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HOLOGRAPHIC RECORDING IN AMORPHOUS CHALCOGENIDE SEMICONDUCTOR THIN FILMS

J. Teteris

Institute of Solid State Physics, University of Latvia, LV-1063, Riga, Latvia

A detailed study of the amorphous As-S-Se and As_2S_3 films as recording media for optical holography and electron beam lithography is presented. The results on R&D of resist based on the amorphous As-S-Se thin films for manufacturing of embossed holographic labels are discussed. The holographic recording of transmission and Bragg gratings were studied.

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1. Introduction

The phenomenon of photo- and electron-beam induced changes in the dissolution rate of a large group of amorphous chalcogenide semiconductor (AChS) films was the basis for extensive development of a new class of inorganic resists [1,2]. Amorphous As-S, As-Se and As-S-Se films have been used recently as promising materials for photolithography in the visible spectrum ($\lambda \leq 650$ nm) with high resolution (>5000 lines/mm) and light sensitivity (~10^{-1} J/cm^2). *Hologramma Ltd* in Riga successfully applies the AChS photoresists in the manufacturing process of embossed rainbow holographic labels. The AChS resists obtained by the thermal deposition method in vacuum are characterized by a very high resolution capability and they have a number of peculiarities that make them attractive for application in many photo- and electron-beam lithographic processes.

Diffractive optical elements (DOEs) manufactured by a holographic or an electron beam lithography method have recently found wide application in various optical and optoelectronic elements and devices [3]. The main advantages of the DOEs are their compactness, compatibility with planar technology and the possibility for an effective control of optical parameters. It is well known that the fabrication of the DOEs with a blazed profile significantly improves the performance efficiency and enables the control of the spectral region for maximum light concentration. Resists with low proximity effect, high sensitivity and linear dependence between the exposed dose and the profile depth are required for the fabrication of the blazed DOEs.

During the studies of the holographic properties of amorphous As-S films doped with bromide, an increase of the diffraction efficiency (DE) after the recording was observed [4]. This phenomenon, called relaxation (or dark) self-enhancement (SE) of holograms (an increase of diffraction efficiency with time without any special treatment), in amorphous As_2S_3 films was explained as a periodic spatial mechanical stress modulation induced by a holographic grating (HG) [5]. The process of self-enhancement of holographic gratings can be stimulated by light. The following hologram enhancement types can be distinguished according to the mechanism and to the properties of this effect: 1) coherent hologram enhancement is due to the holographic recording by the diffracted beam and the readout beam jointly inducing a new index grating or hologram which bears exactly the same information as the existing one, and 2) incoherent enhancement is due to photo-stimulated processes in a photorefractive medium. The studies on the holographic enhancement phenomenon in AChS films suggest that the dark SE and incoherent SE of holographic gratings evidently possess common processes that can be accelerated by illumination or heating [6,7].

The present paper reports some new results in the studies of the As-S-Se and As_2S_3 amorphous films as photo- and electron-beam resists. The purpose is to investigate the dose and

spectral characteristics of the resists, to examine the possibility to amplify the diffraction efficiency after recording, and to estimate the possibility to use these films in holography and fabrication of DOEs.

2. Experimental

Amorphous As_2S_3 and As-S-Se films were obtained by thermal evaporation in vacuum of $\sim 5 \times 10^{-6}$ Torr onto glass substrates. The film thickness was in the range of 1 – 12 μm. The samples for the studies of etching changes were irradiated by Ar^+ and He-Ne laser beams with wavelengths from 457.9 nm to 632.8 nm, as well as on the SEM by an electron beam with energy of 30 keV. The etching rate was determined by monitoring the local thickness of the film using thin film interference. The etchant, which is based on alkaline organic solutions produced by *Hologramma Ltd* , was used in these experiments as a negative developer for the As-S-Se films, and NaOH water solution doped by alkyl sulfonate as a surface active substance was used for amorphous As_2S_3 films as a positive developer.

The transmission holographic gratings (HG) with a period of Λ=0.7-2.5 μm were recorded by two symmetrically incident Ar^+ laser beams (514.5 nm) of equal intensity. The readout of the diffraction efficiency was made at the Bragg angle using a He-Ne laser beam (632.8 nm). The average intensity of the readout beam (I_0) was about 1 mW/cm^2. The diffraction efficiency η is defined as $\eta = I_d / I_0$, where I_d is the intensity of the first order diffracted beam. Both of the lasers had linear vertically polarized beams parallel to the HG lines (s-polarization). The hologram enhancement was determined by the factor $\xi = \eta(t)/\eta_0$, where $\eta(t)$ is the diffraction efficiency at the time t and η_0 is the initial diffraction efficiency of the HG.

