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Fabrication of silicon grating structures using interference lithography and chalcogenide inorganic photoresist

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Abstract. Application of inorganic photoresist based on chalcogenide films for fabrication of submicrometer periodic relief on silicon wafers was investigated. For this purpose, technological process of resistive two-layer chalcogenide-Cr mask formation on a silicon surface was developed, and silicon anisotropic etching was optimized, too. This technology has been used for the fabrication of high-quality diffraction gratings on Si (100) surface with symmetric triangular and trapezium grooves and two-dimentional periodic structures. Relief parameters and diffraction properties of the obtained structures and their dependences on etching time were determined.

Keywords: chalcogenide inorganic photoresist, interference lithography, diffraction grating.

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1. Introduction

Investigations of optical and photostimulated phenomena on the microstructured surfaces of various semiconductor or dielectric materials form the basis for development of such devices as high-sensitivity sensors, photodetectors, solar batteries, elements of integral optics, *etc.* As a rule, structures with a periodic relief of the micron or submicron sizes are used depending on the chosen spectral range or other specifications. Relief with necessary parameters can be created using the selective etching of material through the prefabricated resistive mask on its surface. Such masks are formed using photoresists, *i.e.* the materials that change their properties under light irradiation. After deposition of photoresist on the surface of material that should be subjected to microprofiling, exposure by a light field with necessary distribution of intensity and selective etching, that is removal the unexposed areas of photoresist layer, is carried out. Thus, the resistive mask that provides physical access only to the designed areas of the substrate was obtained. As a result of the next technological operation – etching through the mask – there arises a relief structure already in the material of semiconductor or dielectric.

One of the most technological methods of formation of periodically structured resistive mask is recording the interference pattern from two coherent light beams on the substrate with photoresist. Using this method, it is possible to fabricate a mask with apertures that looks like parallel strips with a period of submicrometer to a few micrometers (holographic diffraction grating). If to carry out the double exposure for two mutually perpendicular orientations of the substrate, we shall obtain a bigrating, *i.e.* mask as periodically located holes or islands (depending on conditions of exposure and etching). This technological method has been named as interferential lithography. Interferential lithography is lately used for fabrication of one-dimensional nanostructures [1], production of the master mold for nanoimprinting lithography [2], formation of grating structures on semiconductor surfaces [3, 4], pre-patterning of the substrate before formation of photonic crystals by electrochemical etching [5] or vacuum deposition [6] *etc*. This process provides formation of submicrometer periodic structures on substrates with a large area using single or double exposition. The technology is much cheaper and simpler than the electron beam lithography.

Characteristics of photoresist are important in technology of interference lithography. As shown in a number of works [7-10], one of the most perspective photoresist for formation of interference relief structures is an inorganic photoresist on the basis of chalcogenide glasses of As-S-Se system. An extremely high resolution (1 nm), vacuum deposition (that allows to obtain homogeneous film of precisely controllable thickness on various surfaces, including the nonplanar ones), sufficient mechanical, thermal and chemical stability are the advantages of this photoresist. Earlier we investigated an application of chalcogenide inorganic photoresists for manufacturing the periodic relief-phase structures on the GaAs single crystals [11], layers of silicon nitride (Si_3N_4) as well as substrate of non-crystalline materials (glass, silica). In this work, the first investigation on application of chalcogenide photoresists for fabrication of periodic relief structures on silicon wafers by using interferential lithography and anisotropic etching were carried out.

2. Experiment

The chromium and chalcogenide layers were deposited sequentially onto polished (100) silicon substrates using the thermal vacuum evaporation at the pressure $2 \cdot 10^{-3}$ Pa. The layer thickness was controlled during deposition process by the quartz-crystal-oscillator monitoring system (КИТ-1) and reached 50 nm for the chromium layer and 100 nm for the photoresist ($As_{40}S_{60}$) one.

The prepared samples were exposed by interferential pattern that was generated by an argon laser ЛГН-503 (wavelength of 476.5 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 (negative etching) to form a relief pattern. The removal of Cr layer using water solution of HCl through a chalcogenide mask was the next step. Thus, the obtained two-layer resistive mask $As_{40}S_{60}$-Cr was used to form a corresponding relief on Si 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 that is neutral to alkaline solutions.

