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Interference lithography using chalcogenide inorganic photoresist

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There was investigated the application of inorganic photo-resist based on three-component chalcogenide films for fabrication of submicrometer periodic relief on silicon wafers using interference lithography. 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 diffraction gratings and two-dimensional periodic structures on Si (100) surface. The obtained relief patterns were used to form photonic structures by oblique deposition of silicon monoxide in vacuum.

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1. Introduction

Last decade interference (interferometric) lithography (IL) was widely used for the fabrication of one-dimensional nanostructures [1], production of the master mold for nano-imprinting 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. IL provides an inexpensive method for the fabrication of nano- and microscale periodic structures over large areas and is ideally suited to a large scale manufacturing environment. The technology is much cheaper and simpler than the electron beam lithography.

The characteristics of photoresist are important in IL technology. 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 As-S-Se glasses. Such chalcogenide photoresists are characterized by 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. Using chalcogenide resist the high-quality holographic gratings were obtained with spatial frequencies in the range of 600 to 6000 mm^{-1} and diffraction efficiencies up to 80 % in polarized light [7,8].

Recently the nano-structuring of chalcogenide glasses using electron-beam lithography has been revealed [11].

In this paper we report the results got during the investigation on application of three-component chalcogenide photoresist for fabrication of periodic relief structures on silicon wafers by using interference lithography and anisotropic etching.

2. Experimental

The samples for IL experiments were deposited sequentially onto polished (100) silicon substrates using the thermal vacuum evaporation of chromium and chalcogenide glass ($As_{40}S_{30}Se_{30}$) at the pressure $2\cdot10^{-3}$ 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 100-300 nm for the photo-resist one. The chalcogenide layers of the same thickness for measurements of photo-resist characteristics were deposited onto polished glass and silica substrates. After deposition, the thickness of the films was measured using a MII-4 micro-interferometer.

The prepared samples were exposed by interferential pattern that was generated by an argon laser (wavelength of 488 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 di-gratings each exposure can be 1.5-2 times reduced. The two-dimensional periodic structures on Si(100) surface was formed by the double exposure and orientation of Si wafer for two expositions differed on 90°. During first exposition Si (100) wafers were aligned by a base cut (a direction [110]) in parallel to interference grating lines. 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 $As_{40}S_{30}Se_{30}$-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.

The investigation of sensitometric characteristics of chalcogenide photoresist was carried out using the highly sensitive quartz resonator method.

The two-dimensional photonic SiO_x structures were produced by thermal evaporation of Cerac Inc. silicon monoxide (with 99.9% purity) in vacuum onto patterned Si surface (di-grating). To evaporate the silicon oxide we used a tantalum evaporator. During deposition, the substrates were oriented at the angle β= 75° between the normal to the substrate surface and the direction to the evaporator. The cross-sections of the obtained structures were investigated by electron microscope ZEISS EVO 50XVP.

3. Results and discussion

As a result of irradiating the chalcogenide layer by light with wavelengths corresponding to the inter-band absorption, many of their properties are changed, in particular, their optical characteristics (shift of absorption edge, changes of refractive index, induced dichroism), mechanical characteristics, solubility, etc. Most studied, however, are changes of their optical properties and solubility, because these changes serve as a basis for using chalcogenide as media for information recording and inorganic resist. The photoinduced changes in vacuum-deposited chalcogenide layers with two components: reversible and irreversible. In As-S-Se layers, deposited by using the thermal vacuum evaporation, irreversible changes are rather substantial and surpass the reversible component. The utilization of these layers as an inorganic resist or as a media for the recording of phase-relief holograms is connected to the irreversible solubility changes. The chalcogenides are well dissolved in many inorganic and organic solvents, such as alkaline and amine solutions. After exposure, the solubility rate of the films is changed, and depending on the film's composition and the type of solvent used, it is possible to obtain various degrees of selectivity defined by the solubility ratio of exposed and nonexposed film areas. In addition, for the different solvents and films, it is observed positive as well as negative etching i.e. the i.e. the exposed areas are dissolved either more rapidly or more slowly than the unexposed areas. In our investigations, the negative etching amine solutions were used.

