Holographic optical element fabrication using chalcogenide layers

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Abstract. Investigations in the field of diffractive optical element (DOE) fabrication using optical methods and registering media based on chalcogenide vitreous semiconductors are reviewed. The peculiarities of the holographic diffraction grating (HDG) fabrication processes using such resists are investigated and the factors that influence the groove profiles are determined. Ways of optimizing media parameters, exposure, and treatment processes are shown. High-quality HDGs are obtained with spatial frequencies in the range 600 to 3600 mm^{-1}, diffraction efficiencies of 80 to 85% in polarized light, and a stray light level of 10^{-6}. The processes of Fresnel lense formation by the holographic method with the consequent diffraction pattern transfer into the substrate are developed and investigated. This provides an opportunity to obtain binary lenses with high numerical apertures and small sizes. The results of investigations of the fabrication processes of DOEs with blazed profiles are discussed. Most promising is the method of direct DOE recording using a sharply focused laser beam, which enables one to obtain kinoform elements with micrometer-sized distant zones. Additional treatment methods (wet or dry) enable one to obtain blazed gratings using the initial HDG with a symmetrical profile fabricated on the base of the chalcogenide layers.

Subject terms: diffractive optical elements; diffraction gratings; Fresnel lenses; asymmetrical profile; registering media; chalcogenide layers.

Optical Engineering 34(4), 1030–1039 (April 1995).

1 Introduction

Diffractive optical elements manufactured by the holographic method have recently found wide utilization and their areas of utilization are constantly widening. Diffractive optical elements (DOEs) are widely used as important parts of various optical and integrated optics devices in various applications: spectroscopy, laser beam shaping, waveguide input-output elements, spatial filtering, optical disk systems, etc.[1–4] The simplest among them, holographic diffraction gratings (HDGs), occupy a stable place in the optical industry. The HDGs have several advantages over ruled gratings, including a low level of stray light; the absence of ghosts; and low production cost, which has stimulated their wide utilization in various spectral devices. Among the currently developed DOEs, substantial interest is attracted by the Fresnel lenses, the analogs of common refractive lenses. Their main advantages, which have led to the growing interest in them among optical device developers, are compactness, low weight, compatibility with planar technology, and the possibility for the effective control of optical parameters and aberration correction.

Recently, vacuum-evaporated inorganic resists based on chalcogenide vitreous semiconductors (ChVS) have shown to be good registering media for DOE fabrication.[4–9] Such media are characterized by high resolution,[10–12] good optical uniformity, and acceptable sensitivity in a wide spectral region. The produced relief can be positive or negative, depending on the nature of selected etchant, the resist utilized, and relief formation method. Among the wide range of photoinduced phenomena exhibited by ChVS, the most frequently used for imaging applications are the photodoping effect[5–8] and the photoinduced ChVS layer solubility changes.[4,6–9] Both effects lead to substantial changes in ChVS layer solubility rates, which makes the production of various relief images possible. These qualities enable such resists to satisfy rather rigid demands (high-resolution capability, sensitivity to the irradiation of available lasers, absence of shrinkage under postexposure treatment), which are applied to the

Paper UKR-06 received Aug. 1, 1994; revised manuscript received Sep. 10, 1994; accepted for publication Sep. 10, 1994. This paper is a revision of a paper presented at the SPIE International Conference on Holography, Correlation Optics, and Recording Materials, May 1993, Chernovsty, Ukraine. The paper presented there appears (unrefereed) in SPIE Proceedings Vol. 2108.

light-sensitive media in which the interference pattern being recorded is directly registered. It is well known that the fabrication of the DOE blazed profile significantly improves the DOE performance efficiency and enables control of the spectral region of maximal light concentration in diffraction gratings. Complex recording schemes or additional treatment after exposure are required for the fabrication of the blazed gratings or analogs of kinoform lenses with blazed zones. This problem currently attracts the attention of many investigators.

In this paper, we report on the results of investigations of DOE fabrication processes using ChVS layers and ChVS-Ag structures performed at the Institute of Semiconductor Physics from 1986 to 1993. Using flat symmetrical gratings as examples, the peculiarities of grating groove formation are considered and the grating characteristics are obtained. We also show the possibility of forming DOEs with asymmetrical profiles for integrated and diffractive optics using direct recording (with a sawtoothlike exposure) or additional relief treatment using such inorganic resists.

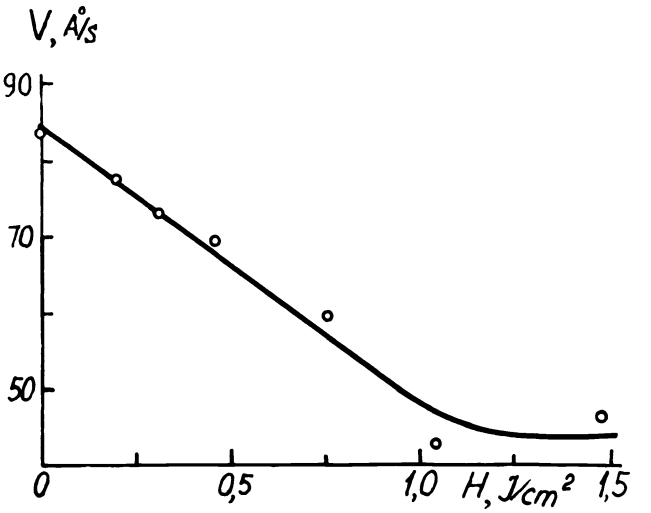


Fig. 1 Dependence of solubility rate V (in amine-based etching solution) of vacuum deposited As_2Se_3 layers from the exposure H for $\lambda = 632.8$ nm.

2 Registering Media and Their Properties

The first images on thin, vacuum-evaporated As_2S_3 layers were obtained[13] as early as 1965. The numerous investigations of photostimulated processes in ChVS layers that followed made it possible to obtain the main characteristics of photostimulated transformations in such layers and to establish their mechanisms.[14] As a result of irradiating the ChVS layer by light with wavelengths corresponding to the interband 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 ChVS as media for information recording and inorganic resist, because these represent the most practical interest.

