, Photo-induced Dissolution

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1. INTRODUCTION

Chalcogenide photoresists based on thermal evaporated amorphous films of chalcogenide glasses (ChG) are characterized by high resolution, optical uniformity, wide spectral range of photosensitivity and the possibility to be used on both planar and non-planar substrates. Additionally, such photoresists possess a high refractive index, ranging from 2.0 to 3.0, and are very perspective for high resolution lithography. But recently it was established [5] that the interference relief structures, formed on such films, undergo parasitic surface nanostructurization, which determines their short-wavelength applicability limit. Such structurization is caused by the initial cluster structure of a ChG film, which leads to spatial variations in its etching rate in a developer. Moreover, sufficiently high etching selectivity is observed in this process only in arsenic-based chalcogenide films, such as As-S, As-Se and As-S-Se.

The samples were prepared by successive thermal evaporation in vacuum at a residual pressure of 2·10⁻³ Pa, with a 6 nm thick (effective thickness) adhesive layer of Cr and ChG layers with thicknesses from 300 nm to 600 nm, deposited onto substrates. Polished glass and silicon (orientation (111)) plates are used as substrates. The layer thickness was controlled during deposition by a KIT-1 quartz thickness meter and measured by MII-4 microinterferometer upon deposition. The deposited films were annealed for 0.5–2 h at temperatures ranging from T₆ – 5°C to T₆ –15°C, where T₆ is the glass-transition temperature of a given chalcogenide.

The etching rates of ChG films were studied using the quartz oscillator method [8] in a quartz cuvette filled with a selective etchant [9] based on an amine solutions. The exposure of the samples during etching was performed in the integral light of a DRSh-250 mercury lamp. Spectral emission lines of the same lamp were selected by filters for investigation of spectral dependencies of photoetching rate. Interference structures on the ChG films were recorded by their exposure to an interference pattern [4] formed by the light of a helium–cadmium laser (wavelength λ = 440 nm) using the holographic setup assembled by the wave-amplitude division method. During exposure these samples were placed also into quartz cuvette filled with selective etching solutions (Fig. 1, a). For decreasing of grating period a glass prism was used (Fig. 1, b). In this method of immersion interference lithography the prism was applied to a quartz cuvette using immersion liquid. This method allow to increase spatial frequency of grating in n time, where n - index of refraction of the prism.

2. EXPERIMENT

The samples were prepared by successive thermal evaporation in vacuum at a residual pressure of 2·10⁻³ Pa, with a 6 nm thick (effective thickness) adhesive layer of Cr and ChG layers with thicknesses from 300 nm to 600 nm, deposited onto substrates. Polished glass and silicon (orientation (111)) plates are used as substrates. The layer thickness was controlled during deposition by a KIT-1 quartz thickness meter and measured by MII-4 microinterferometer upon deposition. The deposited films were annealed for 0.5–2 h at temperatures ranging from T₆ – 5°C to T₆ –15°C, where T₆ is the glass-transition temperature of a given chalcogenide.

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The spectral dependence of the absorption index $k$ near the absorption edge of these films [6,7]. The results we obtained, enable the photoinduced etching of ChGs to be used in the formation of lithographic masks or profiled interference structures [6]. Photolithography, based on this effect, has a number of advantages in comparison with conventional use of ChG films as a photoresist. It can be realized on annealed chalcogenide layers, which are characterized by lower defect concentration than thermally as-deposited films. As an example, figure 3 shows the results of the investigations of the substrate surface roughness and the $\text{As}_{40}\text{S}_{50}\text{Sb}_{10}$ film roughness before and after etching (and photoetching) in the selective etchant. The mean square roughness (rms) of the substrate and the films was determined from the results of AFM studies in an area of 100 μm². Curve 1 shows the surface profile of the silicon substrate. Value of rms roughness of the substrate was 0.3 nm. After deposition of a thin adhesive layer of chromium (effective thickness of about 6 nm) and $\text{As}_{40}\text{S}_{50}\text{Sb}_{10}$ (thickness 360 nm) on silicon wafer, the surface roughness of film compared to substrate increased (curve 2), and rms roughness reached a value of 1.1 nm. This increase in roughness associated with the deposition of thin adhesive film, which has an island structure.

3. RESULTS AND DISCUSSION

Figure 2 shows the kinetic curves $d(t)$ for the etching of Ge$_2$Se$_5$ layers in a selective amine-based etchant [9]. The initial thickness of these layers was $d_0 = 300$ nm ($d$ is the layer thickness upon etching, and $t$ is the etching duration): 1 - as-deposited unexposed layer, 2 - annealed unexposed layer, 3 - as-deposited layer illuminated during etching by integral radiation of mercury lamp (250 Wt) with an energy density of incident radiation $p = 8.8$ mWt/sm², 4 - annealed layer illuminated during etching by the same radiation.

