

APPLICATION OF AMORPHOUS CHALCOGENIDE SEMICONDUCTOR THIN FILMS IN OPTICAL RECORDING TECHNOLOGIES

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A detailed study of the amorphous As-S-Se films as recording media for optical holography and lithography is presented. The holographic recording of transmission and relief-phase gratings were studied. The recording of refractive index and surface-relief modulated gratings with a period of 0.15 – 1.0 μm are demonstrated.

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1. Introduction

During the past 10 years, research in the field of optical materials based on amorphous chalcogenide semiconductors has made significant advances. Much of this research is driven by applied interest and this field of research is extremely broad and active [1,2]. The optical memory effect in amorphous semiconductor thin films was demonstrated a few decades ago [3]. In particular these films have been actively studied as holographic recording media [4,5]. The practical use of amorphous chalcogenide thin films in holography and lithography has probably only just begun, but already produced some promising results. Amorphous chalcogenide layers are thought to be one of the promising media for optical recording of information with high density due to the high resolution and refractive index values of these materials. The maximum values of refractive index photoinduced changes in studied amorphous systems are observed for the compositions $\text{As}_{0.45}\text{S}_{0.55}$ ($\Delta n=0.1$) and $\text{As}_{0.6}\text{Se}_{0.4}$ ($\Delta n=0.73$) at $\lambda=0.6328 \mu\text{m}$. The large values of refractive index changes enable the holographic recording in thin layers with high diffraction efficiency in a real time. The holographic gratings with diffraction efficiency more than 80 % in amorphous As_2S_3 thin film can be recorded. One interesting possibility is offered by application of amorphous chalcogenide materials in nanolithography. Because the effective wavelength inside the material is reduced by the refractive index n , the minimum feature size focused in material is reduced by a factor $1/n$ compared to focusing in air or vacuum. This could be another very fruitful research area with important practical meaning.

The main functional principles and practical application of amorphous chalcogenide photoresists for production of the embossed *rainbow* holograms and holographic optical elements are discussed by a number of authors [6-9]. The laser interference lithography is used as a low-cost method for the exposure of large surfaces with regular patterns like subwavelength-gratings and microsieves [10]. The regular features with the sizes of about 50 nm and less can be fabricated by this method. The Bragg reflection gratings were recorded and studied in amorphous As_2S_3 and As-S-Se films. Formation of Bragg grating structures in the waveguides is an important technology for the development of optical devices applicable to wavelength division multiplexing optical network. Especially the access network requires a low cost and highly reliable waveguide devices. Amorphous chalcogenide thin films are thought to be one of the potential materials for all-optical integrated circuits for the optical communication systems due to their excellent infrared transparency, large nonlinear refractive index, and low phonon energies [11,12].

The present paper reports some new results in the studies of the amorphous As-S-Se films as optical recording media for holography and lithography.

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2. Holographic recording of transmission gratings

Illumination of amorphous chalcogenide thin films by bandgap light leads to appreciable changes of their optical properties. This phenomenon is well-studied and possesses both scientific and technological importance [13]. The photo-induced atomic structure variations modify 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 photo-induced changes of refractive index (Δn) mainly have studied in as-evaporated amorphous As_xS_{1-x} and As_xSe_{1-x} systems [4,5,14]. Due to the large values of the photoinduced changes of optical properties in a real time the thin films of amorphous chalcogenide semiconductors are very promising media for holographic recording, storage and processing of information [15].

The optical properties of thin films of the glass-forming system $(As_2S_3)_{1-x}(As_2Se_3)_x$ recently are extensively studied and data for the absorption coefficient, the band-gap and the refractive index and their changes after illumination are reported by several authors [16-18]. It is known that this system is structurally homogeneous for all values of x ($0 \leq x \leq 1$). Therefore the optical band-gap for thin films of this system can be changed continuously from 1.79 eV ($x=1$; As_2Se_3) up to 2.43 eV ($x=0$; As_2S_3) enabling to optimise the optical properties of the films for the holographic recording.