The photoinduced changes in ChVS layers have two components: reversive and nonreversive. In binary ChVS layers, nonreversive changes are rather substantial and surpass the reversive component. The utilization of ChVS layers as an inorganic resist or as a media for the recording of phase-relief holograms is connected to the nonreversible solubility changes. The ChVS 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; that is, the solubility ratio of exposed and nonexposed ChVS areas. In addition, for the different solvents and films, it is observed in positive as well as negative etching that the exposed areas are dissolved either more rapidly or more slowly than the nonexposed areas.[15] In our investigations, the negative etching solutions were used more often. From our point of view, they are more suitable for the creation of gratings and other DOEs with high-quality relief. Figure 1 presents the typical dependence of solubility rate V of vacuum-deposited As_2Se_3 layers on the exposure H for $\lambda = 632.8$ nm in an amine-based solution. Nonreversible changes in ChVS layers are connected with the structural changes in evaporated layers. For example, the structure of the evaporated As_2S_3 film can be represented in the form of a matrix, which consists of pyramidal units $AsS_{3/2}$ and containing considerable amounts of As_4S_4 and S_2 fragments, that is, As-As and S-S ''wrong'' bonds. In the evaporated films, pores and hollownesses are also present. Under illumination or annealing, polimerization of the molecular groups in the main glass matrix takes place, thus the number of homopolar bonds and hollownesses are diminished.

The light sensitivity of thin-film ChVS-Ag structures is determined by the photostimulated diffusion of metal into the semiconductor.[16,17] During and as a result of the exposure process of such structures in the exposure sites Ag penetrates into the ChVS layer, forming the intermediate doped layer. The properties of such a layer are essentially different from those of the initial ChVS. In particular, photodoped ChVS is highly resistive in relation to alkaline etchants, which rather easily dissolve nondoped ChVS. This makes it possible to obtain relief images depicting the intensity distribution of actinic irradiation.

The spectral light sensitivity distribution of ChVS layers is determined by the absorbed light energy and correlates with the layer's absorption spectra. The wide range of ChVS composition provided and the wide range of light sensitivity spectra, enables choosing the proper sensitivity on the given wavelength λ if necessary. For example, for the As_2Se_3 layers that were among those used in our investigations, the light sensitivity range covers all visible parts of the spectrum, which enables the use of argon ($\lambda = 488.0$ and 514 nm) and helium-neon ($\lambda = 632.8$ nm) lasers. The light sensitivity spectra of ChVS-Ag structures are somewhat extended to the red side of the spectrum in comparison to the light sensitivity of corresponding ChVS layers.

The essential peculiarity of registering media based on ChVS is their extremely high resolution capability. The minimal linewidth achieved on such media using a sharp focused laser[18,19] beam was 0.2 μm, and using electron beam lithography[20] was 30 nm. The angstroms resolution limit was shown in Refs. 10 to 12.

The ChVS-Ag structures provide high enough etching selectivity for not only the liquid treatment but also for plasmochemical treatment.[11]

3 Holographic Diffraction Gratings

3.1 *Experiment*

The HDGs were recorded on ChVS-Ag structures as well as on ChVS layers. The layers were deposited on high-quality polished glass substrates using thermal vacuum evaporation. To provide the necessary adhesion to the glass substrates and to eliminate the interference effects connected with reflectance from the substrate's back surface, a chromium layer (30 to 80 nm) was deposited on the glass prior to the deposition of other layers. The thicknesses of ChVS and metal (Ag) layers are determined by the gratings characteristics (the question of the optimal thickness choice for such structures is considered later). The prepared samples were exposed using the holographic setup assembled by the wave-amplitude division method. The optical scheme provides the formation of the necessary interference pattern (created by two coherent beams with flat fronts). By means of changing the convergence angle of the beams, it was possible in a sufficiently wide range (600 to 3600 mm^{-1}) to change the grating spatial frequency. The recording setting is described in Refs. 5 and 9. After exposure, the samples were chemically treated in alkaline solutions and, as a result, the periodic relief was obtained, corresponding to the recorded interference pattern. The next step is the deposition of the reflective-protecting coating (Al, Ag, MgF_2, etc.) on the obtained gratings. Figure 2 shows the schemes for holographic diffraction fabrication based on ChVS-Ag systems [Fig. 2(A)] and ChVS layers [Fig. 2(B)]. In the figures, for both registering media, (a) is the initial sample, (b) is the exposure, (c) is after chemical treatment, (d) is the reflective-protective coating deposition, 1 is the glass substrate and 2 is the chromium layer. In Fig. 2(A), 3 is the Ag layer, 4 is the barrier layer, 5 is the ChVS layer, 6 is the photodoped layer, and 7 is the Al coating. In Fig. 2(B), 3 is the ChVS layer, 4 is the exposed ChVS, and 5 is the Al coating.

The samples for the scanning electron microscopy (SEM) investigations of the groove profiles, their growth kinetics, etc., were prepared by scoring the gratings on the back, perpendicular to the grooves, whereafter the gratings were cracked. To avoid the relief plastic deformation, the specimens were immersed in liquid nitrogen before cracking. The cross sections were covered with the thin-film (20- to 50-nm) layers of Au or Al. It was considered that these additional layers did not substantially change the grating reliefs. The investigations were carried out using a JSM-35 electron microscope.

The diffraction efficiency η measurements were usually carried out in the setup close to the Littrov scheme and the angle between incident and diffracted beams was about 7 to 8 deg. The grating diffraction efficiency was taken (except for separately described cases) as the ratio of intensity of light diffracted into the first order to the intensity of incident light.

3.2 *Results Obtained and Peculiarities of HDG Recording on ChVS-Ag Systems*

During the exposure process of the ChVS-Ag systems, the initial components are consumed and the thickness of inter-