After removal of the Cr 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 $\eta(\lambda)$ (λ is a wavelength) and angular $\eta(\varphi)$ (φ is an angle of beam incidence) dependences 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.

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. The angular dependence $\eta(\varphi)$ was measured using a helium-neon laser ЛГН-208(λ =632.8 nm) and goniometer Г5М. Both the spectral and angular dependences of η were measured for *s*- and *p*-polarized light *(E* is pendicular and parallel to grooves, respectively).

3. Results and discussion

When fabricating the lithographic mask, an optimization of exposure and time of photoresist etching plays an essential role. The dependence of the groove profile of the interferential structure on exposure for chalcogenide photoresists was investigated in details in [8]. When creating a resistive mask in interferential lithography the mode of small over-exposure is used, what corresponds to the cycloid shape of the grooves. By changing the time of selective etching, it is possible to change the width of strips of the interferential mask and, accordingly, opened intervals between the strips of photoresist. Etching *in situ* is controlled by registration of intensity of the non-photoactive beam diffracted from the formed relief structure, and after the etching – by AFM. In this work, the photoresist masks were formed with the ratio of the strip width to interval close to unity.

For the given photoresist mask, the shape of the groove profile obtained using the anisotropic etching of substrate will be determined by the time of etching and orientation of grooves. In our case, during exposition the Si (100) wafers were aligned by a base cut (a direction [110]) in parallel to grating grooves.

Fig. 1 shows the AFM image of a diffraction grating formed on the silicon (100) surface by the anisotropic etching through $As_{40}S_{60}$-Cr resistive mask (grating period is near 0.9 μm). Time of silicon etching was 60 s (sample 1). Thus, the depth of the relief reaches 0.62 μm, and the groove profile consists of a symmetrical triangular groove with 70.5º apex angle and a small flat top section. The significant depth of the relief modulation (≈ 0.7) and high-quality groove surface were observed.

Fig. 2 shows the spectral dependences of diffraction efficiency for a grating with the profile depicted in Fig. 1. Curves 1 and 2 correspond to *p*- and *s*-polarizations. As it is evident from the figure, the big depth of modulation and non-sinusoidal groove shape of the grating cause shift of the spectral range characterized by high (up to 80 %) η values to the longwave side of the spectrum.

One of the basic characteristics of the diffraction grating is a dependence of the diffraction efficiency on the angle of light incidence. Measurements were carried out for the polarized laser beam (λ = 632.8 nm) for both polarizations. Fig. 3 shows the dependence of $\eta(\varphi)$ for the sample 1. Results both for the first and second orders of diffraction were obtained. Due to the big depth of the grating modulation, values of the diffraction efficiency for the second order are essentially higher than those for the first order (for light of the corresponding polarization type).