The Ar^+ laser 488.0 nm, 501.7 nm, 514.5 nm and 528.7 nm lines were used for recording the Bragg gratings in amorphous as-evaporated As_2S_3 films. A spatially filtered and collimated light beam from the laser was divided into two beams with equal intensity ($I_1 = I_2 = 15.6$ mW/cm^2). The optical setup is illustrated in Fig. 1. A beam 1 is perpendicular to the surface of the sample ($\alpha_1 = 90^o$), but the angle between beam 2 and sample is $\alpha_2 = 88^o$. During the recording process the beam 2 was periodically shut and the diffraction efficiency of recorded Bragg grating was measured by beam 1, i.e. the recording and testing of the gratings was performed with the same wavelength.

A) Optical set-up for recording of Bragg gratings. B) Bragg grating formation in the film.

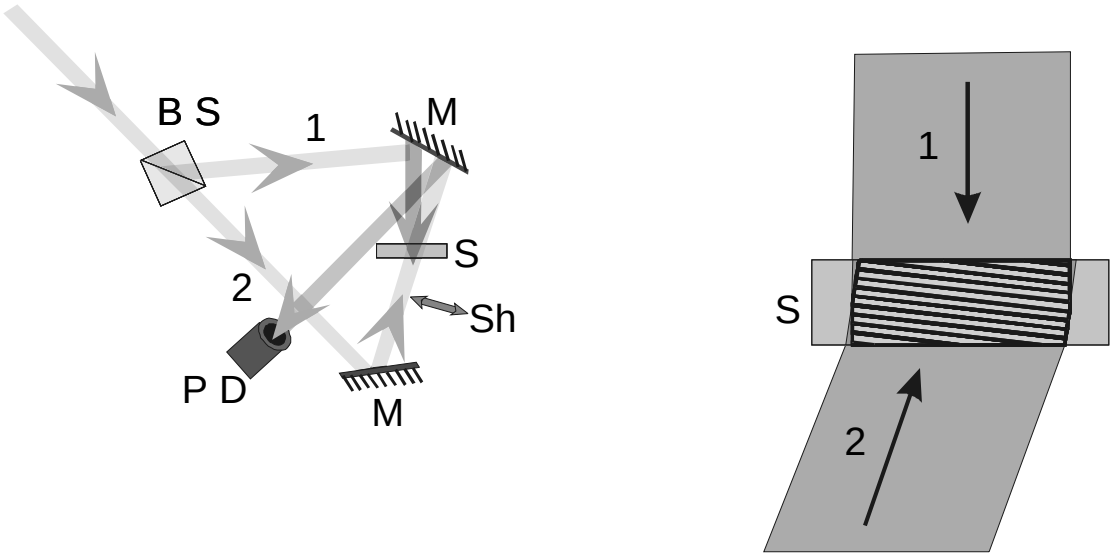

Fig. 1. Experimental setup for Bragg grating recording: BS – beam splitter; M – mirror; S – sample;Sh – shutter; PD – photodiode.

3. Results and discussion

3.1. Real-time transmission holographic recording in AChS films

Irradiation of amorphous chalcogenide semiconductor thin films by bandgap light leads to appreciable changes of their optical properties [8-10]. These changes are connected with the short-range order modification as a result of chemical bond transformation in the material. The atomic structure variations modifies the electronic structure of the disordered system leading to the changes of optical properties in the films – optical band gap (E_g), absorption coefficient (k) and refractive index (n). The photoinduced changes of refractive index (Δn) in as-evaporated amorphous As_xS_{1-x} and As_xSe_{1-x} systems were studied versus arsenic concentration. The values of Δn were measured by a two beam interferometry method at wavelength λ = 632.8 nm. The amorphous As-S and As-Se films were exposed by 514.5 nm and 632.8 nm laser line light, respectively. The obtained results are represented in Fig. 2. The maximum values of PhI refractive index changes in studied amorphous systems were observed for the compositions $As_{0.45}S_{0.55}$ (Δn = 0.1) and $As_{0.6}Se_{0.4}$ (Δn = 0.73).

Real-time holographic recording in amorphous As_2S_3 films versus film thickness, light intensity and grating period was studied. The recording processes and parameters were studied by elementary holographic gratings with the period (Λ) of 0.7 to 2.5 μm. Two different holographic recording-readout conditions in As_2S_3 films were studied: 1) grating recording at λ_1= 514.5 nm and read-out of diffraction efficiency at the same wavelength λ_2=514.5 nm (λ_1=λ_2); 2) grating recording at λ_1=514.5 nm and read-out of diffraction efficiency at λ_2=632.8 nm (λ_1≠λ_2).