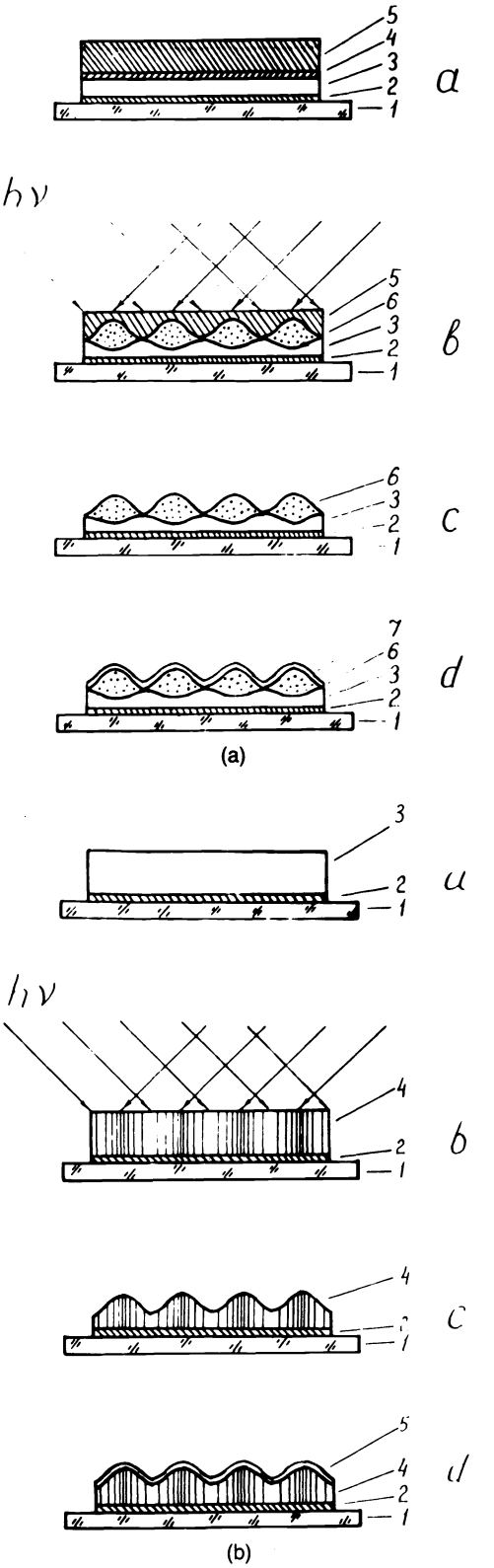


Fig. 2 Schemes of holographic diffraction gratings fabrication on the base of (A) ChVS-Ag systems and (B) ChVs layers. For both registering media: a = initial sample, b = exposure, c = after chemical treatment, and d = reflective-protective coating deposition; 1. glass substrate, 2. chromium layer; for Fig. 2(A), 3. Ag layer, 4. barrier layer, 5. ChVS layer, 6. photodoped layer, and 7. Al coating; for Fig. 2(B), 3. ChVS layer, 4. exposed ChVS, and 5. Al coating.

mediate photodoped layer h increases, the kinetic curve $h(H)$ (the h dependence from exposition $H=It$, where I is irradiation intensity and t is time) has an S-like type, that is, it is characteristic for solid state reactions. The relief depths of gratings recorded on such structures and their groove profiles are determined by the thickness distribution of the photodoped layer. The maximal achievable relief depth is equal to the initial ChVS thickness, if the possible negligible swelling of the ChVS layer under the Ag introduction is not taken into account.

The light intensity distribution on the sample surface under grating recording in the direction perpendicular to the grooves can be described by

$$I=I_0/2[1+\cos(2\pi x/d)] \ , \qquad (1)$$

where I_0 is maximum intensity and d is the interference pattern period, which determines the grating period. The insertion of this expression in the $h=h(It)$ dependence for $t=$ const. gives the cross section of the grating groove profile (note again here that the products of photodoping are almost unsoluble in many utilized alkaline etching solutions). Thus, the grating groove profile in this case is determined by the kinetic curve and the exposure time. To a certain degree, the photodoping kinetics can be changed either by introducing an additional barrier layer or by uniform preexposure. Correspondingly, the grating groove profile will change. A detailed analysis of all these factors and the numerical modeling of the HDG fabrication processes on ChVS-Ag structures is performed in Refs. 5, 21, and 22. With a good approximation, groove profiles can be described by cycloidal dependence, but for the high-frequency grating the grating profile is close to sinusoidal. For example, such was the case during recording of gratings with 3600 mm^{-1} spatial frequency on an As_2Se_3-As_2S_3-Ag structure,[5] where a thin As_2S_3 layer was deposited to prevent or substantially slow the darkness diffusion of Ag into As_2Se_3. The profiles of the gratings obtained were well described by a sinusoid. The gratings with the lower spatial frequencies have profiles that are well described by the cycloidal dependencies, with flat peaks if overexposed. By changing the groove profiles (for a given spatial frequency), it is possible, to a certain degree, to change the spectral distribution of the diffraction efficiency η, correspondingly to the conditions of the gratings used.

The necessary condition to obtain high-quality gratings is the optimization of the initial structure layer thicknesses, exposure, and etching conditions. The ChVS layer thickness must be large enough to provide the necessary modulation depth ($h/d\sim0.3$, where h is groove depth and d is grating period), which provides high diffraction efficiency. However, substantially increasing the ChVS layer thickness over the $h=0.3d$, in addition to unproductive material expenditure, lowers light sensitivity because of screening of the active photodoping areas by the ChVS layer and worsens the relief quality. Taking this into account demands that the ChVS layer thicknesses under grating recording are usually chosen slightly larger than $0.3d$. The Ag layer must be thick enough to provide for the formation of the necessary relief depth. An Ag surplus, however, leads to worsening the grating surface quality because of increased stray light intensity. The optimal correlation between metal and ChVS thicknesses needed for the production of high-quality gratings are determined ex-

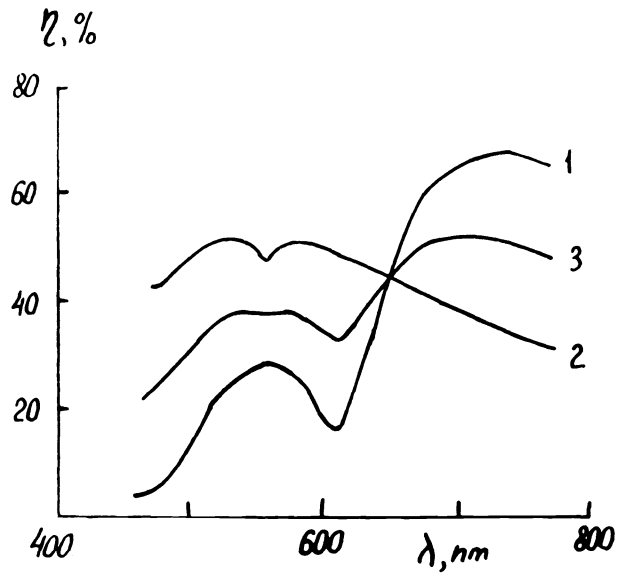


Fig. 3 The spectral dependence of the diffraction efficiency η for the gratings obtained on the base of the As_2S_3-Ag system with the help of dry etching (spatial frequency 1350 mm^{-1}; 1, S-polarization; 2, P-polarization; and 3, nonpolarized light).

perimentally. For example, for a light sensitive As_2Se_3-As_2S_3-Ag structure, this ratio was[5] in the limits 0.05 to 0.1.

