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Influence of the corona discharge on the formation of the diffractive holographic gratings in the $As_{40}S_{60-x}Se_x$ films

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The influence of the corona discharge on the holographic recording and the subsequence chemical etching of the recording holographic gratings in the $Cr/As_{40}S_{60-x}Se_x$ thin film structures was investigated. It was established that applied of the positive corona discharge leads to the increase of the holographic sensitivity during the recording in the As−S−Se films, as well as to the amplification of the diffraction efficiency of the recording gratings and of the relief-phase diffractive gratings obtaining in the result of the consecutive chemical etching. Among the investigated films of the $As_{40}S_{60-x}Se_x$ system, the best results on the application of the Argon laser irradiation (488 nm) was obtaining for the composition $As_{40}S_{39}Se_{21}$. Applied of the corona discharge bring to the increase of the holographic sensitivity more than up two order, and of the diffraction efficiency about three order in the respect of the of the ordinary recording. Reciprocally was reached a amplification of the diffraction efficiency of the relief diffraction gratings formed in the result of the sequent chemical etching up to 30%.

Keywords: chalcogenide vitreous semiconductors, holographic diffractive grating, corona discharge, diffraction efficiency, selective etching.

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Introduction

In modern optical analog holographic technologies, the development of recording media is one of the key aspects. Among the many recording media, much interest is paid to amorphous films of chalcogenide glassy semiconductors (CGS). Recording in CGS films can be based on various physical processes, among which the following are distinguished: photoconductivity in the method of photothermoplastic recording; photostructural transformations (PSP); photodiffusion of metal (PDM) into the CGS layer. The first one has a record sensitivity of $S \sim 10^6\,cm^2/J$ [1]. The second and third, which cause the modulation of optical parameters and etching rate, have lower sensitivity, but have a high resolution (more than 10,000mm^{-1}), low noise, the possibility of selective chemical and ion etching [2].

The importance of holographic sensitivity increases S with optical holographic recording of analog holograms with a large area, along with the resolution of the recording medium. The method of recording in thin films of CGS using PSP is applied in protective holographic technologies and for the creation of holographic optical elements. However, it is characterized by a relatively low value of holographic sensitivity S of the order $\sim 10^1\,cm^2/J$ [3] and a relatively low value of diffraction efficiency η of the order $\sim 1\%$ [4].

The holographic recording in CGS films can be enhanced using a modified method comprising exposing thin-film structures of Me-CGS with simultaneous charging of high-resistance semiconductor layer in the corona discharge field. At the same time, there is a several-fold increase in the value of S, as well as the diffraction efficiency of η holographic diffraction gratings (HDG) formed both during recording and by subsequent chemical etching [4]. The effect of the corona discharge field on the diffraction efficiency of gratings recorded by the holographic method in the $Cr-As_2S_3$ structure with a nanoscale layer thickness of As_2S_3 [5–7] was studied. The use of corona increased η by about 10 and 30 times, respectively, when using layers As_2S_3 with thicknesses equal to 56 and 29 nm, [5].

The peculiarity of triple-composition CGS films As−S−Se consists in a smooth change in their optical and chemical properties by changing the percentage of Se. The width of the band gap (E_g) changes between the values E_g corresponding to As_2S_3 and As_2Se_3 in the most studied system $As_{40}S_{60-x}Se_x$ [8–12] when x changes from 0 to 60 [11,13]. This, in particular, makes it possible to select the composition of the recording film As−S−Se that is most suitable for the laser radiation used. For films $As_{40}S_{60-x}Se_x$, an almost linear increase in the refractive index was observed over the entire range of variation x (from 0 to 60) [11]. It is known [2] that CGS thin films ($\sim 1\,\mu$m) of triple compositions As−S−Se are more preferable for the formation of holographic diffraction gratings and holograms compared to binary films (As_2S_3 and As_2Se_3). The films of the system As−S−Se combine the high photosensitivity inherent in films As_2Se_3 and the stability inherent in films As_2S_3.

The aim of this work was to study the effect of charging amorphous films of the $As_{40}S_{60-x}Se_x$ system in the corona discharge field on the optical holographic recording of diffraction gratings and their subsequent chemical etching.