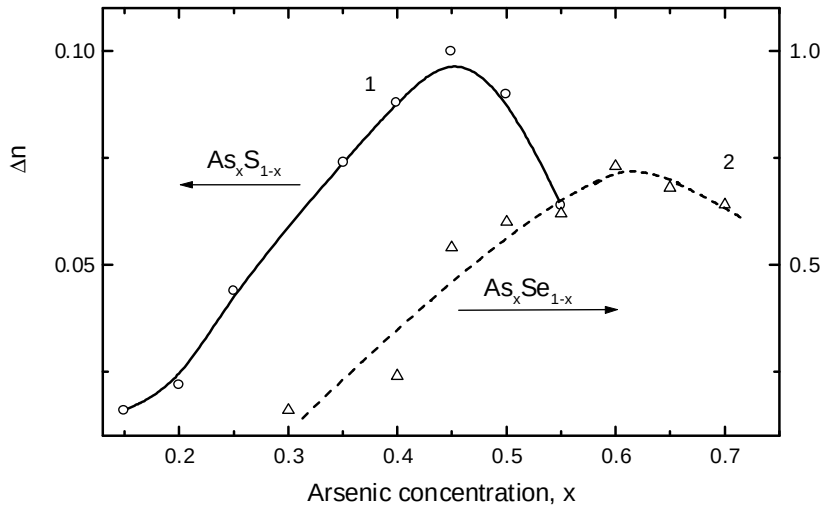

Fig. 2. Photoinduced changes of refractive index in as-evaporated As_xS_{1-x} (curve 1) and As_xSe_{1-x} (curve 2) films versus As concentration.

Some of the experimental curves showing variation in diffraction efficiency vs. exposure dose for various intensities of exciting laser beam can be seen in Fig. 3. These curves were obtained at a grating period of Λ = 0.7 μm. The maximum value of the real-time diffraction efficiency of ~78 % was obtained by recording at λ_1= 514.5 nm with intensity I ≤ 0.4 W/cm^2 and read-out at λ_2= 632.8 nm (curves 1-3). Hologram recording by λ_1=514.5 nm light in As_2S_3 films utilizes photoinduced variation of the absorption coefficient and the refractive index, which are related to photodarkening at wavelengths shorter than the absorption edge. Therefore to escape the absorption losses at hologram regeneration the use of read-out light wavelength longer than recording one, in which only variation of the refractive index plays an important role, is recommendable. In the case of recording and read-out by 514.5 nm light (λ_1= λ_2), when essential absorption of read-out light occurs, the obtained values of diffraction efficiency are considerably lower (curves 4 and 5).

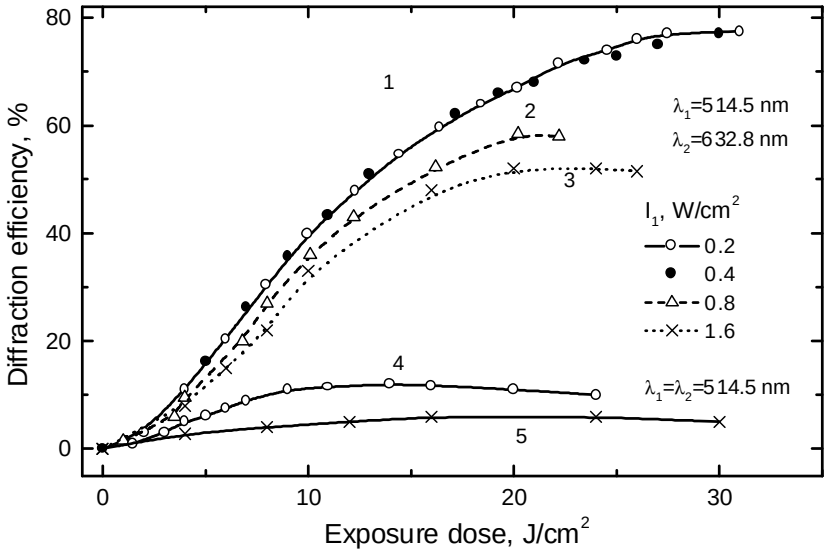

Fig. 3. Diffraction efficiency in As_2S_3 film (thickness d =5.2 μm) as a function of exposure dose for Ar^+ laser 514.5 nm line recording.

