

## INTERFERENCE PHOTOLITHOGRAPHY USING PHOTOETCHING EFFECT IN CHALCOGENIDE FILMS

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The surface roughness of thin amorphous films of chalcogenide glasses (ChG) after photo-stimulated dissolution in amine-based selective etchant has been investigated. It is established that the rms roughness of the annealed and photoetched ChG film substantially smaller than the as-evaporated film and etched in the same selective etchant. This makes it possible to obtain more higher-quality lithographic masks or periodic relief-phase structures using new photoetching effect: photo-induced enhancement in solubility of annealed ChG layers. A possible mechanism for the photoinduced etching of ChGs is discussed. The diffraction gratings on germanium ChG - more environmentally acceptable compounds than traditionally used arsenic chalcogenides, were recorded for the first time by using the effect of photoinduced etching on ChG layers and their characteristics were studied.

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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 immersion lithography, including high resolution interference lithography [1-4]. But recently 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.

In this paper we report on the results of investigation of surface roughness of ChG films which arises during development of this films in amine-based selective etchants using also new photostimulated effect [6] in amorphous chalcogenide films: photo-induced enhancement in solubility of annealed ChG layers. The simultaneous illumination and etching of annealed ChG films results in the photo-induced enhancement in the solubility of chalcogenide in selective etchants. The new photo-induced effect allows realize a photolithography (including the process of interference photolithography) on the ChG layers, annealed near the glass-transition temperature, by the simultaneous irradiation and selective etching of such layers.

### 2. Experimental

The samples for study were prepared by successive thermal evaporation in vacuum at a residual pressure of  $2 \cdot 10^{-3}$  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 film thicknesses were monitored with a KIT-1 quartz thickness meter during deposition and a MII-4 microinterferometer upon

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deposition. Some of deposited films were annealed for 0.5–2 h at temperatures ranging from  $T_g - 5^\circ\text{C}$  to  $T_g - 15^\circ\text{C}$ , where  $T_g$  is the glass-transition temperature of a given chalcogenide.

The etching rates of ChG films were studied using the quartz\_oscillator method [7] in a quartz cuvette filled with a selective etchant [8] based on an anhydrous solution of an organic alkali (amines). The exposure of some samples during etching was performed in the integral light of a DRSh-250 mercury lamp. The spectral dependence of the effect of the photoinduced etching of ChG films was studied by selecting spectral lines of this lamp using filters.

Recording of interference structures on annealed ChG films was carried out by the interference pattern formed with helium-cadmium laser (wavelength  $\lambda = 440$  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 etchants. The profile shape of the obtained structures and surface roughness of ChG films were investigated with a Dimension 3000 Scanning Probe atomic force microscope (AFM) (Digital Instruments Inc.).

The diffraction properties of obtained relief gratings were examined by measuring the spectral dependence of the diffraction efficiency  $\eta(\lambda)$  of samples preliminarily coated with a 40-nm-thick Al reflecting layer. Value  $\eta$  was taken as the ratio of intensities of the diffracted beam to the incident beam, and were measured for s- and p-polarized light (electric vector of light-wave is perpendicular and parallel to grating grooves, respectively). Spectral measurements were performed for the first order of diffraction in the spectral range 400–900 nm using the setup close to the Littrow scheme, the angle between the incident and diffracted beams was near 8 deg.

### 3. Results

Unlike conventional utilization of ChG layers as photoresist, where sufficiently high sensitivity is observed only in thermally as-evaporated arsenic chalcogenide films, photoetching can be realized on annealed layers of chalcogenides (including germanium chalcogenides), which are characterized by lower defect concentration compared with non-annealed films [6]. In this paper the investigation was carried out for ChG films of two compositions:  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  and  $\text{Ge}_{25}\text{Se}_{75}$ . Figure 1 shows, as an example, the kinetic curves  $d(t)$  for the etching of  $\text{Ge}_{25}\text{Se}_{75}$  layers in a selective amine\_based etchant [8]. 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/sm<sup>2</sup>, 4 - annealed layer illuminated during etching by the same radiation.