The irreversible changes in chalcogenide photoresists are connected with the structural changes in evaporated layers. The structure of the evaporated As-S-Se films can be represented in the form of a matrix, which consists of pyramidal units $AsS(Se)_{3/2}$ and contains considerable amounts of As-As, S-S and Se-Se "wrong" bonds. In the evaporated films, pores and hollows are also present. Under illumination or annealing, polymerization of the molecular groups in the main glass matrix takes place, and, thus, the concentration of homopolar bonds and hollows are diminished.

The spectral light sensitivity distribution of chalcogenide layers is determined by the absorbed light energy and correlates with the layer's absorption spectra. The wide range of chalcogenide composition provides the wide range of light sensitivity spectra. This enables choosing the proper sensitivity on the chosen wavelength λ if necessary. For example, for argon laser, used in our investigations (λ = 488.0 nm), the optimum chalcogenide composition is $As_{40}S_{30}Se_{30}$.

Fig. 1 presents the dissolution kinetics of vacuum-deposited $As_{40}S_{30}Se_{30}$ layers. Initial thickness h_0 of the layers was 300 nm, curve 1 – unexposed sample, curve 2 – exposed by integral irradiation of mercury lamp DRCH-250, value of exposure H = 0.5 J/cm^2. The selectivity of etching for this value of exposure is equal 13.

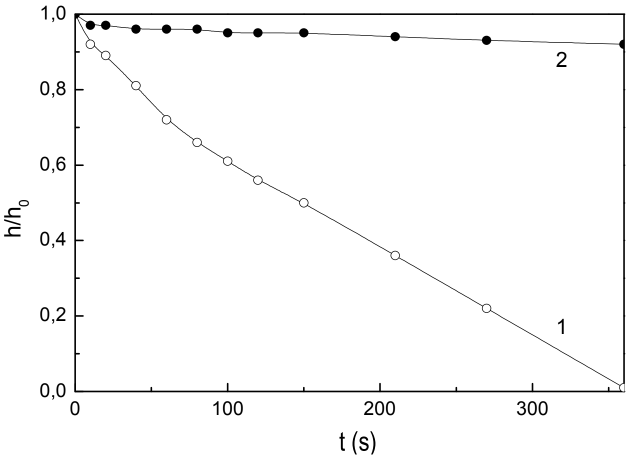

Fig.1. Dissolution kinetics of $As_{40}S_{30}Se_{30}$ layers. Curve 1 – unexposed layer, 2 – exposed by mercury lamp, H=0,5J/cm^2, h-thickness of the layer, h_0-initial thickness.

Fig. 2 shows the characteristic curve (h/h_0 dependence on H in logarithmic scale) for $As_{40}S_{30}Se_{30}$ layer exposed by monochromatic light (λ = 488 nm). It can be seen, that in exposure interval $0.15<H<1.05$ J/cm^2 the dependence of h/h_0 on lg(H) is close to linear. Using characteristic curve it is possible to determine the sensitivity characteristics of the resist for this wavelength – light sensitivity S and contrast γ. Here light sensitivity is defined as $S_{0.5} = 1/H_{0.5}$, were $H_{0.5}$ – exposure value, that corresponds to the level 0.5 on the characteristic curve. Contrast γ - tangent of an inclination of the linear part. For a wavelength of 488 nm γ and $S_{0.5}$ of $As_{40}S_{30}Se_{30}$ photoresist are 0.77 and 2.6 cm^2/J, accordingly.