1. Methods of sample synthesis and investigation

Thin-film samples Cr/$As_{40}S_{60-x}Se_x$ were obtained by sequential vacuum deposition of layers Cr and As−S−Se (thermal evaporation) on flexible polyethyleneterephthalate substrates. The thickness of the semiconductor layers for all compositions was the same and was $0.8\,\mu$m. The thickness of the translucent metal layer Cr, used as the underlying electrode for recording in the corona discharge field, was equal to several tens of nanometers. The distance between the corona electrode (thin ($60\,\mu$m) tungsten filament) and the chromium metal film was 17 mm. The schematic diagram is shown in Fig. 1.

The HDG was recorded using the standard off-axis Leith−Upatnieks scheme on a holographic vibration-proof table. A Ar^+ laser with a wavelength of radiation $\lambda = 488$ nm was used as a coherent radiation source.

The division of the laser beam into two beams of the same intensity was carried out by the method of phase division (by means of a beam-splitting cube). The total illumination of both interfering laser beams was 0.42 mW/cm^2. Both the usual recording and the corona discharge field of diffraction gratings with a period of $1\,\mu$m were carried out. A positive potential of +7 kV was applied to the corona electrode at the same time. The samples were exposed from the film side $As_{40}S_{60-x}Se_x$ (Fig. 1). The diffraction efficiency was monitored in the first order of diffraction during the recording process. After recording, relief-phase diffraction gratings were formed by chemical etching at room temperature in 5% KOH aqueous solution (positive etchant). The etching time was the same for all samples and was 30 s.

The diffraction efficiency of the gratings η_1 was measured in the first order of diffraction for transmission at a wavelength of $\lambda = 0.6328\,\mu$m with a normal incidence of He−Ne-laser beam both during the recording process and after the etching procedure. In the first case, a reading laser beam attenuated with light filters was used to minimize the effect on the recording of HDG. The values of diffraction

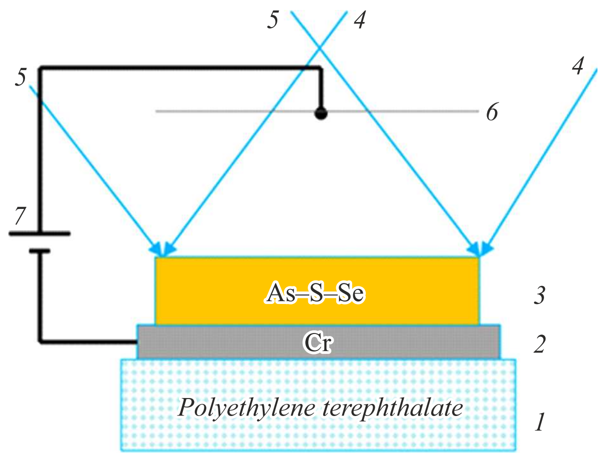

Figure 1. Schematic diagram of HDG recording in the corona discharge field: *1* — flexible dacron substrate, *2* — translucent metal electrode (Cr), *3* — layer HSP, *4, 5* — lagrain bundles, *6* — corona tungsten filament, *7* — high-voltage power supply.

efficiency corresponding to the recording process were determined as the ratio of the intensity of the diffracted beam in the first order of diffraction to the intensity of the beam that passed through the unexposed portion of the sample. This determination of the diffraction efficiency made it possible to exclude the influence of scattering and absorption in the substrate, metal and semiconductor layers on it. The values of the diffraction efficiency of relief-phase diffraction gratings were determined from the ratio $\eta_{et} = I_1/(I_0 + 2I_1)$, where I_1 and I_0 are the light intensities in the first and zero diffraction order, respectively.

The holographic sensitivity S was determined by the formula $S = (\sqrt{\eta})/(HK)$ proposed in [14], where $H = Lt$ — exposure (L — total illumination, t — recording time), $K = 1$ — visibility of the bands (the intensity of the interfering laser beams was the same).

