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Fabrication of submicrometer periodic structures using interference lithography and two-layer chalcogenide photoresist

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Technological process of interference lithography using two-layer chalcogenide photoresist were investigated. Top $As_{40}S_{30}Se_{30}$ layer is photoresist with a high selectivity and can be used for recording of interference pattern and formation of first lithographic mask. Second, more thick $As_4Ge_{30}S_{66}$ layer, almost is not sensitive to light, but dissolves in weak (0.05 %) water solution of KOH. That, optimizing the etchant solutions for both layers, exposure and time of etching it is possible to carry out the technological process of formation of the lithographic mask with high modulation and with the groove form close to rectangular. This technology has been used for the fabrication of one- and two-dimensional periodic structures. Using two-layer $As_{40}S_{30}Se_{30}$-$As_4Ge_{30}S_{66}$ photoresist, we have fabricated the diffraction gratings and two-dimensional periodic structures with elements of submicron size. Relief parameters and diffractions properties of the obtained structures and their dependence on etching time are studied.

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Keywords: Chalcogenide inorganic photoresist, Interference lithography

1. Introduction

One of the most technological method for fabrication of periodic nano- and microstructures, production of the master mold for nanoimprinting lithography, formation of grating structures on semiconductor surfaces, pre-patterning of the substrate and others is interference (interferometric) lithography. As shown in our previous investigations, the thermal evaporated As-S-Se films are perspective photoresists in technology of interference lithography and widely used in production of diffraction optical elements and devices (hologram diffractions gratings, lenses and mirrors, etc.) with the micronic and submicrometer sizes of elements [1-3]. Chalcogenide photoresists are characterized by high resolution, wide spectral range of photosensitivity, they are stable, do not need any thermal treatment [3-6]. Furthermore, chalcogenide films can be deposited very homogeneously using the same technological processes as for deposition of functional layers in microelectronics.

In the case of photoresist exposure by the interference pattern the distribution of light intensity on the photoresist surface is described by a sinusoidal dependence. Accordingly, the groove profiles of the obtained photoresist mask will be close to sinusoidal, or cycloidal [5]. Such form of mask is suitable at fabrication of hologram diffraction gratings and other diffraction optical elements. However for the lift-off lithography, fabrication of two-dimensions relief structures, patterning of substrates, for growing of three-dimensional photonic structures and many other applications must be formed interference relief pattern with the form of grooves more close to rectangular.

For the decision of this task the use of two-layer photoresist that consists of sequentially deposited $As_4Ge_{30}S_{66}$ and $As_{40}S_{30}Se_{30}$ layers was offered. Top light-sensitive $As_{40}S_{30}Se_{30}$ layer can be used for the formation of lithographic mask. Bottom $As_4Ge_{30}S_{66}$ layer is less sensible to light, but dissolves in weak (near 0,05 %) water solution of KOH. That, after the selection of optimum etchants for both layers it is possible to realize three-step technological process: interference exposure, selective etching of $As_{40}S_{30}Se_{30}$, and etching of $As_4Ge_{30}S_{66}$ layer through the lithographic mask of $As_{40}S_{30}Se_{30}$. Thus a relief structure appears with the high modulation, and with the groove form near to rectangular.

In this paper we report the results on the investigation of this two-layer chalcogenide photoresist and its application for fabrication of microrelief structures.

2. Experimental

The samples for measurements and interference lithography experiments were deposited on polished glass and (100) silicon substrates using the thermal vacuum evaporation at the pressure $2 \cdot 10^{-3}$ Pa. To provide the necessary adhesion to the substrate and to eliminate the interference effects connected with reflectance from the glass substrate's back surface, a chromium layer was deposited on the substrate prior to the deposition of other layers. The layer thickness was controlled during deposition process by the quartz-crystal-oscillator monitoring system (КИТ-1) and reached 40 nm for the chromium layer, 300 nm for $As_4Ge_{30}S_{66}$, and 100 nm for As_{40} S_{30} Se_{30} layers. After deposition, the thickness of the films was measured using a MII-4 micro-interferometer.