The optimal exposure value, or irradiation time, under constant intensity is as a rule chosen experimentally. For the concrete parameters of registering media and wavelength, the dependence of diffraction efficiency η on exposure H is investigated. Such dependencies have the form of curves with maxima. The η maxima are achieved under such exposure values, which correspond to saturation, resulting from the creation of product layers through the whole depth of the ChVS in sites corresponding to the maxima of interference pattern. Postexposure structure treatments include removal of the undoped ChVS by selective etching in solutions of inorganic or organic (various amines) alkaline. After that, a reflective coating (usually Al) is deposited.

Optimization of the recording processes and postexposure treatment enables obtaining high-quality gratings in a wide interval of spatial frequencies (1200 to 3600 mm^{-1}) on ChVS-Ag structures. The diffraction efficiency values in polarized light reach 80 to 85% and in nonpolarized light, 50 to 60% (Refs. 5 and 22). These results were obtained mainly in the As_2Se_3-Ag, As_2S_3-Ag, $GeSe_2$-Ag systems.

It is known that doped and undoped regions of ChVS layers drastically differ in etching rates (>100) of dry etching in different plasmas.[11] We investigated HDG production processes using dry etching in CF_4, and SF_6 using ChVS-Ag systems (mainly As_2S_3-Ag and Ag-As_2S_3, which differ in order of layer deposition).[7] With CF_4 and SF_6 plasmas undoped chalcogenide is etched quickly (i.e., a negative resist), whereas regions doped with silver have high resistance. The diffraction efficiency η for nonpolarized light in the maximum of spectral dependence reaches 50%, as can be seen from Fig. 3. The values of η for such gratings were near the values obtained using amine-based solutions. Note here that conditions of the ChVS-Ag system dry development are not

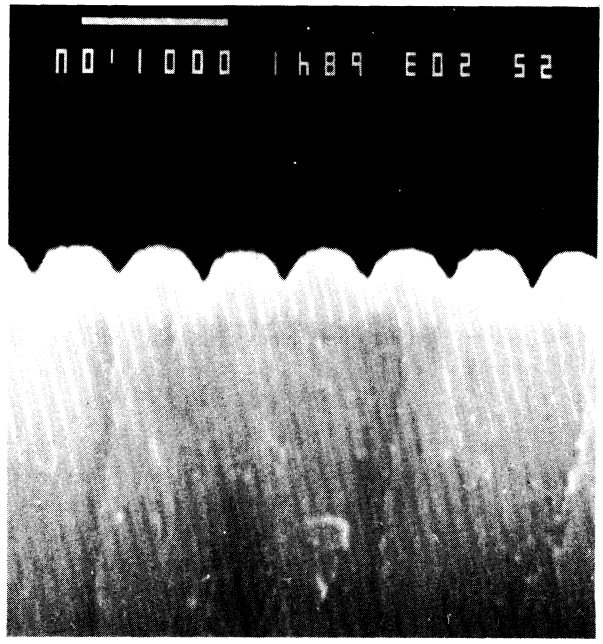
sufficiently optimized, in particular in terms of the quality of the relief obtained.

3.3 *HDG Recording on the ChVS Layers*

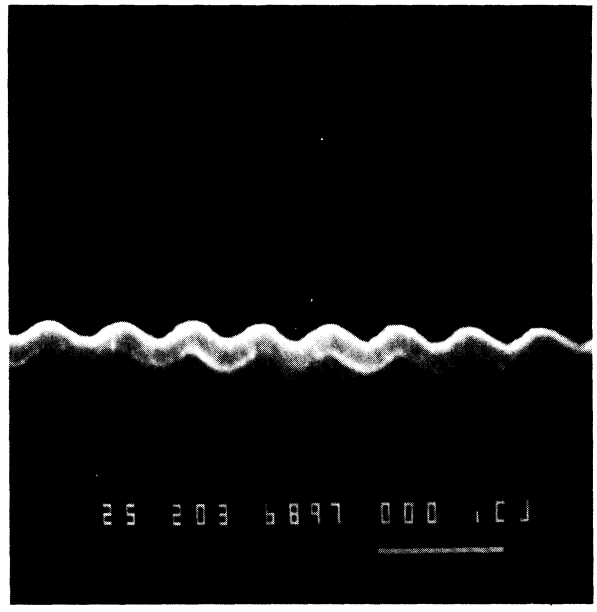
The photostimulated solubility changes of the ChVS layer, that is, the dependence of layer's solubility rate V on absorbed light energy or exposition H: $V=f(H)$ (Fig. 1) serve as a base for relief image formation in the ChVS layers. Such dependence is characteristic for layers of certain composition and certain solvents and may vary under changes of ChVS or the solvents parameters (composition, concentration). In addition, the light intensity distribution in ChVS layer during grating recording is rather nonuniform and, with taking the interference of falling and reflected beams into account, can be expressed in the form

$$I \sim n^2/2\pi \exp(-\alpha h/\cos\theta) \cos^2(kx \sin\theta)[\exp(\alpha z/\cos\theta) + \rho^2 \exp(-\alpha z/\cos\theta) + 2\rho \cos(2kz \cos\theta + \delta)] , \quad (2)$$