2. Experimental results and discussion

The values of the diffraction efficiency of the recorded gratings were used to construct the exposure-contrast characteristics of $\sqrt{\eta} = \varphi(H)$ films $As_{40}S_{60-x}Se_x$. Fig. 2 shows the dependencies of $\sqrt{\eta}$ on exposure for films $As_{40}S_{60}$ (Fig. 2, curves *3, 4*), $As_{40}S_{39}Se_{21}$ (Fig. 2, curves *5, 6*) and $As_{40}S_{18}Se_{42}$ (fig. 2, curves *1, 2*) obtained during normal recording (curves *1, 3, 5*) and in the corona discharge field (curves *2, 4, 6*). The application of the corona discharge during recording led to the strengthening of the formed HDG with all compositions. The values of $\sqrt{\eta}$ changed slightly near the saturation level when the exposure reached $H = 0.2$ J/cm^2 . The values of the holographic sensitivity S of the films used $As_{40}S_{60-x}Se_x$ were calculated for this value H.

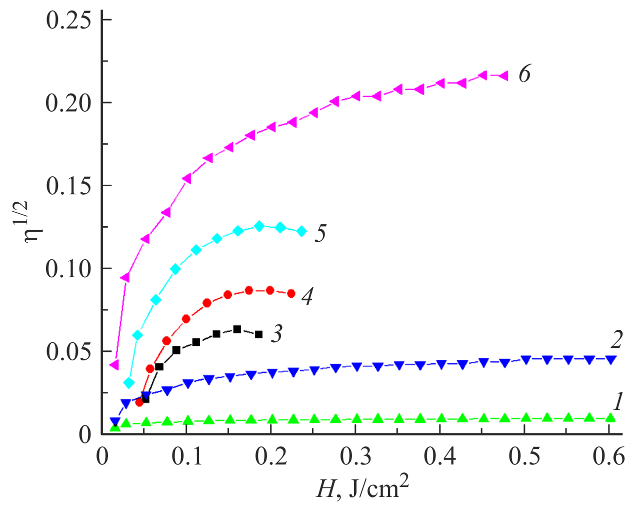

Figure 2. Dependence of diffraction efficiency on exposure: *1, 2* — $As_{40}S_{18}Se_{42}$; *3, 4* — $As_{40}S_{60}$; *5, 6* — $As_{40}S_{39}Se_{21}$. *1, 3, 5* — normal HDG recording; *2, 4, 6* — recording in the corona discharge field.

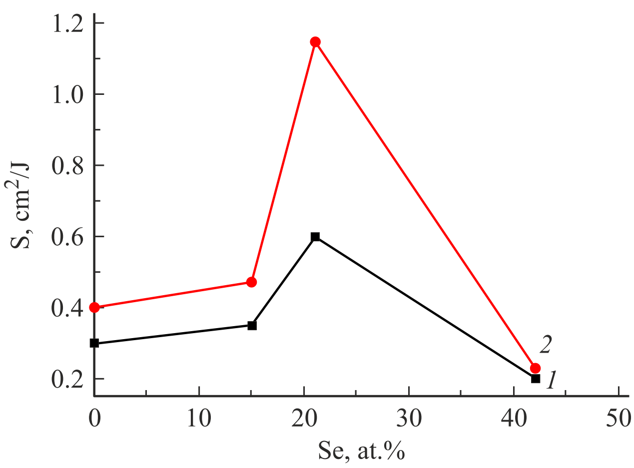

Figure 3. The dependence of the holographic sensitivity on the content Se in $As_{40}S_{60-x}Se_x$ with normal writing (*1*) and in the corona discharge field (*2*).

The effect of the corona discharge field on the holographic sensitivity of films $As_{40}S_{60-x}Se_x$ of various compositions is shown in Fig. 3.

The application of the corona discharge field during recording (Fig. 3, curve *2*) noticeably increased the holographic sensitivity of all the compositions used $As_{40}S_{60-x}Se_x$. The highest values S were obtained for films $As_{40}S_{39}Se_{21}$. In this case, the application of an electric field resulted in a twofold increase of holographic sensitivity.

HDG were first recorded (almost to the maximum of diffraction efficiency, i.e. to saturation) on various compositions of the system $As_{40}S_{60-x}Se_x$ and then they were subjected to chemical etching to study the effect of corona discharge on the diffraction efficiency of relief-phase gratings. The recording was performed both in the corona discharge field and without it. The resulting HDGs were subsequently subjected to chemical etching under the same conditions. The HDG diffraction efficiency before etching was measured on these samples for all the studied compositions (η and η_{cd}, normal recording and recording in the corona discharge field, respectively). These data are provided in Table 1.