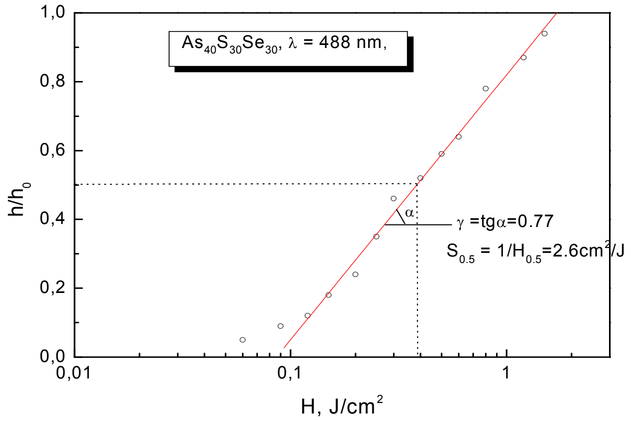

Fig. 2. Characteristic curve of $As_{40}S_{30}Se_{30}$ layer. H – exposure, wavelength of exposure: 488 nm, layer’s thickness: 300 nm.

Spectral dependence of $As_{40}S_{30}Se_{30}$ light-sensitivity well enough correlates with absorption spectrum of this film [9]. With the increase of wavelength light-sensitivity of the photoresist diminishes, however noticeable light-sensitivity is observed up to 600 nm wavelength.

When the lithographic mask is fabricated, an optimization of exposure and time of photoresist etching plays an essential role. The process of the groove profile of the interferential structure formation using chalcogenide photoresists was investigated in details in [7]. The groove profile forms can, in most cases, be approximated by a cycloid, and profiles close to the sinusoidal can also be obtained. It is possible to change the parameters of the cycloid by varying the recording and developing conditions. It was established that groove profiles depend not only on exposure and the thickness of the layer but also on the selectivity of etching solution and time of etching. Thus, to provide the necessary mask parameters, it is necessary to chose the optimal thickness of the initial sample, exposition, selectivity, and etching time. When creating a resistive mask in interference 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 photo-resist. 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.

For the given photo-resist 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.

Fig. 3 shows the AFM image of a diffraction grating formed on the silicon (100) surface by the anisotropic etching through $As_{40}S_{30}Se_{30}$-Cr resistive mask (grating period is near 1.0 μm). On this sample the photoresist mask was formed with the ratio of the strip width to interval width close to unity. The depth of the relief reaches 0.6 μm, and the groove profile consists of a symmetrical triangular groove with 70.5° apex angle and a small flat top section. The significant depth of the relief modulation (≈ 0.6) and high-quality groove surface were observed.

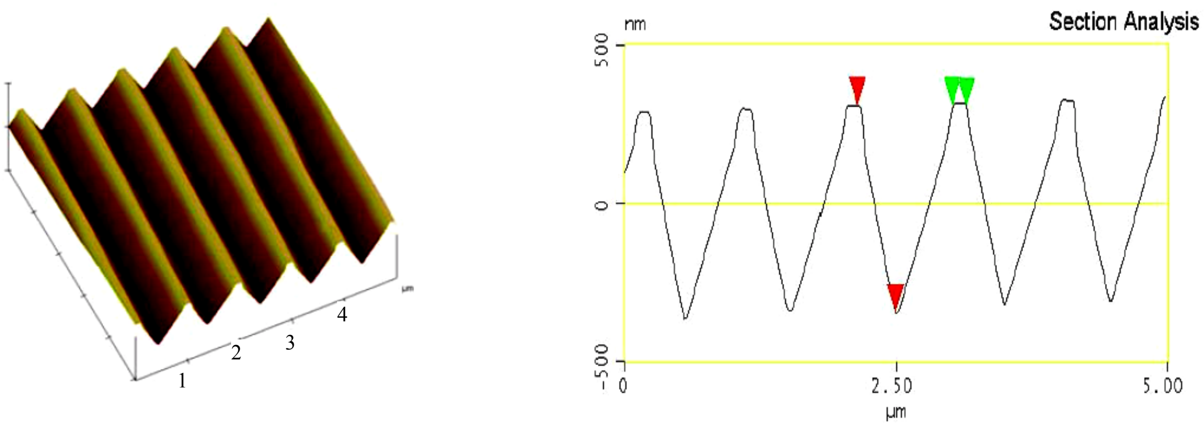

Fig. 3. Relief and groove profile of a grating obtained on Si (100) surface; time of silicon etching: 50 s.