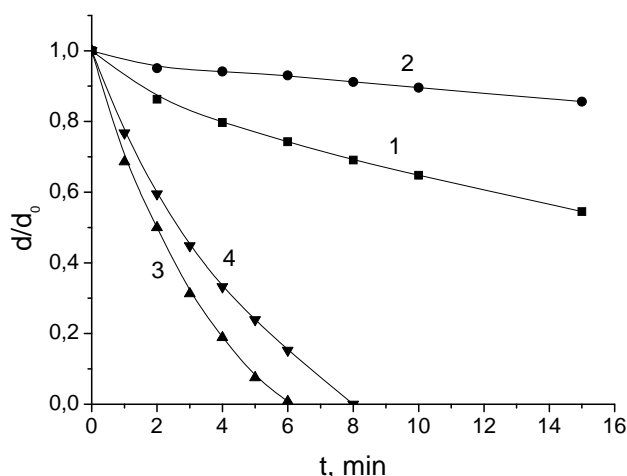


Fig. 1. Dissolution kinetics of  $\text{Ge}_{25}\text{Se}_{75}$  layers in the amine-based etchant: curve 1 – as-deposited unexposed layer, 2 - annealed and unexposed layer, 3 - as-deposited layer exposed during etching by integral radiation of mercury lamp (250 Wt) with an energy density of incident radiation  $p = 8,8$  mWt/sm<sup>2</sup>, 4 - annealed layer exposed during etching in the same conditions.

As can be seen from the figure, the irradiation of the films during etching leads to a significant increase in the rate of dissolution both annealed and as-evaporated layers of germanium chalcogenides. However selectivity of etching for annealed  $\text{Ge}_{25}\text{Se}_{75}$  film more high than on as-evaporated layer. In conventional lithography on ChG unexposed areas of the photoresist are dissolved in the amine-based etchant faster than the exposed areas do, i.e., negative selectivity is observed [4]. In the case of photoinduced etching of the same, but annealed ChG layers, the layers illuminated in the course of etching are dissolved much more rapidly (curves 3 and 4 against curve 2 and 1 in Fig. 1), i.e., positive selectivity is observed for the same etchant (value of selectivity, that defined by the ratio of dissolution rate of exposed and unexposed layers reaches 35).

Similar results with certain quantitative details were obtained for  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  films, but for the arsenic chalcogenide photoetching effect shows up only on annealed layers. With increasing light intensity  $p$ , the dissolution rate grows nonlinearly: a six-fold increase in  $p$  made it possible to reduce the complete dissolution time of an  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film by only a factor of 3.

Control experiments were carried out with similarly annealed samples successively illuminated at the same exposures ( $H = pt$ ) and then etched in the same etchant. The etching rate was close to that for unexposed samples (Fig. 1, curve 2). Thus, the given etchant acts effectively on an annealed ChG film only under exposure to light.

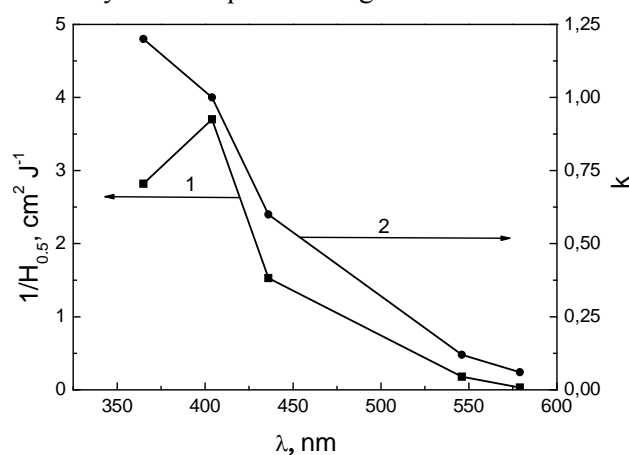


Fig. 2. Spectral dependence of the photoetching efficiency (curve 1) and absorption index ( $k$ , curve 2) [9] of  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film.

Fig. 2 shows the spectral dependence of the photoinduced etching efficiency for an annealed  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  layer, defined as a quantity inverse to the exposure  $H_{0.5}$  at which half of the film thickness is dissolved. On the same figure the spectral dependence of the absorption index  $k$  for an  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film is shown [9]. Rather good correlation between the absorption and the photoinduced etching rate can be noted near the absorption edge; however, at the short-wavelength spectral range photoetching efficiency slightly decreases. This decrease in efficiency may be caused by the absorption of shortwave radiation in the etchant solution.