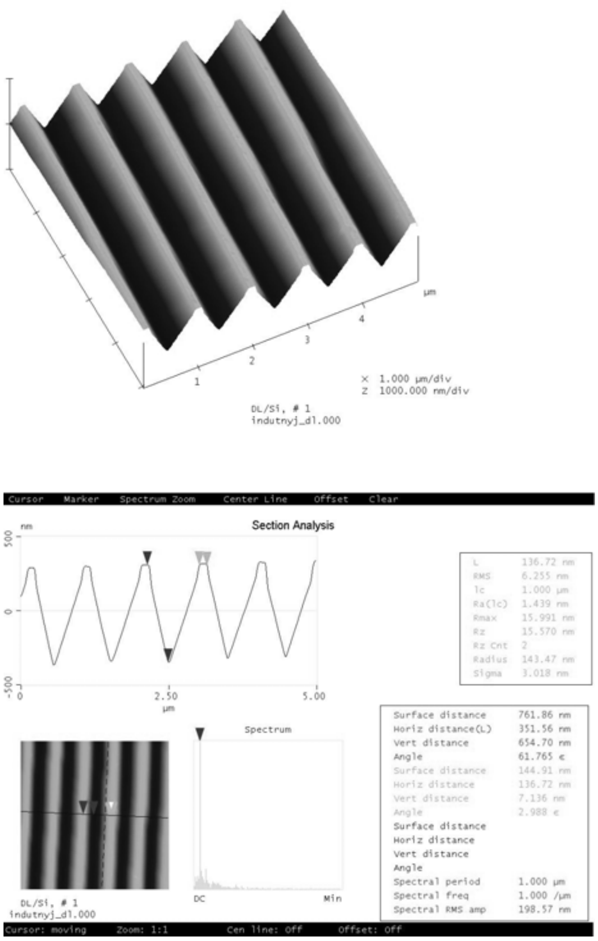

Fig. 1. Relief and groove profile of a grating obtained on Si (100) surface, time of the etching – 60 s (sample 1).

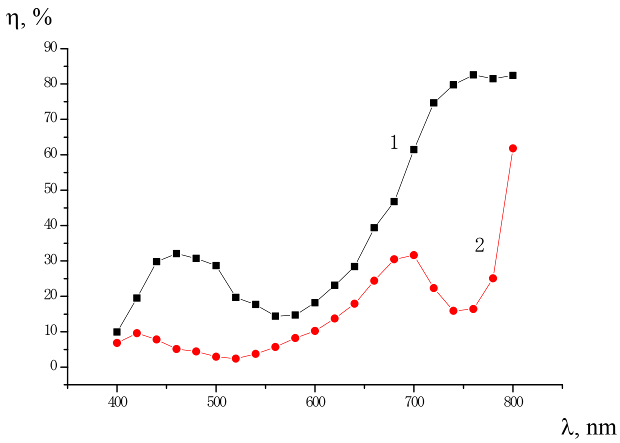

Fig. 2. Spectral dependence of the diffraction efficiency η for *p*- (1) and *s*-polarized (2) light (sample 1).

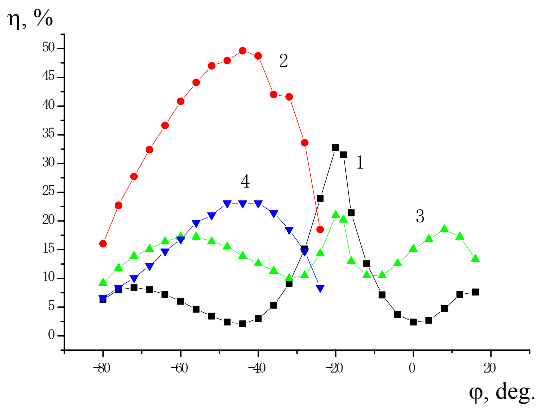

Fig. 3. Angular dependences of the diffraction efficiency for *p*- (1, 2) and *s*-polarized (3, 4) light (sample 1). 1, 3 stand for the first and 2, 4 for the second orders of diffraction.

When reducing the silicon etching time, the shape of grating profile changes accordingly. Fig. 4 shows the relief formed on Si (100) surface by 20 s anisotropic etching (sample 2) through the same mask. The relief depth here is about 0.3 μm, and the groove profile close to trapezium with the same apex angle as in Fig. 1. Since the period of structure remains unchanging (0.9 μm), the depth of modulation reaches approximately 0.33 in this case.

Fig. 5 shows the spectral dependence of the diffraction efficiency measured on the sample 2. In comparison with the previous sample, the much greater difference of η value for *p*- and *s*-polarized light in the longwave part of the spectrum was observed. Such change is connected, obviously, with the change of the groove profile.

Angular dependences of the diffraction efficiency for the sample 2 are plotted in Fig. 6. Here the high η values for *p*-polarized beam in the first order of diffraction and for *s*-polarized beam in the second one are observed, what essentially distinguishes this sample from the previous one.