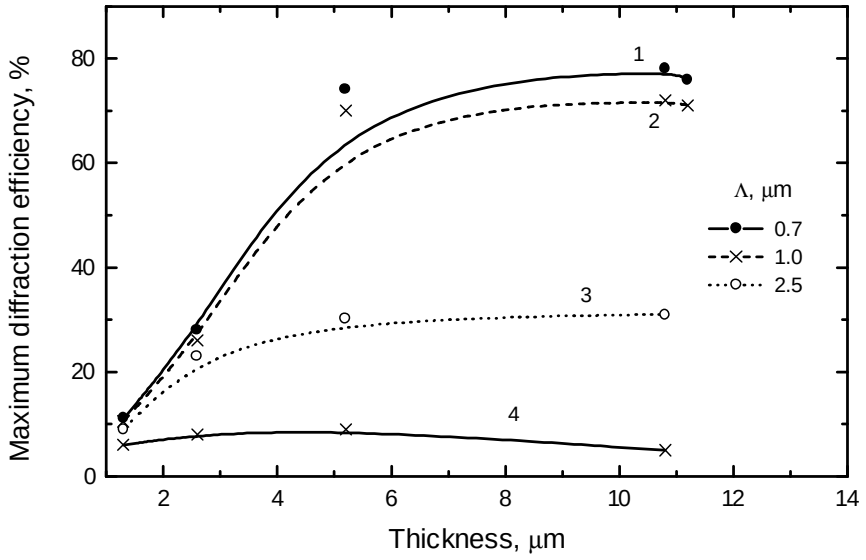

Fig. 4. The influence of film thickness and grating period (Λ) on the maximum diffraction efficiency in As_2S_3: a) recording by λ_1=514.5 nm and read-out of diffraction efficiency at λ_2 = 632.8 nm ($\lambda_1 \neq \lambda_2$) – curves (1-3); b) recording and read – out by λ = 514.5 nm ($\lambda_1 = \lambda_2$) – curve 4.

An increase of recording light intensity above 0.4 W/cm^2 is accompanied by a decrease of maximum diffraction efficiency that can be explained by appearance of thermal processes in the films under illumination with high intensity light. The type of the hologram (thick or thin) is determined by the relationship Λ/d, therefore the maximum diffraction efficiency strongly depends on the film thickness and grating period (Fig. 4). The maximum diffraction efficiency for As_2S_3 films is observed

at following conditions: film thickness $d \geq 5$ μm; grating period $\Lambda \leq 1$ μm; recording by $\lambda_1 = 514.5$ nm with intensity $I \leq 0.4$ W/cm^2.

3.2. Photo-induced changes in chemical reactivity of As-S-Se films

The light irradiation can change not only a number of physical properties of the AChS films but also their chemical reactivity, e.g. the dissolution rate in various alkaline inorganic and organic solvents [11]. The dissolution rate depends on the state and the chemical composition of the AChS films and their etchants. The etching rate of the unexposed and the exposed areas of the AChS films are generally different and the etching process of the films can be strongly influenced by the presence of surface active substances in the etchant.

Fig. 5 shows the dependence of the etching rate of amorphous As-S-Se films on the exposure dose of laser irradiation at different wavelengths. It is seen that the amorphous As-S-Se films are more sensitive for shorter wavelength light. The ratio of etching rate for the exposed (V_{exp}) and the unexposed (V_{unexp}) areas of the films is $\gamma = V_{exp}/V_{unexp} \approx 1/5$. It was found that the as-evaporated As-S-Se films behave as a negative resist for an organic alkaline developer ($V_{exp} < V_{unexp}$), while after the thermal annealing at the glass-transition temperature (~190 ^{o}C) they become positive ($V_{exp} > V_{unexp}$). Fig. 6 illustrates the dependence of diffraction efficiency of a relief-phase grating in an amorphous As-S-Se film on the exposure dose of laser irradiation. Holographic gratings with a period of $\Lambda = 1$ μm were recorded using an Ar^+ laser (488 nm light) with intensity of $I_1 = I_2 = 2.8$ mW/cm^2. The readout of the diffraction efficiency of the gratings after etching in an alkaline organic solution (etching time was 100 seconds) was performed by the same wavelength light (488 nm). The readout laser beam was perpendicular to the grating surface and the intensity of the first reflected diffraction maximum was measured. The resist is linear up to exposure doses of ~ 200 mJ/cm^2.

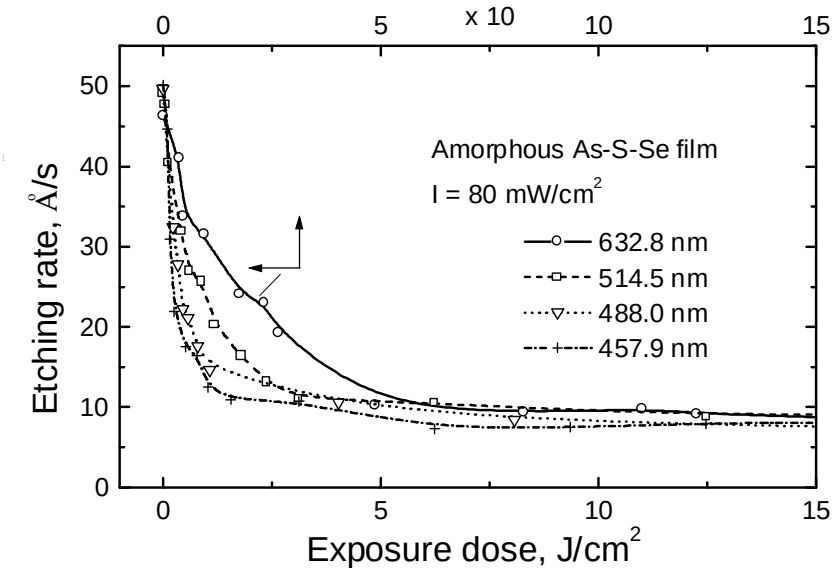

Fig. 5. Dependence of the etching rate in amorphous As-S-Se films on the dose of laser irradiation at different wavelengths.