The investigation of etching characteristics of exposed and non-exposed $As_4Ge_{30}S_{66}$ and As_{40} S_{30} Se_{30} films was carried out using the highly sensitive quartz resonator method .

The prepared samples were exposed by interferential pattern that was generated by an argon laser (wavelength of 514 nm) using the holographic setup assembled by the wave-amplitude division method. The exposure value was near 0.5 J/cm^2, and in the course of formation of bigratings each exposure can be 1.5-2 times reduced. The size of an exposed part of the substrate reached up to 75×75 mm.

After exposure, the samples were chemically treated in non-water alkaline organic solutions [7] (negative etching, i.e. the exposed areas are dissolved more slowly than the unexposed areas) to form a resistive mask in As_{40} S_{30} Se_{30} layer. Next step was etching of $As_4Ge_{30}S_{66}$ layer using KOH water solution.

For patterning of substrate we etch of Cr layer using water solution of HCl through obtained chalcogenide mask. The obtained Cr-chalcogenide resistive mask can be used to form a corresponding relief on substrate surface. Anisotropic etching of silicon was carried out using ethylenediamine solutions. As ethylenediamine actively dissolves chalcogenides, etching of silicon occurred, mainly, through a Cr resistive mask.

The surface patterns of obtained structures were examined with a Dimension 3000 scanning probe microscope (Digital Instruments) in the AFM tapping mode.

Diffraction properties were studied by measuring the spectral η(λ) (λ is a wavelength) dependence of diffraction efficiency (η) of samples that were preliminary covered in vacuum with the reflective thin-film (~ 30 nm) Al layer. The diffraction efficiency was taken as the ratio of intensities of the diffracted to the incident beams, and were measured for s- and p-polarized light (polarization is perpendicular and parallel to grating grooves, respectively). Spectral measurements were carried out for the first diffraction order within the range of 400 to 800 nm using the setup close to the Littrow scheme, the angle between the incident and diffracted beams was near 8 deg.

3. Results and discussion

To obtain the desired effect from the use of two-layer photoresist, that to create the reliable lithographic mask of necessary profile, it is needed to optimize the etchants for both layers. Fig. 1 presents the dissolution kinetics of vacuum-deposited $As_{40}S_{30}Se_{30}$ and $As_4Ge_{30}S_{66}$ layers, initial thickness h_0 of which was 300 nm (h is the thickness of the dissolved layer, t - time of dissolution) in selective etchant for $As_{40}S_{30}Se_{30}$ on the basis of amine solution: curve 1 – unexposed $As_{40}S_{30}Se_{30}$ sample, 1' - exposed $As_{40}S_{30}Se_{30}$ layer (integral irradiation of mercury lamp, value of exposure H = 0.5 J/cm^2), curve 2 - $As_4Ge_{30}S_{66}$ layers (both exposed and unexposed).

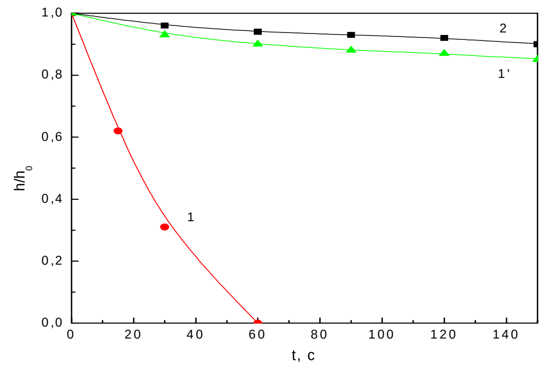


Fig. 1. Dissolution kinetics of $As_{40}S_{30}Se_{30}$ and $As_4Ge_{30}S_{66}$ layers in amine solution. Curve 1 – unexposed $As_{40}S_{30}Se_{30}$ layer, 1' – exposed $As_{40}S_{30}Se_{30}$ layer, 2 - exposed and unexposed $As_4Ge_{30}S_{66}$ layer, h-thickness of the layer, h_0-initial thickness.

