

**PHYSICAL PROPERTIES AND STRUCTURE OF AMORPHOUS
 $\text{Ag}_x(\text{Sb}_{0.33}\text{S}_{0.67})_{100-x}$ PREPARED BY OPTICALLY- INDUCED
DIFFUSION AND DISSOLUTION OF SILVER INTO SPIN-COATED
AMORPHOUS $\text{Sb}_{33}\text{S}_{67}$ FILMS AND THEIR APPLICATION
FOR OPTICAL RECORDING**

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The $\text{Sb}_{33}\text{S}_{67}$ amorphous films were prepared by standard spin-coating technique. Prepared films were stabilized in a vacuum and then annealed in inert argon atmosphere. Silver film was deposited on top of $\text{Sb}_{33}\text{S}_{67}$ film by vacuum thermal evaporation technique. The technique of step-by-step optically-induced diffusion and dissolution of Ag in $\text{Sb}_{33}\text{S}_{67}$ amorphous films has allowed to design films with exact silver concentration. The host $\text{Sb}_{33}\text{S}_{67}$ films were photodoped by dissolution of thin (~ 10 nm) film of silver, which resulted in amorphous films of good optical quality. We have analyzed affect of silver doping in the host materials on their composition, thickness, optical and thermal properties, their structure. Application of such films has been tested. The holographic gratings and optically-induced crystallized spots perspective for optical memories have been produced.

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1. Introduction

Thin films of arsenic, antimony and germanium chalcogenides have been investigated in a numerous applications, such as photoresists [1], gratings [2] and waveguides [3]. Recently, chalcogenides were applied in industrial dimension as recording materials in DVD technique [4]. There is continuing research on suitable thin film optical recording materials and materials for optical memories. Thin films of chalcogenides have been mainly deposited onto the substrates using vacuum coating techniques, i.e. thermal evaporation, sputtering or laser ablation [5, 6]. The optical recording chalcogenide materials are typically ternary or multinary chalcogenides [4]. Silver containing chalcogenides have also good potential to be used in such application. Such materials are technologically difficult to deposit by traditional vacuum techniques due to technological or cost restrictions. Previous studies of e.g. Ag-As-S thin films deposition [5] have mainly been focused on films in As-S system prepared by vacuum evaporation and consequently doped by making use of optically induced silver dissolution and diffusion (OIDD) effect. Previous investigation in various laboratories [7, 8] have also shown that binary chalcogenides can be deposited in technologically useful thin film form by an inexpensive technique of spin-coating deposition from solutions. Such films have demonstrated similar properties and potential applications [9] as vacuum deposited films.

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Ternary films could similarly be prepared by combining spin-coating technique and optically induced silver dissolution (OIDD) of thin Ag film. Amorphous films where As is replaced by Sb could be advantageous as surface oxidation of Sb based amorphous films is significantly reduced. This fact could be of great importance for some applications in optics, microoptics and optically recorded memories. Our aim was to prepare suitable silver-doped amorphous Sb-S films. The technique of OIDD of Ag into Sb₃₃S₆₇ amorphous spin-coated films and properties of such films are studied in this work.

2. Experimental procedure

Bulk chalcogenide samples with composition of Sb₃₃S₆₇ were prepared by standard synthesis from pure elements in evacuated quartz ampoules placed in rocking furnace (T = 900 °C, 24 hours). Melt of the glass was quenched to room temperature. Obtained crystalline samples were powdered and then dissolved in n-butylamine into homogeneous dark brown solution. Thin films were prepared by spin coating of Sb₃₃S₆₇ organic solution for 20 seconds at a spin speed 2000 rpm. The vacuum furnace stabilization of spin-coated samples was carried out by heating at 90 °C during 8 hours. The host Sb₃₃S₆₇ films were photodoped by consecutive dissolving of thin (~10 nm) layers of silver, resulted in homogeneous films of very good optical quality. OIDD was carried out by illuminating the samples either in optical microscope with a lamp house equipped with 100 W tungsten lamp and IR-cut filter.

Microanalysis of samples has been carried out on an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray microanalyser IXRF Systems (detector GRESHAM Sirius 10, accelerating voltage of the primary electron beam 20 kV).

The optical transmission spectra of the films were recorded with Jasco V-570 UV/VIS/NIR spectrophotometer. The optical gap, $E_{g, opt.}$, was determined from the intercept on the energy axis of the linear fit of the high-energy data, in a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, which is a widely accepted procedure (Tauc extrapolation [10]).

Raman spectroscopy has been carried in the As₃₃S₆₇ films, as silver was photo-doped into the host matrix. The Raman spectroscopy study was performed on a Fourier Transformation (FT) Raman spectrometer (Bruker, model IFS/FRA 106). Raman spectra were excited using a laser beam with $\lambda = 1064$ nm having an output power 50 mW. The wavelength of the laser beam was critical to avoid any photostructural changes in these chalcogenide glasses within the time scale of 100 scans. The resolution of the Raman spectrometer was 1 cm⁻¹. The spin-coated films (Sb₃₃S₆₇) and photodoped films (Ag-Sb₃₃S₆₇) were both mechanically peeled from the substrates, and immediately pressed into aluminum targets for the Raman measurements.