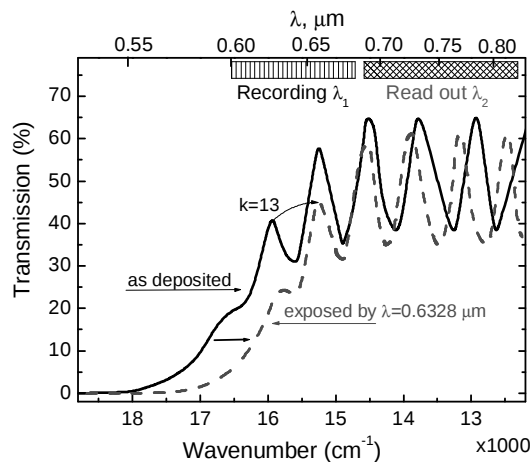


Fig.1. Spectral dependence of transmittance for $As_{40}S_{15}Se_{45}$ film before and after illumination by $\lambda=0.6328 \mu m$ light up to saturation. A shift of the number of interference order ($k=13$) indicates on the refractive index changes. The optimum spectral range for recording (λ_1) and read-out (λ_2) is shown.

In our experiments thin $As_{40}S_{15}Se_{45}$ ($x = 0.75$) films were deposited by thermal evaporation with a deposition rate 30 nm/s and the optical constants were studied. The optical transmission versus wavelength, before and after exposure to light is presented in Fig. 1. The optical band-gap for as-evaporated film $E_g=1.9$ eV obtained from Tauc plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ is in good agreement with results in [18]. It was found that illumination induced the absorption edge shift to the longer wavelengths (an effect of photodarkening) and the photoinduced changes of band-gap $\Delta E_g \approx 0.07$ eV were obtained. The measurement of interference pattern in transmission spectrum and a control of its shift during the illumination process enables calculation of dispersion curve of refractive index both for as-evaporated and illuminated films. The spectral dependence of refractive index and its changes under red light ($\lambda_1 = 0.6328 \mu m$) illumination (5, 15 and 30 minutes at intensity $I = 183 \text{ mW/cm}^2$) are shown in Fig. 2. The calculated value of refractive index at $\lambda_2 = 0.805 \mu m$ for as-evaporated film was $n = 2.49$ and its increase by $\Delta n_{\text{sat.}} = 0.16$ after red light illumination was observed. The value of photoinduced changes of refractive index increases in the direction of shorter wavelengths.

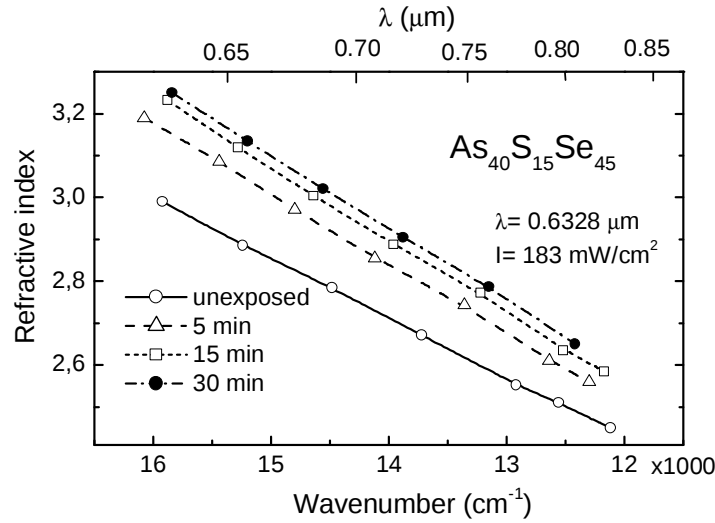


Fig. 2. Spectral dependence of refractive index of $\text{As}_{40}\text{S}_{15}\text{Se}_{45}$ films before and after illumination by $\lambda=0.6328 \mu\text{m}$ light at intensity $I=183\text{mW/cm}^2$ for different exposure time.

The holographic recording in AChS films utilizes the variation of the absorption coefficient and the refractive index, which are related to photodarkening at wavelengths shorter than the absorption edge. The most effective holographic recording with diffraction efficiency up to 100 % can be obtained in thick phase gratings, in which only variation of the refractive index plays an important role. Therefore, a light with a wavelength longer than the absorption edge should be used for hologram regeneration to escape the light absorption losses.