The dependences of diffraction characteristics of gratings on the grating profile and depth of modulation were investigated by many authors [12-14]. In particular, in [14] the spectral dependences of diffraction efficiency of symmetric gratings with the different profile were studied. Authors concluded that changing the shape of grating groove it is possible to control the spectral position of the η peak and width of working interval (spectral range of the high diffraction efficiency). For triangular grooves, the greatest values of η were reached for the modulation depth close to 0.3 and for the wavelength that was some less than the grating period. In the work [12], considered were the diffraction efficiencies of trapezium-type grating with the fixed depth of modulation for the various apex angles. Comparison of the diffraction characteristics of the samples 1 and 2 with the similar characteristics of the modeling structures described in the cited works exhibits their qualitative agreement. In particular, the conclusion is confirmed that diminishing the modulation depth results, as a rule, in a shift of the working interval into a shortwave part of the spectrum.

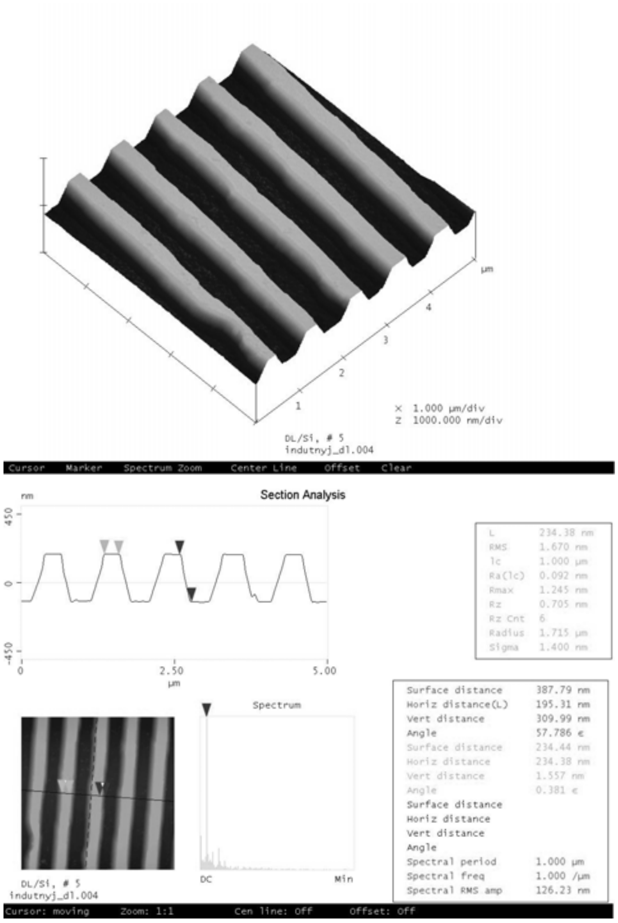

Fig. 4. AFM image and groove profile of a grating obtained on Si (100) surface, time of etching – 20 s (sample 2).

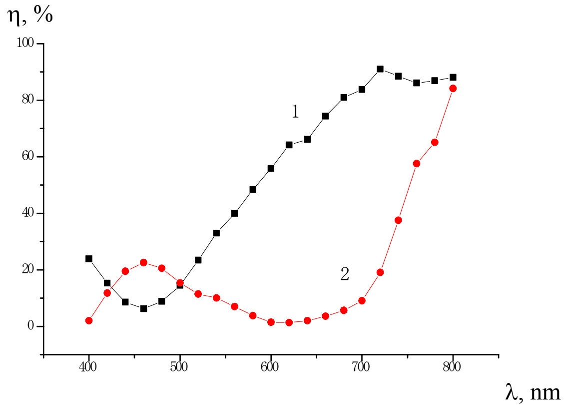

Fig. 5. Spectral dependence of the diffraction efficiency η for *p*- (1) and *s*-polarized (2) light (sample 2).