where ρ^2 and δ are the reflection coefficient and phase shift at the ChVS substrate interface, $k=2\pi n/\lambda$, n and α are the refractive index and absorption coefficient of the layer at the recording wavelength, and θ is the angle of incidence of interfering beams in ChVS. The XOZ plane is chosen perpendicular to the grooves and the substrate, the OX axis is along the substrate, and the coordinate center is at the ChVS-substrate interface. Thus, the solubility rate of the exposed layer V will be described by the 2-D distribution $V(x,z)=f[I(x,z)t]$. Using these data, the numerical modeling of the relief formation processes under the grating recording on ChVS layers (As_2Se_3) was carried out.[6,22] The numerical results of the evolution of grating reliefs are in good correlation with the experimental contours obtained using an electron microscopy. The groove profile forms can, in most cases, be approximated by a cycloid, and profiles close to the sinusoidal can also be obtained[9] (Fig. 4). It is possible, to a certain degree, to change the parameters of the cycloid by varying the recording and developing conditions, which lead to changes of the diffraction efficiency spectral distribution. It was established that groove profiles depend not only on exposure and the depth of the layer but also on the $V(H)$ dependence and on the time of etching. Thus, to provide the necessary grating parameters, it is necessary to chose the optimal thickness of the initial sample, exposition, selectivity, and etching time. The thickness of the initial ChVS layer in addition to spatial frequency (ν) is also determined by the selectivity of the etching solution; the thickness is greater if selectivity is diminishing. Exposure time and etching time are chosen experimentally, and the diffraction efficiency value of the grating is used as the criterion. The η dependencies on exposure H and on etching time t form the curve maximum, which is chosen as an optimal condition. On ChVS layers of various compositions (As_2Se_3, As_2S_3, As-S-Se, etc.) high-quality gratings were obtained[6–9] with spatial frequencies from 600 to 3600 mm^{-1}. Figure 5 shows the η spectral dependence of a grating with $\nu=1800$ mm^{-1} obtained on As-S-Se layers for nonpolarized light.[9] The η values for S polarization (perpendicular to the grooves) on the long-wavelength side of the spectra are close to the reflection coefficient of the grating coating. The level of stray light is 10^{-6}.



(a)



(b)

Fig. 4 Form of the groove profiles of the gratings obtained on the base of ChVS layers: (a) cycloidal and (b) sinusoidal.

4 Fresnel Lenses

For the holographic recording of Fresnel lenses in a quality registering media, mainly As_2Se_3 layers and also some compositions from the As-S-Se line were used. The methods of sample preparation and postexposure treatment were the same as for the diffraction gratings. But holographic relief, obtained under lens recording, was used as a mask for the image transfer into the glass substrate and formation in the glass phase binary zone plate.[7,8] Under these conditions the chromium sublayer also serves as a masking layer, increasing the resistivity of holographic mask under substrate etching.

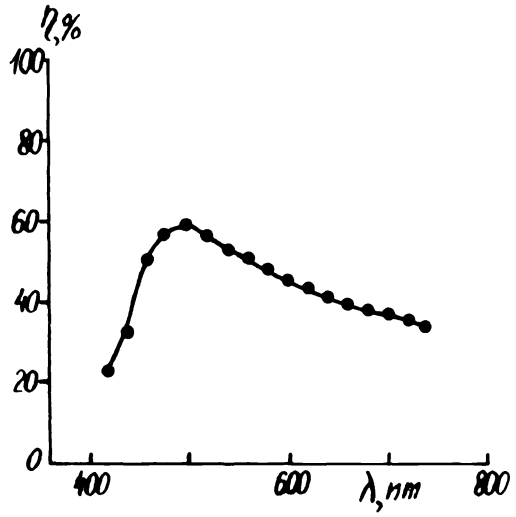


Fig. 5 Spectral dependence of diffraction efficiency η of the grating obtained on the base of As-S-Se layers (spatial frequency 1800 mm^{-1}, nonpolarized light, and absolute values).

With some scheme methods, the holographic method of DOE fabrication enables compensation for lense aberrations.[23] For the perfection of the technological aspects of the phase lense fabrication in glass, however, we used a simple scheme that consisted of a mirror collimator, flat mirrors, two beamsplitters, and an étalon lense, as described in Ref. 8. In the samples plane, the interference pattern that was formed was a system of circular zones. Refractive focusing lenses were used in the étalon element. The recording was carried out using an argon laser ($\lambda = 488$ nm) with exposure values of 0.1 to 0.4 J/cm^2. Postexposure selective etching of the exposed ChVS layers was more durable than under grating fabrication to provide the creation of open windows in the mask. The etching time was chosen in such a way that the width of open zones (a1) was approximately equal to the width of closed (protected) zones (a2), that is, the ratio

$$S = a1/(a1 + a2) = 0.5 \ . \tag{3}$$

Note here that the S value was practically independent of the distance from the center and the zone width changes while going from the lense center to the edge by almost two orders of magnitude. After the substrate etching and the removal of the mask, the axial diffraction lenses were obtained, the structure of which represented circular zones in the form of bulges and hollows in the substrate. The transfer of the image into the substrate took place uniformly over the whole surface, and the relief depth was practically independent of the zone widths. The zone profile form was close to rectangular or to trapezoidal (Fig. 6). Figure 7 presents a fragment of the diffraction lense obtained in a glass substrate. As is known, such zone plates for each wavelength have a set of focus distances, multiples of the first focal distance $f1$. Diffraction efficiency in the first order is determined by the relief depth h[24]:

$$\eta_{+1} = 0.405 \ \sin^2[\pi h(n-1)/\lambda] \ , \tag{4}$$

where n is the refractive index of the substrates material. With an increase of h, the effectivity η grows, reaches a maximum, and then diminishes, in accordance with the previously mentioned dependence. The maximal η values we obtained, however, were somewhat less than the theoretical ones, which is apparently connected with the presence of stray light (the technological processes were not optimized on a full scale). Maximal η value obtained in our experiments was 33%, whereas theoretical value is 40.5%.

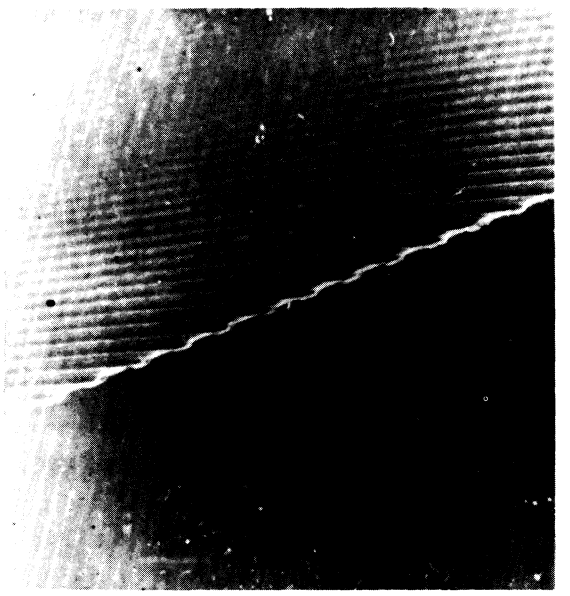


Fig. 6 Form of zone profiles for the binary Fresnel lenses in the glass.