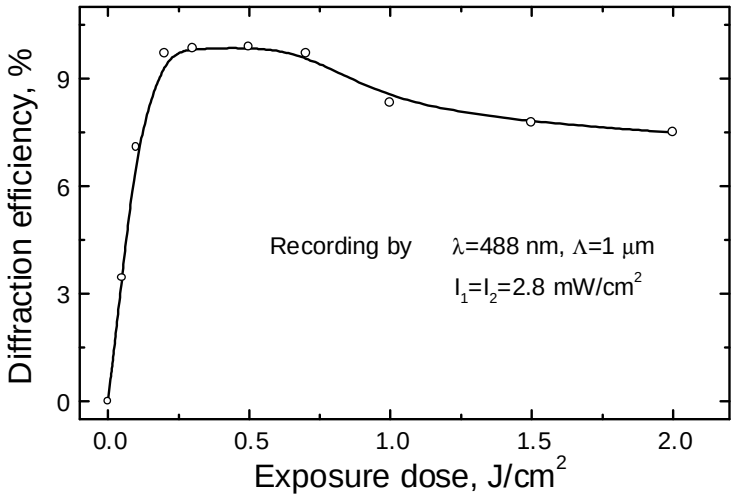

Fig. 6. Dependence of the reflection diffraction efficiency for a relief-phase grating in amorphous As-S-Se films on the dose of laser irradiation.

The AChS photoresists possess many advantages, such as very high resolution, photosensitivity in the visible and near IR spectral range, and the ability to be used as positive or negative resists depending on the resist chemical composition and the developer. The AChS photoresists can be used for the production of embossed holograms. The negative photoresist developed at the Institute of Solid State Physics (University of Latvia) possesses a light sensitivity of 100 mJ/cm^2 and a spectral sensitivity range at $\lambda \leq 700$ nm. Thus it is possible to realize holographic recording in AChS resists by means of a diode pumped solid state laser ($\lambda = 532$ nm).

3.3. Electron beam induced changes in chemical reactivity of AChS films

The modern electron beam lithography (EBL) technique enables the realization of increasingly sophisticated diffractive optical elements, which are based on the diffraction of the light by microstructured surfaces. One of the critical aspects of the EBL process is the selection of a suitable resist material, especially if highly efficient DOEs with a continuous surface profile are to be fabricated. An ideal resist for this purpose has a high resolution and sensitivity, a linear dependence of the profile depth on the electron dose, and a good repeatability of the profile-shape. The resist should also be suitable for the preparation of the nickel shim masters, which are used in the low-cost replication processes for the DOEs.

The dependence of the etching rate on exposure dose for amorphous As-S-Se and As_2S_3 films exposed by electrons with energy of 30 keV is represented in Fig. 7. It is seen that the as-evaporated As-S-Se films behave as a negative resist for an alkaline organic developer, while the As_2S_3 film behaves as a positive resist for a NaOH water solution doped with alkyl sulfonate as a surface active substance. The etching rate ratio of the exposed and the unexposed areas for amorphous As_2S_3 films is $V_{exp}/V_{unexp} \approx 15$.

A linear dependence of the profile depth on electron dose was obtained for both the as-evaporated and thermally annealed As-S-Se films, which makes this resist useful for recording of multilevel diffractive elements, at least if the period of the gratings is a few micrometers (Fig. 8). A profile depth of 1.25 μm was obtained for 2 μm thick films. This depth means that the maximum profile depth is about two read-out wavelengths for a He-Ne laser (632.8 nm) and elements with high diffraction efficiency can be fabricated [12]. The as-evaporated As-S-Se films behave as a negative resist for the alkaline organic developer, whereas the films annealed at 190 ^{o}C behave as a positive resist.

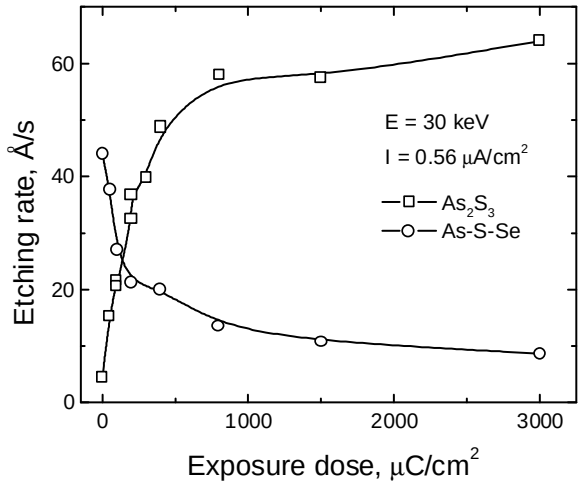

Fig. 7. Dependence of the etching rate in amorphous As_2S_3 and As-S-Se films on the dose of electron irradiation.