It can be seen in Fig. 2 that selected non-water etchant based on amine solution is characterized by good selectivity for the annealed Ge$_2$Se$_5$ layer (value of selectivity, that defined by the ratio of dissolution rate of exposed and unexposed layers reaches 20). But in contrast to traditional lithography on ChG photoresists which use thermally deposited (and non-annealed) ChG layers and where there is a negative selectivity (unexposed photoresist areas are dissolved faster, than exposed), in the photoetching case those layer dissolve faster, which are illuminated in the process of etching (curves 3 and 4, compared with curves 1 and 2). Dissolution rate increases with increasing radiation intensity non-linearly: sixfold increasing of $p$ results in 3 times reducing of the time of complete film dissolution. For germanium chalcogenides the photoetching effect shows up both on annealed and as-evaporated layers, but selectivity of etching is slightly high on the annealed layers.

The spectral dependence of the photoinduced etching efficiency for ChG layers correlates well with the spectral dependence of the absorption index $k$ near the absorption edge of these films [6,7]. The results we obtained, enable the photoinduced etching of ChGs to be used in the formation of lithographic masks or profiled interference structures [6]. Photolithography, based on this effect, has a number of advantages in comparison with conventional use of ChG films as a photoresist. It can be realized on annealed chalcogenide layers, which are characterized by lower
Curve 3 shows the profile surface of as-deposited As$_{40}$S$_{50}$Se$_{30}$ film (initial thickness ~ 300 nm) exposed for 2 minutes by irradiation of mercury lamp, and then etched in the selective etchant for 3 minutes (film thickness is reduced by etching by about 30 nm). It is seen that the surface roughness of etched films is much higher than the original, with rms roughness reaches 3.7 nm. This is in agreement with the results of paper [5], where it was shown, that this roughness is caused by the initial cluster structure of a ChG film, which leads to spatial variations in its etching rate.

Surface profile of annealed and photoetched for 2 minutes the same As$_{40}$S$_{50}$Se$_{30}$ film is shown by curve 4 in Fig. 3. During the photoetching this film is illuminated by integral radiation of mercury lamp having an energy density of incident radiation of 8.8 mWt/sm$^2$, and the film thickness is reduced by half. The rms roughness of the annealed and photoetched film reaches 2.6 nm, i.e., surface roughness substantially less than the as-evaporated film, and etched in the same selective etchant. This result is explained by the fact that the annealed ChG films are more uniform and characterized by lower defect concentration compared with thermally deposited and non-annealed layers. This makes it possible to obtain more higher-quality lithography masks or periodic relief-phase structures using photoetching effect.

This effect has been used for the fabrication of diffraction gratings on germanium ChG - more environmentally acceptable compounds than traditionally used arsenic chalcogenides.

Fig. 3 shows AFM - picture of the diffraction grating which was formed on the annealed Ge$_{25}$Se$_{75}$ film (the initial thickness of this layer was $d_0$ = 200 nm) by photoetching method with using the same amine-based etchant. The spatial frequency of grooves in the recorded grating is 1700 mm$^{-1}$; the profile depth is 65 nm. The shape of the groove profile of the grating is nearly sinusoidal. The recording time of the grating is 20 min, and its size is 30x30 mm at a laser power of 25 mW. During exposure to the absorbing radiation of a helium–cadmium laser (wavelength $\lambda$ = 440 nm), the diffraction efficiency of the grating being formed was monitored in situ with the nonphotoactive light of a helium–neon laser ($\lambda$ = 632.8 nm). The increase of photoetching time (or power of laser) allows to obtain gratings with higher relief depth liquid (Fig. 1).

Fig. 4 shows AFM image of obtained diffraction grating formed on the Ge$_{25}$Se$_{75}$ film by this method of immersion interference lithography with photoinduced etching. The spatial frequency of grooves in the recorded grating is 4330 mm$^{-1}$; the profile depth is 25 nm. The shape of the groove profile of the grating is nearly sinusoidal also. The recording time (by helium–cadmium laser, $\lambda$ = 440 nm) of the grating is 50 min, and its size, is 30x30 mm at a laser power of 25 mW.

For increasing the spatial frequency of the gratings we used a glass prism with $n = 1.5$, which was applied to a quartz cuvette using immersion.

This method also makes it possible to form on the surface of the photoresist complex two-dimensional relief-phase structure, or lithographic masks (Fig. 6) to profile surfaces of metals, semiconductors up to nanodimensions.

4. CONCLUSIONS

The simultaneous illumination and etching of as-evaporated and annealed Ge-based ChG films results
in the photo-induced enhancement in the solubility of the chalcogenides in selective etchants. It was shown that negative-action etchants based on amines dissolve illuminated portions of a chalcogenide film, i.e., act as positive etchants.

The effect of photo-stimulated dissolution has been used for the fabrication of diffraction gratings on germanium ChG films by interference immersion photolithography. Relief parameters of the obtained structures are studied. The photoetching technique used to form interference periodic structures onto chalcogenide layers a simple, inexpensive, and adaptable to large-scale manufacturing.

REFERENCES