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Ion treatment in technology of diffraction optical elements *

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Problems of ions treatment in diffraction optical elements (DOE) technology with ion beam and refractive ion beam systems are discussed. Etching is carried out with a particular screening of the ion beam on contact protecting masks, which are films of organic (light sensitivity composition on the novolac basis) and inorganic (vacuum deposited films of Al, ZnS, Nd_2O_3, AS-3) materials. Microstructure parameters and optical-technical characteristics of DOE produced on the surface of optical glasses (binary synthesized holograms, phase filters, phase modulating elements of kinoform type of high efficiency) are reported.

1. Introduction

Diffraction optics was tempestously developed during last years. A new method of wavefront formation due to diffraction of light passed through a thin phase plate becomes the basis in this field. DOEs constitute the basic elements of the new optics. DOE is a phase element of variable optical thickness which is formed by using materials of either graded refractive index or by producing a microrelief on their surface or in a thin layer.

The application of the diffraction structures for image formation and transformation of light beam was started with Fresnel and Wood zone plates. The last ones were made first in 1898. Fundamental development of diffraction optics was initiated by theoretical research of Soviet scientists (Slyusarev and Tudorovsky). In 1957, Slyusarev proposed modified zone plates for correction of secondary spectrum in objective system [1]. At the same time Tudorovsky proposed special multistep phase filter which allowed us to remove secondary spectra for achromatic objective [2]. But the systems proposed by Slyusarev and Tudorovsky were not realized for technological reasons in fifteeth and sixteeth. The next step in diffraction optics development was stimulated by creation of coherent light sources and holography. Gabor [3] produced holographic amplitude and phase lenses allowing concentration of up to 34% of the light in the first order. At the present time, possibilities of holographic optical elements have been considerably extended thanks to computer generated holograms which allow us to create any required wavefronts including

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the ones of not existing objects. The research in the field of computer-generated holograms resulted in creating of new optical structure-kinoform [4].

As one of new methods for wavefront formation, DOE may be applied to obtain standards of wavefront of complex shape, to create aberration-free optical systems, to perform specified wavefront transformation, to control the quality of optical surfaces for aspherical mirrors and lenses, and to focus the irradiation into certain space point. DOE allows us to develop complex optical systems of small size and weight. In this case, elements made of unstable materials of reversed dispersion are excluded [5]. It is interesting to use DOE in systems with laser sources [6]. Analysis of DOE possibilities, manufacturing and application is reported in [7]–[11].

The basic feature of DOE is a microrelief on the surface of optical material or in a thin layer. Among the existing methods of microrelief formation – mechanical [12], optical [13], holographic [14], photolithographic [15] – the ion technology is the most universal and prospective one [16]. The tool in this technology is the ion beam. Ion beams are easily controllable in a wide range during treatment and allow us to process the surfaces of any shape and size with high regularity under automatic control. Ion technology is a process of high purity. Ion beam is particularly screened during bombardment by contact protecting masks of certain profile and topology. The mask structure is formed by one of the following methods: photolithography, holography, electronography or grooving method.

Ion technology guarantees obtaining microstructures of high resolution; it saves microstructure topology and allows us to control the microstructure profile during the formation process.

The main steps of DOE manufacturing are: deposition of protecting layer on samples, formation of mask structure, ion treatment. The last step removes the mask structure from the working surface of the optical element.

The present paper is devoted only to problems of ion treatment with ion beam and reactive ion beam etching systems used in DOE technology.

2. Experimental cases

Organic mask-photoresists were deposited onto optical working elements by using the centrifuge method. The mask structure was formed in a standard manner with the help of UV-irradiation or holography followed by development in special solvents. Widely used positive photoresists on the basis of novolac resine with different light sensitive additions were employed.

Inorganic mask films were deposited by electron beam in vacuum. The structure of inorganic masks was formed by photolithography with wet chemical etching. The thickness of the mask layers was determined by an interferometric method.