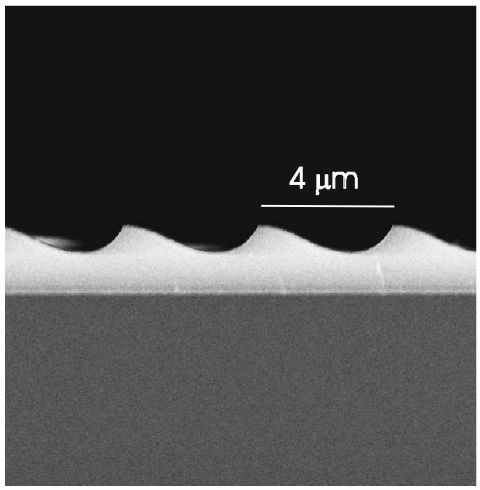

Fig. 8. Scanning electron micrographs of an eight-level-exposed slanted grating with a period of 4 μm recorded in an as-evaporated As-Se-S film.

3.4. Enhancement of holographic recording

Holographic recording in the AChS films possesses a unique property, the so-called self-enhancement (SE) of the holograms. An increase of the diffraction efficiency after the holographic recording over time without any special treatment (so called dark SE) has been observed. The changes of the diffraction efficiency in the amorphous As_2S_3 were studied as a function of aging time, initial diffraction efficiency, recording light intensity, temperature and the material of the substrate [13]. The dark self-enhancement process of the diffraction efficiency of the holographic gratings can be accelerated either by heating at the temperatures up to 100 ^oC or by an additional illumination after the holographic recording (Fig. 9) [6,7]. For the holographic gratings with the initial diffraction efficiency of $\eta_0 \approx 0.02$ % the enhancement factor up to $\xi = \eta/\eta_0 \approx 1000$ was gained (Fig. 10). The possibility of the light- and thermo-induced amplification of diffraction efficiency of the holograms after their recording is especially important for a further improvement of the light sensitivity of the AChS photoresists. The self-enhancement phenomenon is explained by the presence of the internal

mechanical stresses in the amorphous films, arising during the process of their preparation by thermal deposition in vacuum.

The observed light- and thermo-induced increase of the holographic grating self-enhancement can be explained in the following way. According to *Trunov* [14] internal mechanical stresses appear in amorphous As_2S_3 films during their formation and these stresses may be decreased by the light illumination. Thus in holographic recording process periodic distribution of internal mechanical stresses is formed. The stress distribution depends on the HG period and the recording light intensity. During holographic recording photo-induced decrease of compressive stress takes place in HG maximum. As a result a mechanical stress gradient arises between the HG maximum and minimum. It is suggested that smoothing of the gradient with time is the main origin of the appearance of the holographic self-enhancement phenomenon in amorphous As_2S_3 films. It is believed that viscous flow is responsible for the stress relaxation in strained glasses. This flow of the material is determined mainly by viscosity. The light- or thermo-induced weakening of intermolecular forces causes the essential decrease of the viscosity of amorphous As_2S_3 and the relaxation processes in the amorphous film are released.

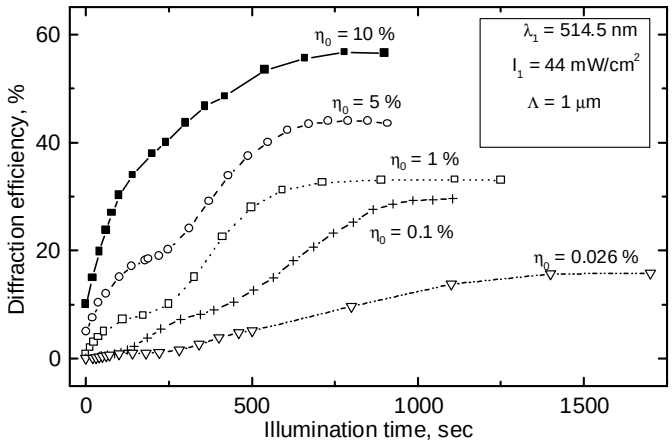

Fig. 9. Dependence of the light-stimulated HG enhancement in amorphous As_2S_3 films on the illumination time and initial diffraction efficiency. The illumination was performed by λ_1 = 514.5 nm and the readout by λ_2 = 632.8 nm. Both the lasers were set at the Bragg angle.