The type of the hologram (thick or thin) is characterized by an expression $Q = 2\pi\lambda_2 d / n_0 \Lambda^2$, where λ_2 is regeneration wavelength at Bragg angle and Λ grating period, but d and n_0 denote a thickness of grating and refractive index of the film, respectively. The values of $Q \leq 0.3$ and $Q \geq 10$ correspond to the Raman-Nath diffraction (thin phase grating) and the Bragg diffraction (thick phase grating), respectively. Consequently, to obtain thick phase holographic recording in amorphous AChS films, the minimum grating thickness should be at least $d \approx 5 n_0 \Lambda^2 / \pi\lambda_2$. This value for the thick phase grating (if $\Lambda = 1 \mu\text{m}$ and $\lambda_2 = 0.805 \mu\text{m}$) in amorphous $\text{As}_{40}\text{S}_{15}\text{Se}_{45}$ films is of $d \approx 5 \mu\text{m}$. The grating thickness is determined by the penetration depth of recording light λ_1 in the film during the holographic recording process. On the one hand the recording light must be effectively absorbed by the film to decrease the exposure dose, on the other hand the recording light must be penetrated in the film deep enough to provide the conditions of thick grating to obtain high value of diffraction efficiency. The optimum values of the absorption coefficient of the film for recording wavelength λ_1 are in the range of $5 \cdot 10^2 - 5 \cdot 10^3 \text{ cm}^{-1}$ depending mainly on the grating period. The average penetration depth of recording light λ_1 in the film depends on the value of absorption coefficient (α) at this wavelength according to $d=1/\alpha$. The conditions for recording of thick phase gratings can be optimised by changing the chemical composition of the film or recording light wavelength to get the optimum for $\alpha=1/d$. The read-out light (λ_2) must be inactive regarding the amorphous film to escape the erasing of the recording and absorption losses during the regeneration process. Therefore the light with wavelength longer than recording one ($\lambda_2 > \lambda_1$) should be used for holographic recording read-out and the absorption coefficient of the amorphous film for this wavelength must be $\alpha < 10 \text{ cm}^{-1}$.

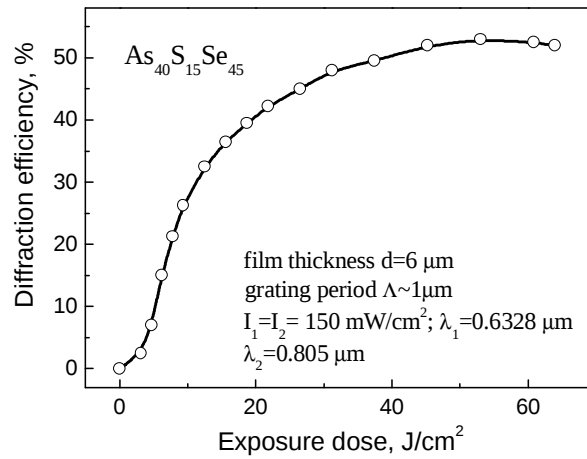


Fig. 3. Diffraction efficiency of holographic grating in amorphous As₄₀S₁₅Se₄₅ film as a function of exposure dose. Recording and read – out at Bragg angle was performed with wavelengths $\lambda_1 = 0.6328\ \mu\text{m}$ and $\lambda_2 = 0.805\ \mu\text{m}$, respectively.

Diffraction efficiency for thick phase holographic gratings can be expressed as

$$\eta = \sin^2(\pi d \Delta n / \lambda_2 \cos \Theta), \quad (1)$$

where Θ is Bragg angle and Δn is the refractive index modulation amplitude for read out light λ_2 . The calculations show that the maximum of this expression for $\Lambda=1\ \mu\text{m}$, $d=5\ \mu\text{m}$ and $\lambda_2=0.805\ \mu\text{m}$ can be obtained for $\Delta n = 0.047$. The maximum available photoinduced changes of refractive index in amorphous As₄₀S₁₅Se₄₅ films for a light with wavelength $\lambda_2=0.805\ \mu\text{m}$ as it is mentioned above are 0.16. Consequently, the amorphous As₄₀S₁₅Se₄₅ films can be successfully applied for holographic recording of thick phase gratings with high diffraction efficiency (see Fig. 3).