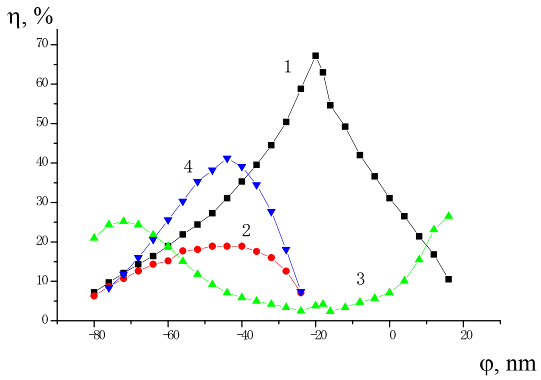

Fig. 6. Angular dependences of the diffraction efficiency of the sample 2 for *p*-(1, 2) and *s*-polarized (3, 4) light. 1, 3 are for the first and 2, 4 – for the second orders of diffraction.

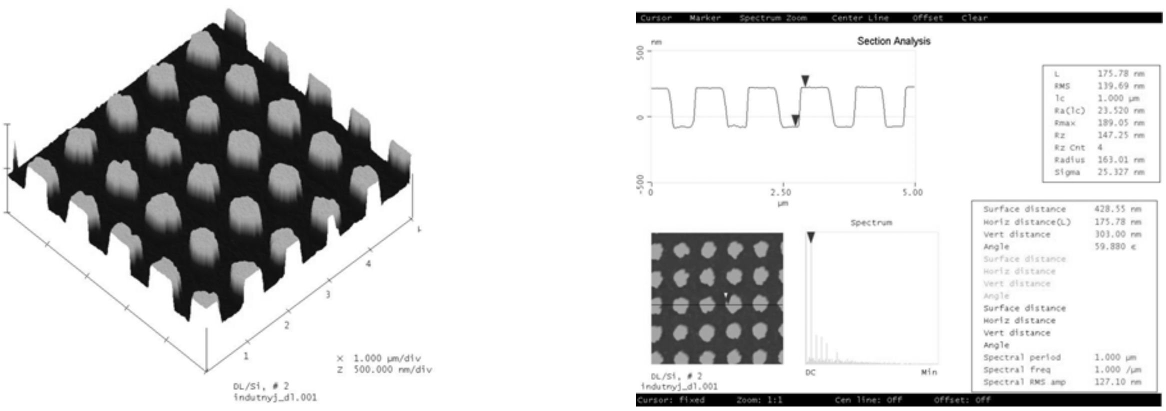

Fig. 7. AFM image and profile of bigrating obtained on Si (100) surface.

Thus, inexpensive technology of interferential lithography based on inorganic chalcogenide photoresist allows to form high-quality Si gratings with the diffraction efficiency close to the theoretical limit and necessary sizes. Such silicon gratings with symmetric triangular or trapezium grooves are used, in particular, in wavelength demultiplexers [3] and tunable lasers [4].

The two-dimentional periodic structure on Si (100) surface was formed using the double exposure by an interferential picture from two coherent beams, with the orientation of Si wafer for two exposures differed by 90º. The value of exposures and time of selective etching of chalcogenide photoresist were chosen so that the lithographic mask looked like periodically located islands of photoresist with the size 0.5 μm (the structure period in two mutually perpendicular directions makes 0.9 μm). The etching time of silicon was 20 s. Elements of obtained Si structure looked like hillocks about 0.5 μm in diameter and ~0.3 μm height (Fig. 7). The form of hillocks was close to cylindrical.

The obtained structures can be used to form bulk photonic structures if applying the modulated electrochemical etching [15] or glancing angle deposition in vacuum [6], or for growing of the ordered matrixes of silicon nanowires [16].

4. Conclusions

We have shown that the chalcogenide photoresists that is widely used for production of relief-phase hologram optical elements can be successfully applied in the interferential lithography to form the submicron relief structures on Si wafers by using the anisotropic etching. Using the $As_{40}S_{60}$-Cr resistive mask and anisotropic type alkaline etchant, we have fabricated the high-quality diffraction gratings on Si (100) surface with the symmetric triangular and trapezium grooves and diffraction efficiency up to 90 % for polarized light, as well as two-dimentional periodic structures with submicron size elements. It was shown that the simple and inexpensive interferential lithography with application of chalcogenide photoresists allows to form the submicron semiconductor relief structures of the significant sizes (in our case up to 75×75 mm).

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