Table 1. Diffraction efficiency of recorded and etched HDG in $As_{40}S_{60-x}Se_x$

Composition		$As_{40}S_{60}$	$As_{40}S_{45}Se_{15}$	$As_{40}S_{39}Se_{21}$	$As_{40}S_{18}Se_{42}$
After recording	η, %	0.4	0.5	1.5	0.18
	η_{cd}, %	0.7	1.2	5.6	0.23
After etching	η_{et}, %	9.3	11.2	17.7	5.7
	$\eta_{et,cd}$, %	12.5	14.6	22.7	7.4

The diffraction efficiency after etching was also measured: η_{et} — relief-phase HDG obtained with conventional recording, η_{et}, η_{cd} — HDG obtained using a corona discharge at the recording stage (Table 1).

An increase of the diffraction efficiency of the HDG is observed for all compositions like in Figure 2 when using a positive corona discharge. As can be seen from the table, the highest value of diffraction efficiency both after normal recording and after recording in the corona discharge is achieved for the composition $As_{40}S_{39}Se_{21}$. With normal recording, the diffraction efficiency value for this composition is 1.5%, and when writing in the corona discharge field 5.6%. After subsequent etching, the diffraction efficiency increased and amounted to 17.7% for normal recording and 22.7% for recording using a corona discharge.

Let us proceed to discuss the results obtained. First of all, let us estimate the magnitude of the electric field that is created in the CGS films under study when they are charged in the corona discharge field. The surface potential formed on the surface of thin CGS films when they are charged in the corona discharge field is approximately $\approx 100-200$ V [7,15]. Since the thickness of semiconductor films $As_{40}S_{60-x}Se_x$ is 0.8 μm, the electric field strength E generated in them is in the order of $E \gtrsim 10^6$ V/cm. With such strong electric fields, the Franz–Keldysh and Pool–Frenkel effects can be manifested, causing an increase in photoabsorption and concentration of nonequilibrium carriers (in our case holes), which leads to a photoinduced increase of the refractive index Δn [16]. As the experiment shows, the effect of the Franz–Keldysh effect can be neglected. Photoabsorption increases slightly when charging structures in the corona discharge field. It should be noted that in such strong electric fields, the value of the quantum yield increases [17], i.e., the ratio of the number of nonequilibrium carriers born to the number of absorbed photons.

To date, the impact of the electric field and the wavelength of light on the photogeneration of free charge carriers in amorphous selenium films has been studied in detail. It has been experimentally found [18–21], that the application of an electric field E leads to an increase of the quantum yield. At the same time, for all wavelengths with an increase of E, a monotonous increase in the quantum yield was observed, approaching unity under short-wave illumination and $E > 10^7$ V/m. For example, the quantum yield of C at high fields (for selenium greater than $3 \cdot 10^4$ V/cm) is approximated by the Pool–Frenkel $C \sim \exp(\beta E^{1/2}/kT)$ theory for selenium, where $\beta = (4e^3/\varepsilon)^{1/2}$ [17].

Basically, the dependence of the quantum efficiency on E was explained using [18–20] models based on the Frenkel theory [22]. At the same time, a model based on the theory of Onzager [23] is considered, and the advantage of using this theory to describe experimental results is shown in [21]. The application of this model gave a good match with the experimental and calculated dependence of the quantum yield on E in a wide range of changes in the wavelength of light initiating the formation of electron-hole pairs. Calculations made in all the considered models predict an increase in the probability of thermal separation of a photoinduced electron-hole pair in an electric field into free charge carriers. According to both theories (Frenkel and Onzager), this is attributable to a decrease in the thermal ionization energy required for the separation of charge carriers bound by Coulomb attraction.

The corona discharge field initiated an electric field $E \approx 10^9$ V/cm in the film As_2S_3 with a thickness of 100 nm under the conditions of the experiment conducted in [7]. The number of photoinduced charge carriers N_c in an applied high electric field according to Frenkel's theory is represented by the authors [7] using the formula

$$N_c = N_0 \exp\left[\frac{(e^3E)^{1/2}}{nk_\mathrm{B}T}\right],$$

where N_0 is the number of nonequilibrium charge carriers without an applied electric field; n is the refractive index.