3. Holographic recording of surface-relief gratings

The copying of surface-relief microstructures by replication techniques such as hot embossing, moulding or casting is a key technology for the low-cost mass-production of diffractive optical elements (DOEs) and other optical elements with micrometre- or nanometre-sized features. Replication technology is used for the commercial production of submicron grating structures (hot embossed diffractive foil and security holographic labels) and data storage microstructures (injection moulded compact discs). The basic replication process involves the copying of a surface-relief microstructure from a metal form into a formable material such as a thermoplastic or curable polymer. The original microstructured element is fabricated in the so-called resist material by optical or electron-beam microstructuring technology. It is then electroformed to a nickel shim used in replication process.

The light irradiation can change not only a number of physical properties of the amorphous chalcogenide films but also their chemical reactivity, e.g. the etching rate in various alkaline inorganic and organic solvents enabling to use these materials as photoresist. The etching rate of exposed and unexposed areas of the amorphous chalcogenide films is generally different and depends on the state and chemical composition of the films and their etchant. The factors that influence the etching rate including film deposition method and rate, layer chemical composition, exposure conditions, etchant type and concentration, temperature etc. were studied by a number of research groups [8,14,19,20]. The etching process of the films can be strongly influenced by the presence of surface-active substances in the etchant. The obtained values of etching selectivity, the ratio of etching rate for

exposed and unexposed areas, can attain hundreds. The amorphous chalcogenide films can be used as a positive (the etching rate increases with exposure) or negative (the etching rate decreases with exposure) photoresist depending on chemical composition of the film and applied etchant properties. The photoresists based on amorphous chalcogenide films are successfully applied in the manufacturing process of embossed rainbow holographic labels by a number of holographic companies (Hologramma Ltd, HoloGrate) [9]. The negative photoresist based on As-S-Se system possesses a light sensitivity of $\sim 100 \text{ mJ/cm}^2$ and a spectral sensitivity range at $\lambda \leq 650 \text{ nm}$. The main advantage of amorphous chalcogenide photoresists is that holographic recording can be performed by strong lines of Ar^+ laser (488 or 514.5 nm) or diode pumped solid state laser (532 nm).

The fringe period for two intersecting coherent light beams can be expressed as

$$\Lambda = \lambda_0 / 2 n \sin \theta, \quad (2)$$

where λ_0 is the wavelength of laser light in vacuum, n is refractive index of the medium that surrounds the resist and θ is the half-angle between the laser beams. The smallest period that can theoretically be obtained is for $\theta = 90^\circ$ and is equal to $\lambda_0 / 2 n$. Fig. 4a illustrates how the interference pattern can be created by two coherent laser beams on the resist surface in air. In this case $n \approx 1$ and grating period is determined by laser light wavelength and angle between the beams. The decrease of the grating period can be realized mainly by using shorter recording laser wavelength. The angle between laser beams does not exceed 120° because an increase of half-angle above 60° is accompanied by drastic increase of reflection losses for recording beams and the same time the numerical changes of $\sin \theta$ for $\theta > 60^\circ$ are negligible. The gratings were recorded in As-S-Se based photoresist using Ar^+ laser line $\lambda = 0.488 \mu\text{m}$ and angle 90° between laser beams. After recording the etching of photoresist was performed to obtain surface-relief grating, and the grating period and profile was measured by AFM. If Ar^+ laser 488 nm line was used for recording and angle between the beams was equal to 90° , the grating with a period of $0.345 \mu\text{m}$ was obtained (Fig. 4a).