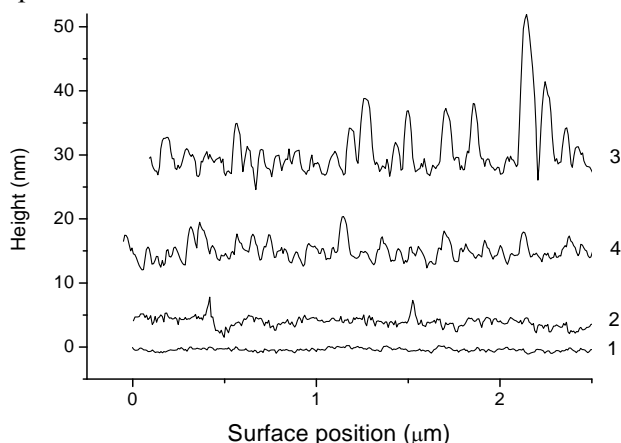


Fig. 3. The surface profile of the samples: 1 - silicon substrate, 2 -  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film with Cr sublayer deposited on the substrate, 3 - as-deposited, exposed and etched  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film,

Fig. 3 shows the results of the investigations of the substrate surface roughness and the  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  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  $100\ \mu\text{m}^2$ . 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  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  (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.

Curve 3 shows the profile surface of as-deposited  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  film 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 CG film, which leads to spatial variations in its etching rate.

Surface profile of annealed and photoetched for 2 minutes  $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$  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  $8,8\ \text{mWt}/\text{sm}^2$ , and the film thickness is reduced by half. The rms roughness of the annealed and photoetched film reaches 2.6 nm, ie, 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 lithographic masks or periodic relief-phase structures using photoetching effect.

Another advantage of photolithography using photoetching effect is that the processes of etching and exposure in this method are combined, that diminishes the number of technological operations in photolithographic process. In photoetching lithography for deposition of chalcogenide films more technological methods can also be used: electron-beam evaporation, laser or high-frequency magnetron sputtering, deposition on the substrate from solutions.

This effect has been used for the fabrication of diffraction gratings on germanium ChG - more environmentally acceptable compounds than traditionally used arsenic chalcogenides. Figure 4a shows the AFM image of a diffraction grating formed on an annealed  $\text{Ge}_{25}\text{Se}_{75}$  film by photoinduced etching in the same amine-based etchant. The spatial frequency of grooves in the recorded grating is  $1700\ \text{mm}^{-1}$ ; the profile depth is 65 nm. The shape of the groove profile of the grating (Fig. 4b) is nearly sinusoidal. The recording time of the grating is 20 min, and its size, is  $30 \times 30\ \text{mm}$  at a laser power of 25 mW. During exposure to the absorbing radiation of a helium-cadmium laser (wavelength  $\lambda = 440\ \text{nm}$ ), the diffraction efficiency of the grating being formed was monitored *in situ* with the nonphotoactive light of a helium-neon laser ( $\lambda = 632\ \text{nm}$ ).