Apparently, experimental and theoretical results obtained for amorphous selenium films and As_2S_3 can be used to explain the increase in the holographic sensitivity of films $As_{40}S_{60-x}Se_x$ and the diffraction efficiency of the HDG during optical recording in the corona discharge field compared to conventional recording. The main effect of the electric field is to increase the quantum yield during photogeneration of free charge carriers.

Obtaining the best results for films $As_{40}S_{39}Se_{21}$ is consistent with the results of studying the optical properties of films of the system $As_{40}S_{60-x}Se_x$ [11], as well as their applications for optical recording [9]. The growth of the photoinduced increase in the refractive index reached an area of the weak change with $x \approx 20$ with an increase of the proportion of Se content[11]. It is shown [9] that amorphous films of the system $As_{40}S_{60-x}Se_x$ ($x = 20\ldots40$) are characterized by high holographic sensitivity. The holographic sensitivity of the composition corresponding to $x = 20$ was much higher than for $x = 30$ and 40 when diffraction gratings were recorded with a wavelength of 0.44 μm. The highest diffraction efficiency of the grating was also obtained for the composition $As_{40}S_{39}Se_{21}$ Due to the correlation of photoinduced changes in the optical and chemical properties of CGS films.

Table 2. Sensitivity and diffraction efficiency at recording and etching HDG formed in structures $Cr{-}As_{40}S_{39}Se_{21}$ and $Cu{-}As_2Se_3$

Composition	Mechanism recording	Gain S and η during recording in corona discharge field		
		After recording		After etching
		S_{cd}/S	η_{cd}/η	η_{cd}/η
$Cr{-}As_{40}S_{39}Se_{21}$	Photostructural transformations	2	3.6	1.3
$Cu{-}As_{40}Se_{60}$	Photo diffusion metal	1.6	2.5	2.5

Apparently, the observed rather significant (by several times) increase of diffraction efficiency during holographic recording of gratings in the corona discharge field compared to conventional recording (Fig. 2) can be qualitatively explained taking into account the Pool–Frenkel effect. It can also be assumed that the increase in diffraction efficiency in the corona discharge field is influenced by a decrease in the longitudinal photodiffusion of nonequilibrium carriers (holes) from the illuminated portion of the CGS film to the nonradiated region due to the existing internal transverse electric field in the semiconductor layer.

It should be noted that the use of a corona discharge (negative) also leads to an increase in holographic sensitivity and diffraction efficiency not only with PSP, but also with PDM in the films of CGS [24–26]. For comparison, Table 2 was compiled on the basis of the data obtained in this work and given in works [24–26],.

As can be seen from the table, the holographic sensitivity when recording in the corona discharge S_{cd} is higher than the sensitivity obtained with conventional recording S. It should be noted that if the gain of S and η when using a corona discharge for the composition of $Cr{-}As_{40}S_{39}Se_{21}$ (recording by PSP) is higher than for the composition of $Cu{-}As_{40}Se_{60}$ (recording using PDM), then for diffraction efficiencies after etching GDR, such gain is, on the contrary, higher, almost by 2 times, for the composition of $Cu{-}As_{40}Se_{60}$. The latter fact can be explained with the peculiarity of etching of thin films of CGS at PDM [2].

Taking into account the above results, it can be assumed that for all high-resistance photosensitive thin films based on CGS, the use of a corona discharge will ensure an increase in their photosensitivity, diffraction efficiency and depth of surface relief. So, in particular, for the multilayer nanostructure As_2S_3/Se, consisting of alternating nanoscale layers As_2S_3 and Se [27], charging in the corona discharge field can be very effective for increasing their holographic sensitivity S, diffraction efficiency η and surface relief depth h. The following work will be devoted to the verification of the last assumption.

Conclusions

1. The application of a positive corona discharge during optical holographic recording in films $As_{40}S_{60-x}Se_x$ resulted in an increase in the holographic sensitivity and diffraction efficiency of both recorded gratings and relief gratings formed by subsequent chemical etching.

2. Among the studied films $As_{40}S_{60-x}Se_x$ the best results when recording at a wavelength of 488 nm were obtained for $As_{40}S_{39}Se_{21}$. For this composition, the use of a positive corona discharge led to an increase of about 2 times in holographic sensitivity, more than 3 times in diffraction efficiency during recording, and after subsequent chemical etching by about 30%.

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Conflict of interest

The authors declare that they have no conflict of interest.

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