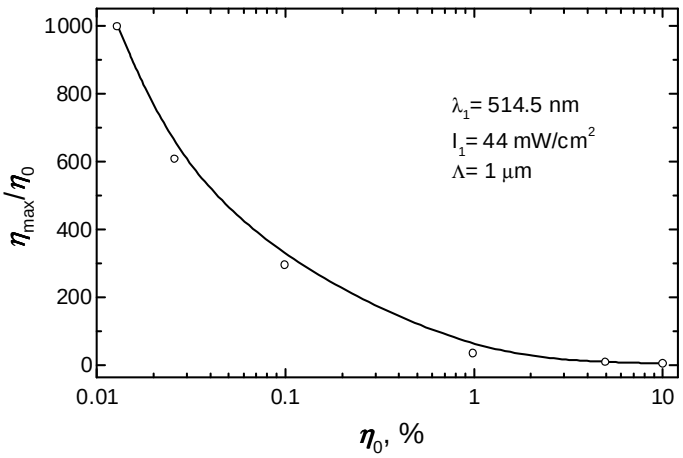

Fig. 10. Dependence of the light-stimulated HG enhancement factor in amorphous As_2S_3 films on the initial diffraction efficiency. The illumination was performed at λ_1 = 514.5 nm and the readout at λ_2 = 632.8 nm.

3.5. Fabrication of Bragg grating structures

The Ar^+ laser 488.0 nm; 501.7 nm; 514.5 nm and 528.7 nm lines were used for recording the Bragg gratings in amorphous as-evaporated As_2S_3 films. A spatially filtered and collimated light beam from the laser was divided into two beams with equal intensity ($I_1 = I_2 = 15.6$ mW/cm^2). The recording and testing of the Bragg gratings was performed with the same wavelength. Fig.11 shows typical dependence of diffraction efficiency changes during the recording process. A rapid increase of diffraction efficiency (reflectivity) of Bragg grating is observed in the beginning of recording process. After reaching the maximum a decrease of reflectivity of gratings follows. The time required for recording the maximum diffraction efficiency decreases with the increase of the film thickness.

Amorphous As_2S_3 films are high refractive index material with $n = 2.6$ at $\lambda = 514.5$ nm and remarkable photo-induced changes ($\Delta n \approx 0.15$) are observed in these films under Ar^+ laser illumination. The period of Bragg grating is determined by expression $\Lambda = \lambda / 2n \sin\theta/2$, where λ is laser wavelength; n - refractive index of As_2S_3 film and θ is angle between laser beams inside the film. Consequently, if the angle between laser beams is $\theta = 180^o$, we obtain Bragg grating with the period $\Lambda = 0.0989$ μm for $\lambda = 514.5$ nm. Due to the high value of the film refractive index an increase of the period is insignificant by decreasing the angle between laser beams. If the angle between the laser beams in air is $\alpha_1 + \alpha_2 = 90^o$ the value of the period increases up to $\Lambda = 0.1028$ μm.

Fig.12 illustrates the dependence of the maximum diffraction efficiency on the film thickness. It is seen that the diffraction efficiency increases with the sample thickness, passing a maximum at around 2 – 4 μm, and then decreases. The initial increase of diffraction efficiency can be related to an increase in the reflector thickness, while the decrease of diffraction efficiency for thicker As_2S_3 films may be related to the increase of read out laser light absorption. The calculated light sensitivity of the As_2S_3 films with thickness of 2 – 4 μm for Bragg grating recording with $\lambda = 514.5$ nm is of ~0.6 J/ %·cm^2.

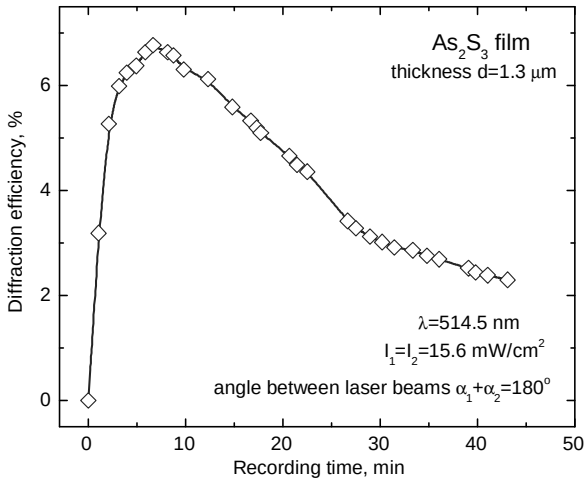

Fig. 11. Dependence of diffraction efficiency (reflectivity) on recording time.