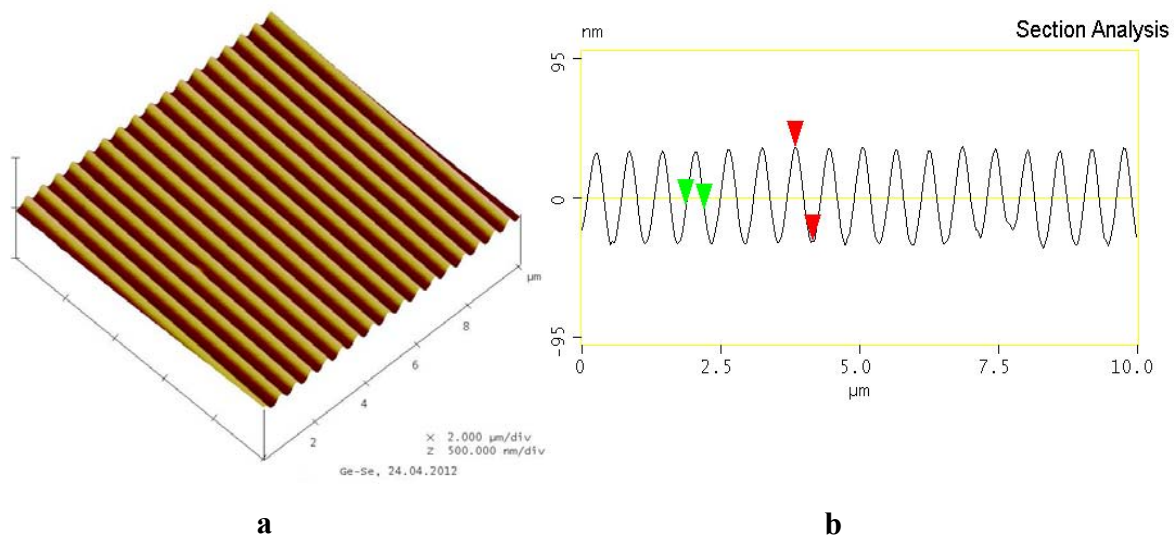


Fig. 4. AFM image and groove profile of diffraction grating, obtained on annealed  $\text{Ge}_{25}\text{Se}_{75}$  film by photoetching method.

Thus formed diffraction structure has corresponding properties of holographic diffraction gratings. Fig. 5 shows the spectral dependences of diffraction efficiency for a grating with the profile shown on Fig. 4 that coated with reflective Al layer (40 nm thickness). Curves 1 and 2 correspond to perpendicular and parallel orientation of the electric vector of light-wave relative to the grating grooves. Surface of this grating is characterized by a lower rms roughness than the gratings which were recorded on as-evaporated ChG layers. This will allow to produce with the help of photoetching and immersion interference lithography more high-frequency relief-phase structures of good quality.

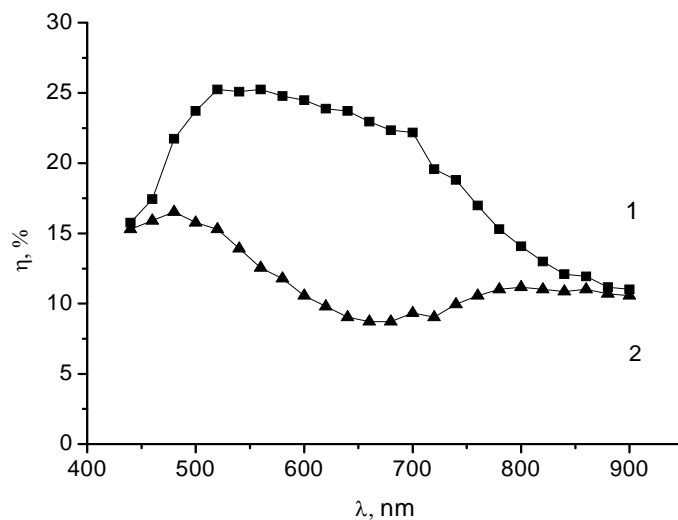


Fig. 5. Spectral dependence of the diffraction efficiency  $\eta$  for the grating formed by photoetching of annealed  $\text{Ge}_{25}\text{Se}_{75}$  film (the same sample as on Fig. 4): curves 1 and 2 correspond to perpendicular and parallel orientation of the electric vector of light-wave relative to the grating grooves.

#### 4. Discussion

Most photostimulated effects in ChG were investigated on as-deposited, annealed and/or exposed films. However, as investigations have shown [10, 11], during the exposure of the ChG films transient photostimulated changes in the structure are also observed, which exist only during the illumination of the film and quickly relax after switching off the light.

Transient change of ChG structure during illumination is confirmed also by the phenomenon of photostimulated fluidity (photoplasticity) in binary chalcogenide films and selenium, which was studied by many researchers [12 - 14]. It is characterized by decreasing viscosity and increasing fluidity of ChG films which are illuminated by light of sufficient intensity, and observed only during exposure of ChG. A few microscopic mechanisms of photoplasticity are offered [14, 15]. Fritzsche [14] suggest that photoplasticity is caused by cumulative effect of recombination-induced atomic motions and bond changes during illumination. The recombination-induced bond rearrangements continue as long as ChG is exposed to electron-hole pair producing light and this dynamic state is comparable to that near the glass-transition temperature. Other authors [15] based on in situ EXAFS and Raman experiments propose two possible mechanism: first, an interchange of covalent bonds through bond rupture and rebonding (which is supported by EXAFS results [16]), second, weakening of the intermolecular and interchain bonds (which agree with Raman measurements [17]). Such transient structure changes, as shown by our investigations [6], accompanied by a change in the solubility of chalcogenide in selective etchants. It can be assumed that the photodissolution of ChGs is, in all probability, stimulated just by bond switching during their exposure to photoactive light.