Ion and reactive ion etching of working samples were performed in vacuum chamber equipped with cold cathode autonomic ion source. IR-, UV-optical spectroscopy were used for investigation of structure changes due to temperature treatment in photoresist films (SF-16, USSR, SPECORD-75, Germany). XPS with depth profiling (PHI 5400 Perkin–Elmer) was applied to study the inorganic

masks after ion beam treatment. Surface topology and profile structure of DOE were controlled by electron microscope (EM-14, USSR) observations.

3. Organic masks in DOE technology

The main problem for the examined materials is connected with increasing ion resistance under inert or chemically active particle beam. The ion resistance includes both low etching rate and ability of mask to preserve both the initial surface morphology and the mask adhesion to the support. These properties determine the main power quality and the optical-technical characteristics of DOE.

In the present work, the task of ion resistance increasing was solved by preliminary thermal treatment of the formed relief masks. Widely used convective thermal treatment of photoresists in the air allows us to reduce the etching rate by several times. But in this case, it is impossible to achieve uniform drying of maks, while the significant heating of the element under ion treatment produces local defects in mask layer, adhesion losses and consequently poor quality of DOE. To avoid this effect, it is necessary to cool the working elements under ion bombardment to the temperature not higher than 100 – 150 °C. From this point of view, the drying of the mask "layer by layer" starting from the support is a more effective process. It is possible to create an optimal heat field in photoresist mask with controlled IR-radiation. In the present work, the vacuum thermotreatment of the formed photoresist mask by near IR-irradiation was used. Optimal temperature-time conditions are individual for each type of photoresist. The efficiency of chemical structure changes in the mask layer resulting in an increase of the ion resistance is checked by optical spectroscopy: complete decomposition of additions responsible for light sensitivity and formation of bonds between molecules in polymer component. As an exemple, a positive photoresist produced on the basis of novolac resine and anphtohinondiazide (NHD) derivative, is discussed as a light-sensitive component. Figures **1a** and **b** show the UV- and IR-spectra of the initial photoresist.

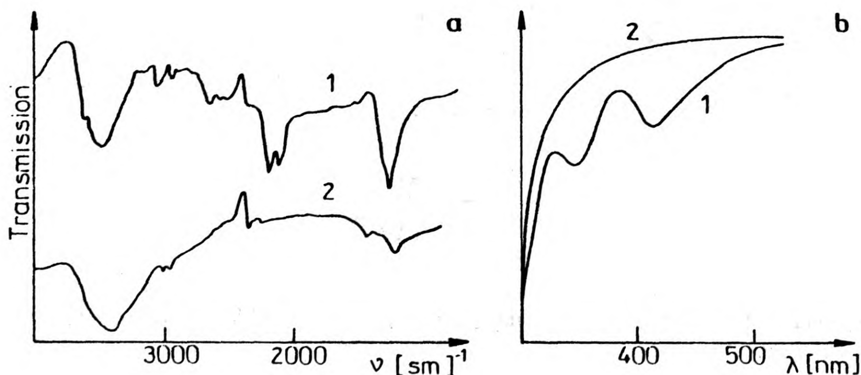

Fig. 1. UV- (a) and IR-spectra (b) of photoresist (curve 1 – initial, curve 2 – treated by IR-irradiation in vacuum)

Characteristic bands of NHD derivative in UV-field lay at 350 nm and between 400 and 420 nm, while in IR-field – at 2139 cm^{-1}. The disappearance of those bands in spectra of thermostated samples means that the light sensitivity addition has been decomposed. Expansion of the band near 3200–3600 cm^{-1} region in the IR-spectra corresponds to formation of new bonds between polymer chains. IR vacuum treatment allows us to reduce etching rate by 3–4 times in either inert or fluorine gases and to produce good masks on the surface of optical materials during DOE manufacturing.

4. Inorganic mask materials

Protective masks from inorganic materials in DOE technology allow us both to intensify significantly the ion treatment process and to reduce the damages due to sample cooling and pressure of residual gases in the vacuum chamber.