It can be seen, that chosen non-water etchant [7] on the basis of amine solution is characterized by good selectivity for $As_{40}S_{30}Se_{30}$ layer (value of selectivity, that defined by the solubility ratio of exposed and nonexposed film areas, achieves 13), and almost does not dissolve $As_4Ge_{30}S_{66}$ layer, both exposed and unexposed. It enables on the second step to form sinusoidal interference relief on the top photosensitive $As_{40}S_{30}Se_{30}$ layer.

Fig. 2 shows the dissolution kinetics of $As_{40}S_{30}Se_{30}$ and $As_4Ge_{30}S_{66}$ samples in 0.05 % KOH water solution (etchant for $As_4Ge_{30}S_{66}$) (notation the same, as on Fig.1). As it is evident from the figure, this etchant is actually neutral for $As_{40}S_{30}Se_{30,}$ not dissolving neither exposed nor unexposed films (curves 1, 1' on Fig. 2). At the same time $As_4Ge_{30}S_{66}$ layer dissolves with high speed (curve 2 on Fig. 2) that gives possibility to form on this two-layer chalcogenide structure more deep relief with the form of groove near to rectangular.

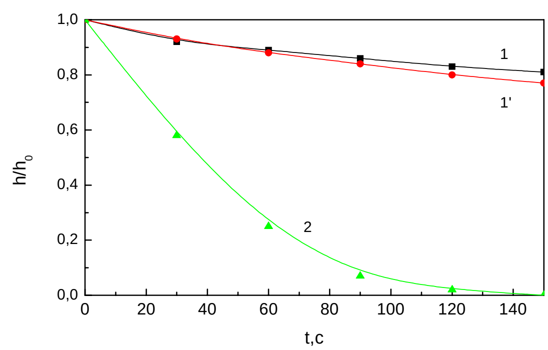


Fig. 2. Dissolution kinetics of $As_{40}S_{30}Se_{30}$ and $As_4Ge_{30}S_{66}$ layers in alkaline solution. Curve 1 – unexposed $As_{40}S_{30}Se_{30}$ layer, 1' – exposed $As_{40}S_{30}Se_{30}$ layer, 2 - exposed and unexposed $As_4Ge_{30}S_{66}$ layer, h-thickness of the layer, h_0-initial thickness.

Fig. 3 shows the AFM image of the periodic relief, formed by interference exposure and two-step etching of two-layer chalcogenide photoresist. Obtained diffraction grating have a period near 0,76 mkm. Time of $As_4Ge_{30}S_{66}$ layer etching was 45 c, relief depth achieves 0,17 mkm, and trapezium groove profile close to rectangular is observed. There is a significant depth of the relief modulation (≈ 0.23) and high-quality groove surface are observed. It is necessary to notice also, that Ge-chalcogenide glasses are characterized by higher thermal and mechanical durability as compared to As-S-Se glasses, it is also important at their use as lithographic masks. In particular, it allows to produce the copies of such elements on standard stamping technology, or with the use of photopolimers .