This value is many times less than recording energy of Bragg grating reflector by He-Ne laser light (632.8 nm) [15,16], where exposure time for recording by light intensity of 100 W/cm^2 is 0.5-1 h. It is well known that the photo-induced changes of optical properties in amorphous As_2S_3 films are more effective for light in the region of optical absorption edge [8]. With regard to the photo-induced changes, the most remarkable difference may be that the 632.8 nm light (1.96 eV) is absorbed in Urbach tail region, whereas the quantum energy for Ar^+ laser lines (2.35-2.54 eV) is compared with the band-gap energy of As_2S_3 (2.4 eV) [17]. As a result, the values of the refractive index change are different: $\Delta n \approx 10^{-2}$ for recording by He-Ne laser [16] and $\Delta n \approx 0.15$ for recording by Ar^+ laser light. Hence, in the amorphous As_2S_3 films, efficient Bragg filters can be formed in more short distance by recording with Ar^+ laser light (2-4 μm, see Fig. 12) comparing with recording by He-Ne laser light, when the optimum thickness of the samples is 100 μm.

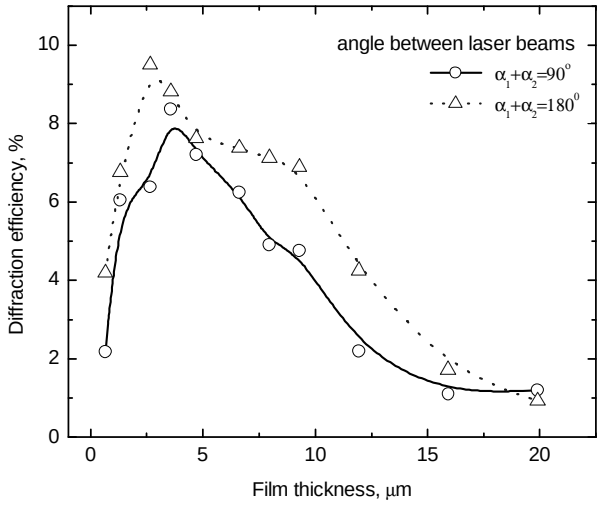

Fig. 12. Dependence of maximum diffraction efficiency on the film thickness.

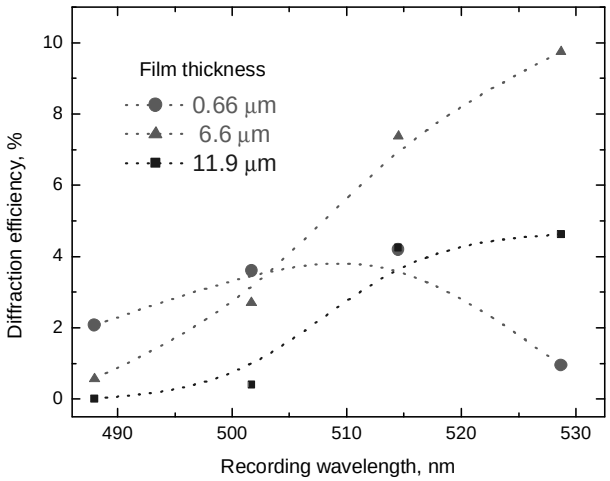

Fig. 13. Dependence of maximum diffraction efficiency on recording wavelength.

Fig. 13 shows the dependence of the maximum diffraction efficiency on the recording wavelength of Ar^+ laser for three different thicknesses of the As_2S_3 film samples. An increase of diffraction efficiency is observed for longer recording wavelengths. Only for very thin films (0.66 μm) the diffraction efficiency for $\lambda > 520$ nm decreases that can be explained by decrease of a number of reflector layers in the film.

It is known that the most effective holographic recording of transmission holograms in amorphous chalcogenide semiconductor films can be obtained by so-called two-wavelength method [18]. The grating recording is performed by Ar^+ laser light that is absorbed by the As_2S_3 film, but read-out is performed with longer wavelength light to escape the absorption. As a result, a holographic recording with high diffraction efficiency can be obtained.

Further studies of Bragg grating recording in As_2S_3 films by two-wavelengths method are in progress.

4. Summary

Amorphous As-S-Se and As_2S_3 films were studied as a recording media for optical holography and electron beam lithography. It is shown that the as-evaporated As-S-Se films can be used as a negative resist with light sensitivity ~100 mJ/cm^2 and spectral sensitivity in the visible spectral region $\lambda \leq 650$ nm. Thus it is possible to realize the holographic recording by strong lines of Ar^+ laser (lines 488.0 nm and 514.5 nm) or diode pumped solid state laser (532 nm). The amorphous As-S-Se resist has been successfully applied for the manufacturing of embossed holographic label [19]. The linear dependence of the profile depth on the electron irradiation dose makes these resists useful for recording the multilevel diffractive optical elements by electron beam lithography.
The transmission holographic gratings with high diffraction efficiency (~ 80%) can be recorded in amorphous As_2S_3 films. To escape the absorption losses at hologram regeneration the read-out light wavelength longer than recording one was applied. After recording an enhancement of the diffraction efficiency of the holograms is possible.

It is shown that Bragg grating structures with the period $\Lambda \approx 0.1$ μm can be recorded in amorphous chalcogenide semiconductor thin films.

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