The choice of inorganic materials for masks under usual etching in inert gases is mainly determined by material sputtering coefficient. The usage of the materials which reduce their etching rate under some oxygen addition increases the protection efficiency. This films of Al provide an example.

XPS study of Al films before and after interaction with Ar ion beam clears up the chemical structure changes in those films and their influence on etching rate. Initial film 0.7–0.75 μm thick contains 50–60% of oxide in the 20 Å surface layer and 10% of oxide in the film volume. After Ar ion treatment with 1–2% residual oxygen content, the significant amount of Al_2O_3 was found on the surface and in the film volume, the penetrating depth being increased with the increase of the ion treatment time and is greater by several times than the average penetration depth of the bombarding ions.

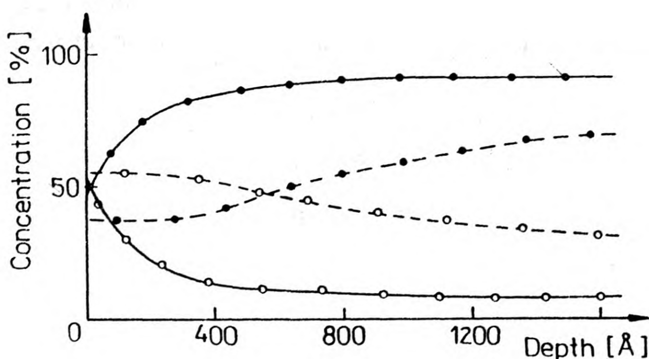

Fig. 2. Al (•) and O (○) XPS depth profiles (—— initial Al film, – – – Al film treated during 10 min with ion beam (Ar+1% O))

In Figure 2, the concentration of oxygen and Al vs. depth profile is demonstrated. The results obtained allow us to suppose that the ion bombardment activates the

the surface of the film and provokes not only the oxide formation due to residual oxygen, but also the ion-stimulated oxide diffusion into the film. The formation on the Al surface of the significant amount of oxide having low sputtering coefficient results in significant reduction of the etching rate for Al mask layer. This has been confirmed by experimental data. Al film etching rate is reduced by three times after 10 min treatment. The similar effect was demonstrated in the case of thermal oxidation of the vacuum deposited layers of arsenic sulphide when kept in the air. The etching rate of this mask is reduced by ten times being equal to 2–3 μm per hour [17].

An effective inorganic mask for reactive ion etching could be obtained by employing the materials which form stable and non-voltaic compounds in reaction of surface atoms with chemical active plasma particles. This was the reason why we have examined by vacuum deposited Al, ZnS and Nd_2O_3 films. XPS study of those films shows that their etching in fluorine containing gases results in the formation of a changed surface layer, 50% of metal atoms being bonded with F, another 50% either being preserved in the initial state or having reacted with oxygen (if added in vacuum chamber). Fluorine depth penetration does not exceed 20–25 nm. The formation of non-volatile fluorides allows us to use the Al, ZnS and Nd_2O_3 films as mask materials of high efficiency in fluorine containing gases for optical glasses.

Our results concerning the ion resistance of organic and inorganic materials allowed us to use them as protecting masks in technology of DOE of resolution less than 1000 lines per mm, such as: binary computer-generated holograms, phase filters, kinoforms, etc. With the help of one step masking and ion treatment, the binary holograms for controlling the aspherical surfaces were manufactured. Such holograms are of binary circumferential structures of variable period. The produced elements are of the following parameters: working wavelength 630 nm, element diameters 13–100 mm, ring zone number up to 10000, zone width 3–500 μm, depth of structure 0.4–1.3 μm.

By applying the many-step masking and ion treatment multilevel kinoform correctors for optical TV, photography and microscope objectives were manufactured. The DOE parameters are the following: number of levels 4–12, element diameters 13–180 mm, working wavelength 480–950 nm. Optical technical testing showed that the diffraction efficiency of those kinoform correctors is very close to the theoretical one and reaches 90% for 6 level, and 93% for 8 level phase structures [11], [18].

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