The two-dimensional 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 (the structure period in two mutually perpendicular directions makes 1.25 µm). The size of photoresist islands depends on the value of exposure, and the form of islands depends on the ratio of exposures in two mutually perpendicular directions.

Elements of obtained Si structure looked like hillocks rhomb-shaped form in the section and height of these elements depends on etching time of silicon. Fig. 4 shows the di-grating structure that was formed using both exposure of 0.3 J/cm^2. Here photoresist islands were symmetrical and the ratio of the island diameter to interval width between islands close to unity. Time of silicon etching was 15 s. Depth of the obtained relief is 0.15 micrometers.

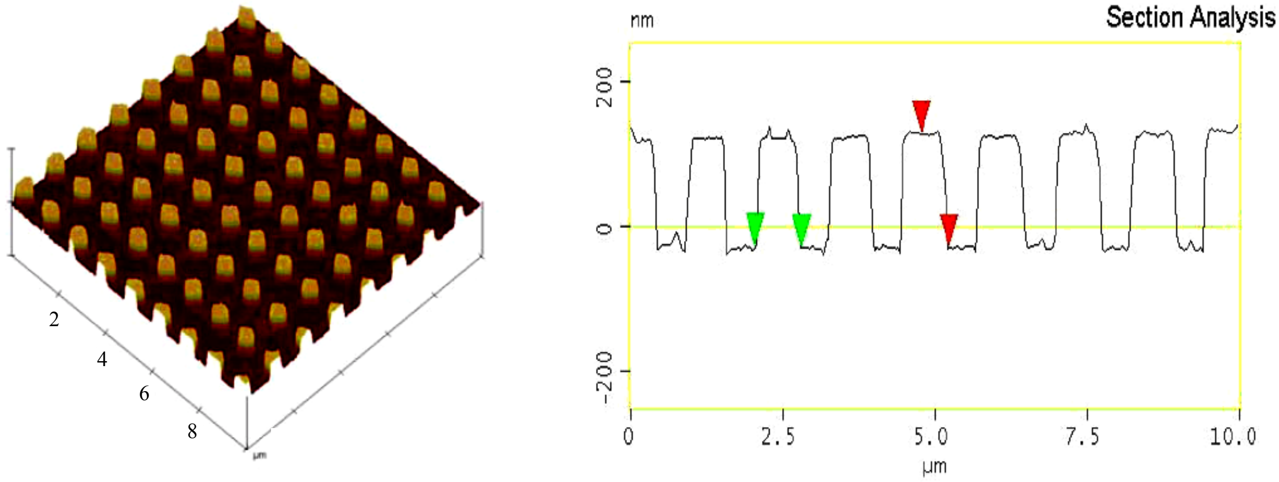

Fig. 4. AFM image and profile of bigrating with symmetrical elements obtained on Si (100) surface. Time of silicon etching – 15s.

Fig. 5 shows the structure that was formed using sequential double exposure of 0.3 and 0.5 J/cm^2. Here photo-resist islands were elongated and interval width between islands depends on direction. Duration of silicon etching was 25 s and depth of the relief was 0.3 microns.