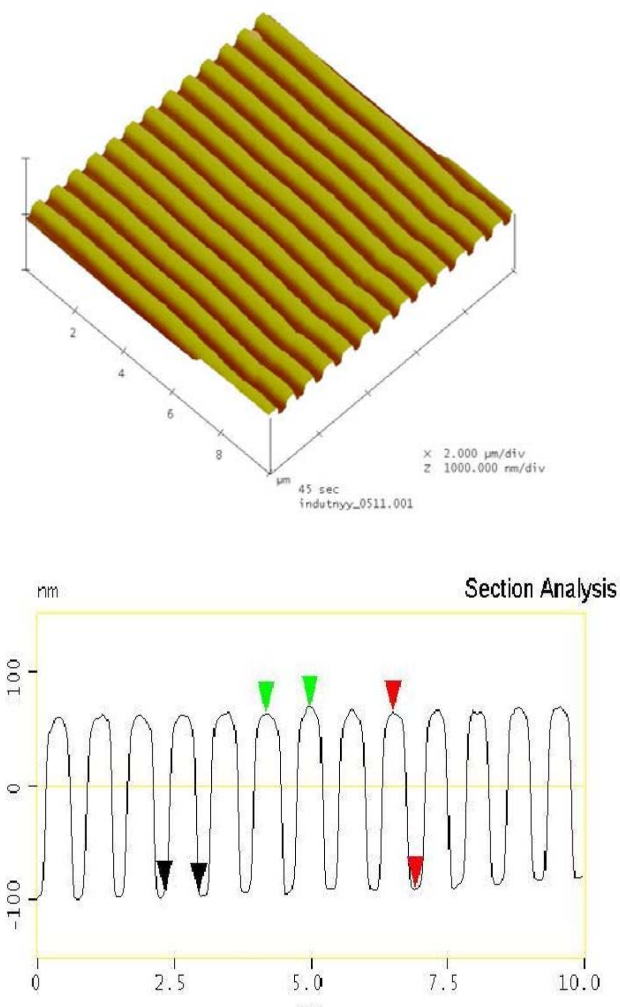


Fig. 3. Relief and groove profile of grating formed on two-layer chalcogenide photoresist.

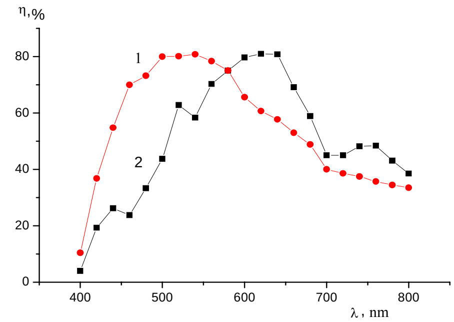
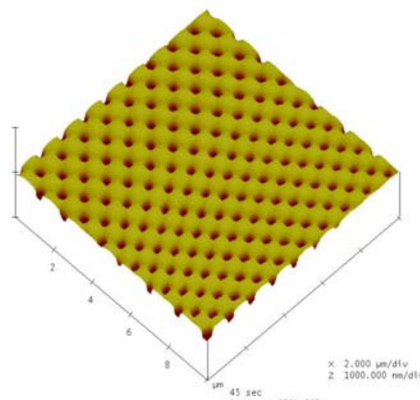


Fig. 4. Spectral dependence of the diffraction efficiency η for p- (1) and s-polarized (2) light (the same sample as on Fig. 3).

Fig. 4 shows the spectral dependences of diffraction efficiency for a grating with the profile depicted in Fig. 3. Curves 1 and 2 correspond to *p*- and *s*-polarizations. As it is evident from the figure, the significant depth of modulation and non-sinusoidal groove shape of the grating cause high (up to 85 %) η values in visible and IR spectral range.



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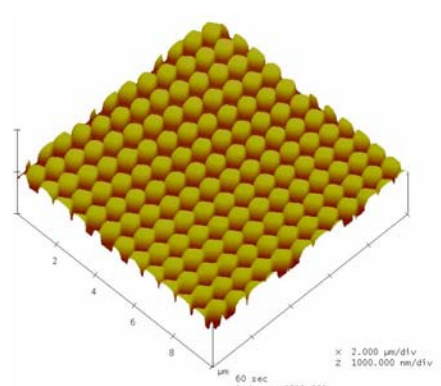

b

Fig. 5. AFM image of bigratings with symmetrical elements obtained on two-layer chalcogenide photoresist.

Dependence of diffraction characteristics on groove profile and relief depth of diffraction gratings was explored by many authors [8, 9]. In particular in [9] spectral dependence of diffraction efficiency of symmetric gratings with the different form of relief is investigated theoretically. Authors state, that by changing the form of groove profile it is possible to control spectrum of diffraction efficiency, and working spectral interval of gratings. Diffraction efficiency of gratings with trapezium groove profile and different slope of trapezium side is investigated in [8]. At comparison of η spectra of our samples with similar model structures described in [8], there is their qualitative similarity.