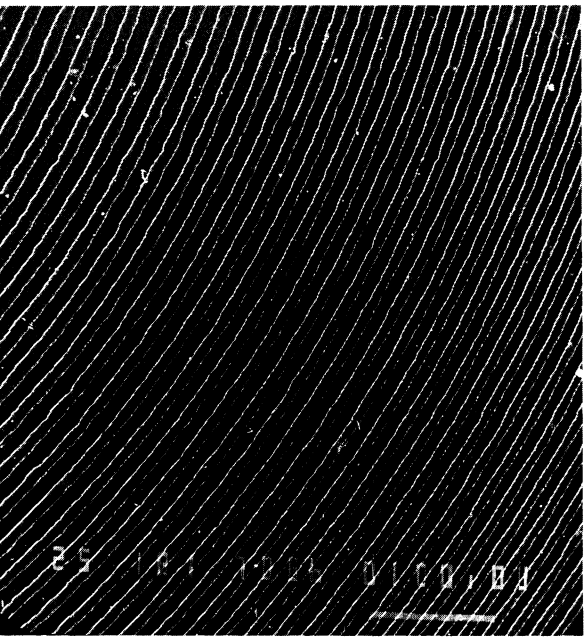


Fig. 7 Fragment of the diffraction lens obtained in the glass substrate.

5 Obtaining of the DOE with Blazed Profiles

As is known, the fabrication of a DOE blazed profile can be carried out by the photolithographic, photoraster methods,

using various recording schemes, with additional treatments, by direct laser or electron-beam exposure of material surfaces, etc. We investigated the possibility of recording of holographic diffraction gratings with an asymmetrical groove profile form using the light sensitive semiconductor-metal system[25] (As_2Se_3-As_2S_3-Ag). The recording was conducted in intersecting beams. The dependencies of grating diffraction efficiency ($\nu = 1060$ mm^{-1}) on the beam angle incidence for S and P polarizations have shown clear asymmetry (η values differed by two to five times for conjugated first orders of diffraction). Spectral η distribution in the 280- to 600-nm range was also typical for the blazed gratings. With decreasing λ values, the η values increased and were about 50% in nonpolarized light in the λ region 280 to 290 nm. In this paper, we consider the recent results for fabrication of DOE (gratings) with the asymmetrical profile in As-S-Se inorganic resists using direct laser beam exposure (using the sawtooth-like exposure distribution) and, in the second case, by means of additional treatment of initially formed symmetrical relief.

5.1 *Direct Laser Beam Exposure*

We previously discovered that by using laser lithography on ChVS layers it is possible to obtain narrow (0.2 μm) lines, the width of which is substantially narrower than the exposure beam half-width.[18,19,26] The laser beam (476 or 532 nm wavelength) was focused on the rotating substrate. The cross sections of light beam intensity on the substrate surfaces has Gaussian distribution:

$$I = I_0 \exp[-(r/r_0)^2] \ , \tag{5}$$

where, in our case $r_0 = 0.8$ μm, I_0 is the intensity at the beam center and r is the distance from the center.

Under focused laser irradiation, the light sensitivity S values of ChVS layers are substantially higher than those under low exposure intensity. At 476-nm wavelength exposure the S value is approximately 10 times higher, and at 532 nm, S rises about two orders of magnitude in comparison to the S value at normal exposure intensity. The increase of S is initiated by the local heating of the exposed areas of the ChVS layers. Light sensitivity S dependence on the temperature T is given by

$$S = S_0 \exp(-E_a/kT) \ , \tag{6}$$

where E_a is the activation energy.

The distribution of exposure H in the line perpendicular to the beam trajectories on the sample surface,

$$H(z) = H_0 \exp(-z^2/r_0^2) \ , \tag{7}$$

determines the temperature T distribution under ChVS layer exposure,

$$T(z) = T_0 + \Delta T \exp(-z^2/r_0^2) \ , \tag{8}$$

where z is the distance from the beam's center and ΔT is the temperature increase at the center of the beam. The spreading of heat is not taken into account because the characteristic heat spreading distance (for the exposure time near some microseconds) is smaller than r_0. Thus, the degree of photostructural transformations M in the ChVS layers is determined by the product of exposure H and light sensitivity S:

$$M = BH(z)S(z) \ , \tag{9}$$

where B is a coefficient. The estimates show that the dependence of M on z is substantially more abrupt and has smaller half-width than $H(z)$ and, as a result, we obtain much narrower lines under the increased sensitivity (which is a rare case for photosensitive media).[26] Such "self-focusing" enables production of lines with widths of 0.2 to 0.3 μm using the laser beam with parameter $r_0 = 0.6$ to 0.8 μm, and so the production of a blazed profile using several grades of exposure values under rather high spatial frequency becomes possible.

The ChVS layers (200 nm thickness) were vacuum evaporated on the disk substrate (130 mm in diameter) with a previously deposited chromium layer (100 nm). The exposure was carried out by means of line scanning when an intensity-modulated focused light beam was moved along the resist surface. The resist exposure was carried out under the substrate rotating frequency 10 Hz and it was simultaneously moved along the radius relative to the recording spot. The light intensity within one period was changed linearly and consisted of the eight exposure grades. Exposure wavelength was 476 nm and period was 3.2 μm. After the exposure the selective etching in amine-based solutions was carried out.

The blazed profiles obtained in this manner on As-S-Se layers are shown in Fig. 8. It can be seen from the figure that using direct laser beam exposure (utilizing a sawtoothlike exposure distribution), blazed profiles can be fabricated using chalcogenide inorganic resists. The spatial frequency of blazed profiles made in this way may be not less than 1000 mm^{-1}, with the proper choice of recording period.[27]

Thus, the chalcogenide inorganic resists can be considered possible media for DOE blazed profile fabrication with rather

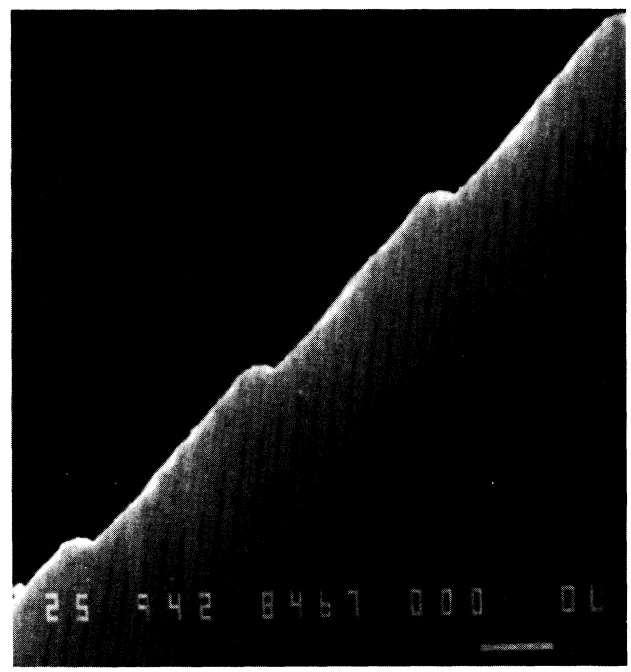


Fig. 8 Blazed grating obtained on the As-S-Se layers with the help of sawtoothlike exposure distribution.