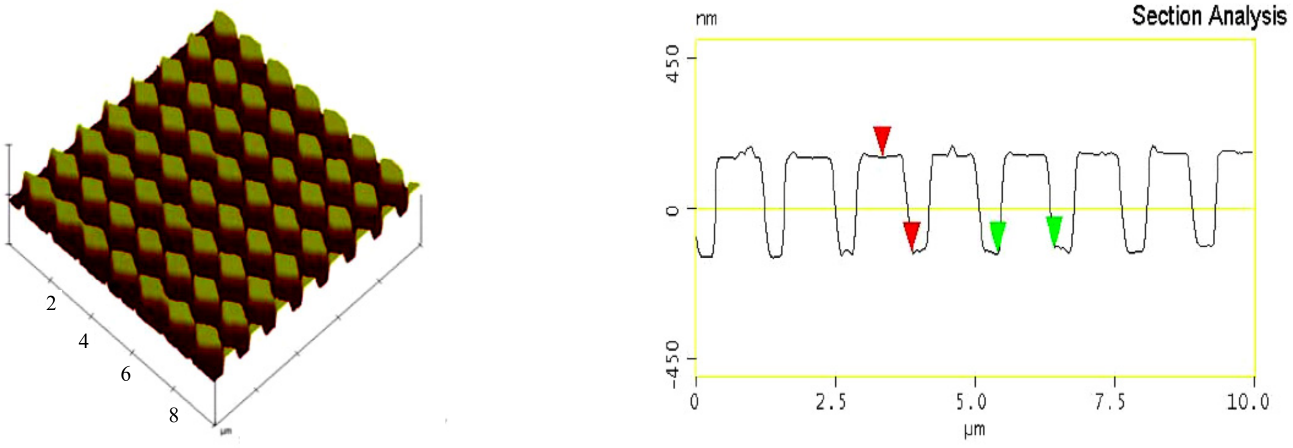

Fig. 5. AFM image and profile of bigrating with elongated rhomb-shaped elements obtained on Si (100) surface. Time of silicon etching – 25 s.

The obtained relief patterns can be used to form photonic structures if applying the modulated electrochemical etching [10], glancing angle deposition in vacuum [6], or for growing of the ordered matrices of silicon nano-wires [12]. It is known [13, 14], that during oblique deposition of Si monoxide, thermally evaporated in vacuum, SiO$_x$ films with a porous (nano-column-like) structure are formed, with the nano-column diameter depending on the deposition angle. Using the patterned Si substrate shown in Fig. 5 we obliquely deposited porous

SiO_x film (deposition angle β= 75°).

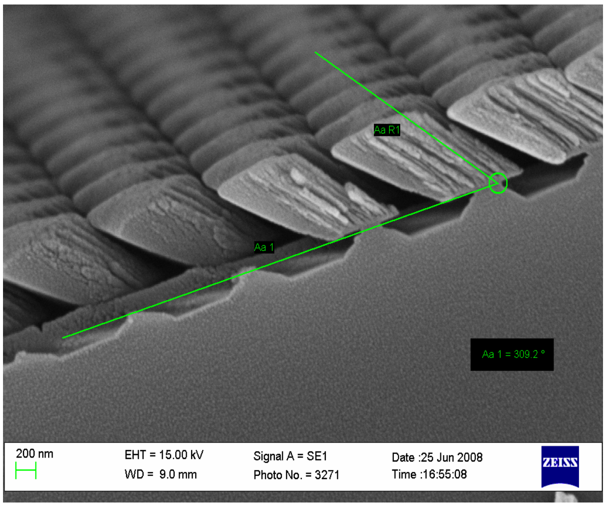

Fig. 6. Cross-sectional SEM micrographs showing porous SiO_x columns (nanorods) on patterned Si substrate.

Fig. 6 shows the cross-section of the prepared photonic structure. This two-dimensional structure is made of an ordered array of broadened up SiO_x columns which are grown on Si hillocks. The diameter of SiO_x column in its bottom coincides with the diameter of Si hillock. Each SiO_x column is inclined and have porous structure (the nano-column diameter 10–100 nm). The porosity of SiO_x column is near 58%, the composition is x = 1.51, and the density of SiO_x is 0.88 g/cm^3 [12]. The inclined columns have anisotropic optical properties, and such structures have potential application as photonic crystals, polarizing filters, etc.

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 interference lithography to form the submicron relief structures on Si wafers by using the anisotropic etching. Using the $As_{40}S_{30}Se_{30}$-Cr resistive mask and anisotropic alkaline etchant, we have fabricated the diffraction gratings and two-dimensional periodic structures with submicron size elements on Si (100) surface. The obtained relief patterns were used to form photonic structures by oblique deposition of silicon monoxide in vacuum.

It is shown, that simple and inexpensive interference lithography with use of the three-component chalcogenide photoresist allows forming the periodic semiconductor relief structures of the different frequency, significant sizes and various applications.

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