Fig. 5 presents the AFM image of the periodic relief formed in two-layer chalcogenide photoresist by double interference exposure and two-step etching. Orientation of the sample for two exposure by an interferential picture from two coherent beams differed by 90°. The value of exposures and time of selective etching of two-layer chalcogenide photoresist can be chosen so that the lithographic mask looked like periodically located holes in photoresist layer (Fig. 5, a). The diameter of holes can be changed depending on the value of exposure and time of etching (the structure period in two mutually perpendicular directions makes 0.8 mkm). That, such method give the possibility to form a well-organized microporous structure with controlled porosity.

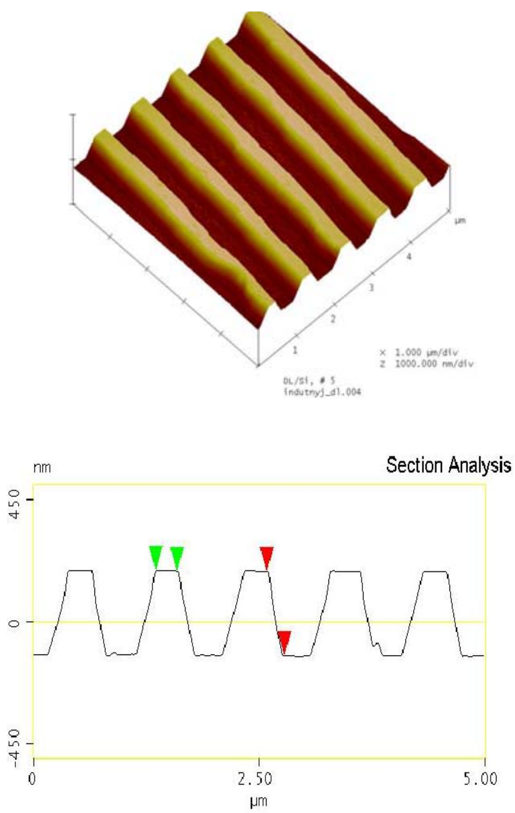

Fig. 6. AFM image and groove profile of a grating obtained on Si (100) surface, time of silicon etching – 20 s .

By increase of etching time of photoresist layer and optimization of exposure it is possible to obtain structures, which looked like hillocks, rhomb-shaped form in the section (Fig. 5b). Dimensions of obtained relief elements (both Fig. 5a and b) depends mainly on time of etching and thickness of chalcogenide layers. Thus there were obtained structures with the submicrometer sizes of elements on the substrates with the sizes of up to 75*75 mm.

The obtained structures can be used as diffractions optical elements [5, 10], stamps for copying of nano- and microstructures [9, 11], as patterned substrates for growing of three-dimensional photonic structures [12, 13], ordered matrixes of silicon nanowires [14], and as resistive mask for surface profiling of different semiconductor or dielectric materials by direct or lift-off lithography [1, 2]. As an example, Fig. 6 shows the AFM image of diffraction grating formed on the silicon (100) surface by the anisotropic etching through $As_{40}S_{30}Se_{30}$-$As_4Ge_{30}S_{66}$ -Cr resistive mask (grating period is near 0.9 mkm). Time of silicon etching in ethylenediamine solutions was 20 s. The depth of the relief reaches 0.3 mkm, and the groove profile is close to trapezium with 70.5° apex angle and a flat top section. Such silicon gratings with symmetric triangular or trapezium grooves are used, in particular, in wavelength demultiplexers [15] and tunable lasers [16].

4. Conclusions

We have shown that the two-layer chalcogenide photoresist can be applied in the interference lithography to form the submicron relief structures with the high depth modulation, and with the groove form near to rectangular. Using the two-layer $As_{40}S_{30}Se_{30}$-$As_4Ge_{30}S_{66}$ photoresist and two-step etching, we have fabricated the high-quality diffraction gratings with the groove's section close to rectangular and diffraction efficiency up to 85 % for polarized light, as well as two-dimentional periodic structures with submicron size elements. It was shown, also, that inexpensive interference lithography with two-layer chalcogenide photoresist can be used for submicrometric patterning of semiconductor or dielectric substrates by direct or lift-off lithography.

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