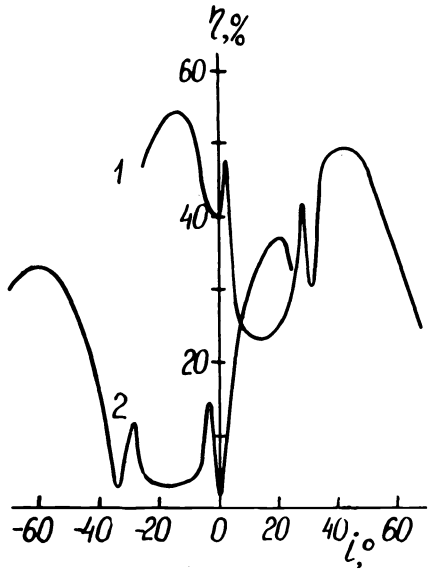


Fig. 9 The angular dependencies of diffraction efficiency η for the first conjugated diffraction orders (S-polarization, $\lambda = 441.6$ nm grating on the base of As_2Se_3 layers).

high spatial frequencies and with high aperture under direct laser beam exposure.

5.2 *Additional Treatment*

In this case, the initial gratings (or holographic masks) were made holographically by means of interference registration, formed by coherent laser beams in the ChVS layer. The grating recording was carried out using argon laser irradiation (488 nm) in the scheme described in Refs. 5 and 9. The exposure values were 0.2 to 0.5 J/cm^2. After chemical treatment, gratings with symmetrical groove profile forms were obtained (which also can be used as a holographic mask for the formation of asymmetrical grating in the substrates material).

Additional 200- to 500-nm-thick ChVS layers were deposited on the obtained grating. Then this structure was irradiated using 488-nm wavelength argon laser under the angles to the substrates surface close to $90-\alpha$, where $\alpha = \arcsin[\lambda(v)(m/2)]$ (where v is grating spatial frequency; in our case, 1200 mm^{-1}; m is the diffraction order; and λ is the used monochromatic wavelength). Then, the gratings were chemically treated in amine-based solutions and consequently covered with the reflective coating (Al).

The asymmetry of the obtained gratings is well pronounced in angular (Fig. 9) and spectral dependencies of diffraction efficiency η. In Fig. 9 the η angle dependencies are presented for the first conjugated diffraction orders for the case of S polarization. The measurements were carried out using the He-Cd laser irradiation (441.6 nm). Curve 1 corresponds to a larger facet and curve 2 to a smaller one. It is clearly seen from the figure that the obtained gratings have clearly pronounced asymmetry. At normal incidence for the conjugated first orders, η differs by about 20 times.

The increase in η is clearly pronounced in the short-wavelength region, in the near-IR region, η values are[28] close to 90%. In experiments on obtaining asymmetrical gratings in the substrate material (glass) by using masks formed by the holographic method and ion etching, blazed gratings were also produced.[7]

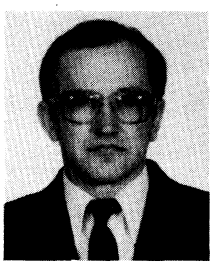
6 Conclusions

The investigations that were carried out show that registering media based on ChVS layers are rather promising for DOE fabrication. Holographic methods enable recording high-quality reflective diffraction gratings on such media with a wide range of spatial frequencies and fabrication protective masks for the production of phase-zone plates—diffractive lenses. Application of additional treatment or recording schemes in intersecting beams provides for the fabrication of gratings with blazed profiles. Highly promising is the method of laser lithography on ChVS layers, if the "self-focusing" effect in such media is taken into account, under exposure by a sharp-focused laser beam. This method enables recording optical elements with micrometer-sized distant zones, that is, with high numerical aperture. Thus, the obtained results show that ChVS layers are good media for the production of holographic optical elements with asymmetrical profiles.