## 5. Conclusions

The rms roughness of the annealed and photoetched ChG film substantially smaller than rms of the as-evaporated film and etched in the same selective etchant. This decrease in roughness is caused by that the annealed ChG films are more uniform and characterized by lower defect concentration compared with thermally deposited, non-annealed and exposed layers. The simultaneous illumination and etching of annealed ChG films results in the photo-induced enhancement in the solubility of chalcogenide in selective etchants. The new photo-induced effect allows realize a photolithography (including the process of interference photolithography) on the ChG layers, annealed near the glass-transition temperature, by the simultaneous irradiation and selective etching of such layers.

The effect of photo-stimulated dissolution of annealed ChG films has been used for the first time for the fabrication of diffraction gratings on germanium ChG films. Relief parameters and diffractions properties of the obtained structures are studied. It is assumed that the photostimulated ChG dissolution is stimulated by bond switching processes between ChG atoms during illumination by photoactive radiation.

The photoetching technique used to form interference periodic structures onto chalcogenide layers a simple, inexpensive, and adaptable to large-scale manufacturing.

## References

- [1] Y. Mizushima and A. Yoshikawa, Photoprocessing and lithographic applications // Amorphous Semiconductors Technol. and Devices.-Y.Hamakawa, Ed.- OHM,Tokyo , and North-Holland, Amsterdam 277 (1982).
- [2] G.H. Bernstein, W.P. Liu, Y.N. Khawaja, M.N. Kozicki and D.K. Ferry, J. Vac. Sci. Technol. **B6**, 2298 (1988).
- [3] K. Saito, Y. Utsugi and A. Yoshikawa, J.Appl.Phys. **63**, 565 (1988).
- [4] V.A. Dan'ko, I.Z. Indutnyi, V.I. Min'ko, and P.E. Shepelyavyi, Optoelectronics, Instrumentation and Data Processing **46**, 483 (2010).
- [5] S. N. Koreshev and V. P. Ratushnyi, Optics and Spectroscopy **106**, 288(2009).
- [6] V. A. Dan'ko, I. Z. Indutnyi, V. I. Min'ko, P. E. Shepelyavyi, O. V. Berezn'ova, O. S. Litvin, Semiconductors, **46**, 504 (2012).
- [7] K. Shtekhelmaher, In "Thin-film microelectronics", ed. By L. Hollend, M. Mir, (1968).
- [8] Pat. Russia № 2008285, МКИ5 C 03 C 15/00, 23/00 (1994).
- [9] A.I. Stetsun, Optical properties of photodoped calcogenide layers, Ph. D. diss., (1994).
- [10] A.V. Kolobov , K. Tanaka, Phizika I Tehnika Poluprovodnikov (Russia) **32**, 899 (1998).
- [11] Ashtosh Ganjoo, H. Jain, S. Khalid, Journal of Non-Crystalline Solids **354**, 2673 (2008).
- [12] M. L. Trunov, P. M. Lytvyn, P. M. Nagy, and O. M. Dyachyns'ka, Appl. Phys. Lett. **96**, 111908 (2010).
- [13] K. Tanaka, N. Kawakami, and A. Odajima, Jpn. J. Appl. Phys., Part 1 **20**, 1874 (1981).
- [14] H. Fritzsche, Solid State Communications **99**, 153 (1996).
- [15] Alexander V. Kolobov and Kazunobu Tanaka, in Handbook of Advanced Electronic and Photonic Materials and Devices, edited by H. S. Nalwa (Academic, San Diego), **5**, Chap. 2, (2001).
- [16] A.V. Kolobov, H. Oyanagi, K. Tanaka and Ke Tanaka, Phys. Rev. **B 55**, 726 (1997).
- [17] V.V. Poborchii, A.V. Kolobov, and K. Tanaka, Appl. Phys. Lett. **74**, 215 (1999).