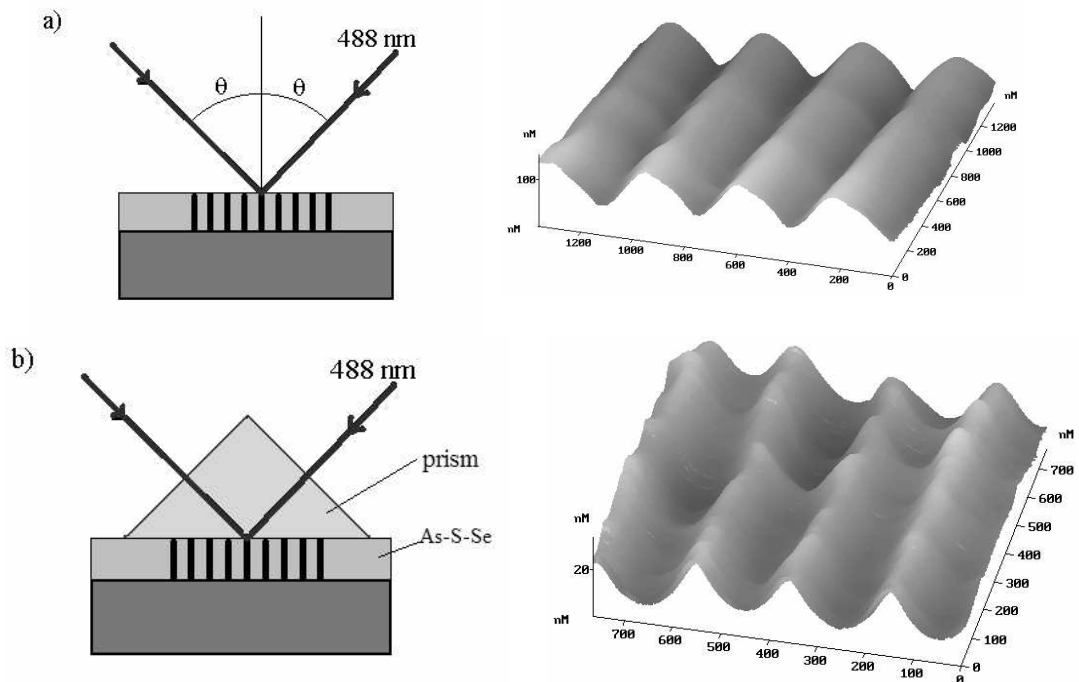


Fig. 4. Interference pattern recording ($\lambda = 0.488 \mu\text{m}$, $\theta = 45^\circ$) and AFM picture of the grating after etching in As-S-Se resist. An intersection of the laser beams in: a) air ($n = 1$), grating period $\Lambda = 0.345 \mu\text{m}$; b) prism with $n = 1.75$, grating period $\Lambda = 0.197 \mu\text{m}$.

If the intersection of the laser beams is performed in media with refractive index of 1.75, using right angle prism, the obtained value of a grating period is $0.197\ \mu\text{m}$ (Fig. 4b). It is seen that an application of the prism decreases the period of the recorded grating n times according to expression (2). It is worthy mentioning that the depth-of focus of laser interference lithography method is dependent on the coherent length of the light and can be of the order of metre and more, compared to microns for conventional optical lithography systems. As a result, the demands on substrate flatness and resist layer positioning are not critical. The regular features with the sizes of about 50 nm and less can be fabricated by this method using the prisms with refractive index of 3 and more as well as decreasing the recording laser wavelength. This method is perfectly suitable for production of regular patterns like subwavelength-gratings and microsieves. It should be mentioned that such recording method could be realized only using resists with high refractive index to escape the total reflection by the prism-resist interface. The demands for resist refractive index are as follows – $n_r > n_p \sin \theta$, where n_p is a refractive index of material for used prism and θ is the half-angle between the laser beams inside the prism. For example, if a prism with $n_p = 3$ and the half-angle $\theta = 60^\circ$ are used in the recording process, a resist with $n_r > 2.6$ must be applied. As seen in Fig. 2 a resist based on As-S-Se system can fulfil this requirement.

4. Conclusions

The use of amorphous chalcogenide thin films in holography and lithography has probably only just begun, but already produced some promising results. Amorphous chalcogenide layers are thought to be one of the promising media for optical recording of information with high density due to the high resolution and refractive index values of these materials. The large values in photoinduced changes of refractive index enable the holographic recording in thin layers with high diffraction efficiency. One interesting possibility is offered by the application of amorphous chalcogenide materials in nanolithography. Because the effective wavelength inside the material is reduced by the refractive index n , the minimum feature size focused in material is reduced by a factor $1/n$ compared to focusing in air or vacuum. This could be another very fruitful research area with important practical meaning.

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