References

1. U. Krackhardt, J. Schwider, M. Schrader, and N. Streibl, "Synthetic holograms written by a laser pattern generator," *Opt. Eng.* **32**(4), 782–785 (1993).
2. M. C. Hutley, R. F. Stevens, and S. J. Wilson, "Manufacture of blazed zone plates in germanium for the use in 10 μm spectral region," *Opt. Eng.* **30**(7), 1005–1010 (1991).
3. J. P. H. Benschop and H. Steinhauser, "Design and manufacture of holographic optical elements," *Proc. SPIE* **1983,** 670–671 (1993).
4. B. Mednikarov, A. G. Poleschchuk, and E. G. Churin, "Application of As_2S_3 films for the fabrication of phase-relief diffractive elements," *Autometria* (Russia) (4), 87–93 (1993).
5. I. Z. Indutnyi, M. T. Kostishin, P. F. Romanenko, and A. V. Stronski, "Recording of holographic diffraction gratings on lightsensitive semiconductor-metal systems," *J. Inf. Rec. Mater.* **19**(3), 239–248 (1991).
6. I. Z. Indutnyi, I. I. Robur, P. F. Romanenko, and A. V. Stronski, "Holographic diffraction gratings on the base of chalcogenide semiconductors," *Proc. SPIE* **1555,** 248–257 (1991).
7. A. V. Stronski, P. F. Romanenko, I. I. Robur, I. Z. Indutnyi, and P. E. Schepeljavi, "Application of vitreous chalcogenides in diffractive optics," in *Optics as a Key to High Technology, Pt. II, Proc. SPIE* **1983,** 647–675 (1993).
8. P. F. Romanenko, I. I. Robur, A. V. Stronski, I. Indutnyi, P. Schepeljavi, S. Kastioukevitch, and L. Kostrova, "Holographic optical elements, holograms production on the base of chalcogenide vitreous semiconductor layers," in *Holography, Correlation Optics, and Recording Materials, Proc. SPIE* **2108,** 110–114 (1993).
9. A. V. Stronski, P. F. Romanenko, I. I. Robur, I. Z. Indutnyl, P. E. Shepeljavi, and S. A. Kostioukevitch, "Recording of holographic optical elements on As-S-Se layers," *J. Inf. Rec. Mater.* **20**(6), 541–546 (1993).
10. A. Joshikawa, S. Hirota, O. Ochi, A. Takeda, and Y. Mizushima, "Angstroms resolution in Se-Ge inorganic photoresists," *Jpn. J. Appl. Phys.* **20**(2), L81–L83 (1981).
11. Y. Mizushima and A. Yoshikava "Photoprocessing and lithographic applications," in *Amorphous Semiconductors Technol. and Devices,* Y. Hamakava, Ed., OHM, Tokyo, and North-Holland, Amsterdam, pp. 277–295 (1982).
12. Y. Utsugi, "Chemical modification for nanolithography using scanning tunneling microscopy," *Nanotechnology* **3,** 161–163 (1992).
13. M. T. Kostishin, E. V. Michailovskaya, P. F. Romanenko, and G. A. Sandul, "About the photographic sensitivity of the thin semiconductor layers," *J. Sci. Appl. Photogr. Sinematogr.* **10**(6), 450–451 (1965).
14. N. Mott and E. Davis, *Electron Processes in Non-Crystalline Materials,* Clarendon Press, Oxford (1979).
15. B. T. Kolomietz, V. M. Ljubin, and V. P. Shilo, "Photostimulated solubility changes of chalcogenide glasses," *Phys. Chem. Glasses* **4**(3), 351–357 (1978).
16. M. T. Kostishin, E. V. Michailovskaya, and P. F. Romanenko, "On the effect of photographic sensitivity of the thin semiconductor layers deposited on metal substrates," *Sov. Phys. Solid State* **8**(2), 571–572 (1966).

17. I. Z. Indutnyi, M. T. Kostishin, O. P. Kasjarum, V. I. Minko, E. V. Mikhaylovskaya, and P. F. Romanenko, *Photostimulated Interaction in Metal-Semiconductor Structures,* Naukova Dumka, Kiev (1992).
18. I. Z. Indutnyi, S. A. Kostioukevitch, A. V. Stronski, and P. E. Schepeljavi, "Formation of optical disk direction paths and optical master disks with the help of inorganic resist," in *Optics as a Key to High Technology, Pt. I, Proc. SPIE* **1983,** 464–465 (1993).
19. S. A. Kostyukevitch, "Laser lithography on the layers of chalcogenide glasses," in *SET'92 Catalolgue and Symp. Progr., 3rd Mid-European Symp. & Exhib. on Semiconductor Engineering and Technology,* October 12–14, Warsaw, Poland, pp. 304–305 (1992).
20. B. Singh, S. P. Beamont, A. Webb, G. Bower, and C. D. W. Wilkinson, "High resolution patterning with Ag_2S/As_2S_3 inorganic electron-beam resist and reactive ion etching," *J. Vac. Sci. Technol. B* **1**(4), 1174–1177 (1983).
21. M. T. Kostishin, P. F. Romanenko, I. Z. Indutnyi, T. M. Kolomiets, and O. P. Kasjarum, "Peculiarities of holographic diffraction gratings recording on lightsensitive semiconductor-metal systems," *Fundamental Base of Optical Memory and Media,* Vol. 14, pp. 85–94, Viszha Shkola, Kiev (1983).
22. I. Z. Induntyi, I. I. Robur, P. F. Romanenko, and A. V. Stronski, "Formation of the holographic optical elements in lightsensitive structures on the base of chalcogenide semiconductors," in *Fundamental Base of Optical Memory and Media,* Vol. 22, pp. 3–11, Lubid, Kiev (1991).
23. G. I. Greisukh, I. M. Efimenko, and S. A. Stepanov, *Optics of Gradient and Diffractive Elements,* Radio and Svjaz, Moscow (1990).
24. V. V. Dontsova, G. A. Lenkova, and I. A. Michaltsova, "Investigation of parameters of the diffractive microobjectives," *Avtometrija* (2), 87–96 (1989).
25. M. T. Kostishin, P. F. Romanenko, and A. V. Stronski, "Recording of holographic diffraction gratings with the asymmetrical form of groove profile on lightsensitive semiconductor-metal systems," *Ukr. J. Phys.* **29**(4), 510–513 (1984).
26. I. Z. Indutnyi, S. A. Kostioukevitch, V. I. Minko, A. V. Stronski, and P. E. Shepeljavi, "Laser lithography utilizing As_2S_3 layers," in *Optoelectronics and Semiconductor Technique,* Vol. 25, pp. 52–59, Naukova Dumka, Kiev (1993).
27. A. V. Stronski, S. A. Kostioukevitch, P. E. Schepeljavi, I. Z. Indutnyi, P. Romanenko, and I. I. Robur, "Asymmetrical profile fabrication of diffractive optical elements with the help of chalcogenide inorganic resists," in *Diffractive and Holographic Optics Technology, Proc. SPIE* **2152,** 333–337 (1994).
28. P. F. Romanenko, I. I. Robur, A. V. Stronski, and I. Z. Induntyi, "Investigation of the processes of obtaining of holographic diffraction gratings with the asymmetrical form of grooves profile with the help of inorganic resists on the base of chalcogenide semiconductors," *Abstr. of IVth. Int. Conf. Physics and Applications of Chalcogenide Glassy Semiconductors in Optoelectronics,* pp. 86–87, Shtiintsa, Kishinev (1993).



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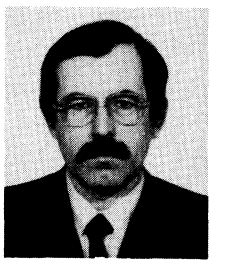

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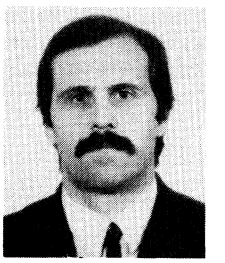

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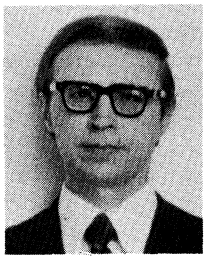

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