The recent temperature-modulated differential scanning calorimetry (TMDSC, TA Instruments Q100) technique has been applied to the measurement of the thermal properties of amorphous Ag-Sb-S films. All samples in this work were exposed to the same temperature-modulated heating schedules with the average heating rate of 5°C/min in DSC regime. The total heat flow (HF) and a glass transition temperature T_g were obtained. Thermal gravimetry analysis (TGA) produced by TA Instrument (Q500) has been used to check the thermal region where residual solvent is released from the spin coated films during the heating schedule. The films were mechanically peeled from the substrates for the MDSC and TGA measurements, and immediately weighed into aluminium crimped pans and platinum pan, respectively. A typical film sample weight was less then 1 mg.

Holographic grating preparation was carried out by holographic illumination of the bilayer (Ag/Sb₃₃S₆₇) samples with monochromatic light from Ar⁺ ion laser ($\lambda = 514$ nm, with power 98.7 mW in one beam). The period of the intensity distribution was 1.5 μ m. Diffraction efficiency of prepared gratings was measured at a wavelength of 633 nm to an accuracy of ± 0.3 %. The grating surface and film thickness were measured with an atomic force microscope (AFM ULTRA Objective SIS company) with a resolution of ± 1 nm in the Z direction.

Spot laser exposure Ar⁺ ion laser ($\lambda = 514$ nm, P = 845.5 mW, I = 89 W/cm²) has been used to test optical recording ability of prepared films.

3. Results

Prepared bulk material with starting composition $\text{Sb}_{33}\text{S}_{67}$ and spin coated films with composition of $\text{Sb}_{33}\text{S}_{67}$ and Ag-Sb-S were analyzed by EDX analysis. The results of EDX quantitative analysis together with other important parameters ($E_{g, \text{opt}}$ and thickness) are summarized in Table 1. It is clear that ~15 at.% of Ag was photo-dissolved during OIDD process in Sb-S film.

Table 1. The composition, optical constants and other parameters of the source Sb-S sample and prepared spin coated films.

sample	Ag [nm]	composition [at.%]			$E_{g, \text{opt}}$ [eV]	film thickness [nm]
		Ag	Sb	S		
bulk Sb-S	0	-	33.5	66.5	-	-
film Sb-S	0	0	34.8	65.2	1.53	234
film Ag-Sb-S	10.1	15.3	29.1	55.6	1.48	240

Thermal properties of prepared binary films Sb-S film measured in TGA and DSC regime are compared in Fig. 1. TGA and TGA derivative curves show that stabilized spin coated films (see experimental part for explanation) decreases their weight in two thermal regions. First one is between 30 and 80 °C and second one is related to glass transition temperature. Glass transition region seems to be observable in DSC curves of the binary films between 127 and 152 °C and of ternary Ag-Sb-S films between 125 and 133 °C (Fig. 1).

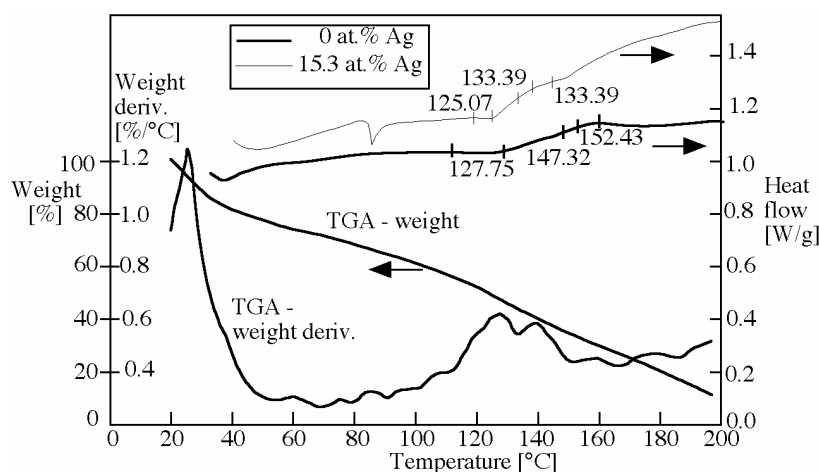


Fig. 1. TGA and DSC curve of studied spin coated films.

The typical optical transmission curves before and after OIDD and the calculated values of optical band-gap, $E_{g, \text{opt}}$, of prepared films are in Fig. 2 and Table 1, respectively. It is clear that as a consequence of silver dissolution in $\text{Sb}_{33}\text{S}_{67}$ spin coated films, there is a significant decrease of $E_{g, \text{opt}}$, from 1.51 eV down to 1.48 eV with 15 at.% Ag content in the films, can be noticed as a red shift on transmission curve. Deeper modulation of interference fringes on transmission curve of silver containing film means that index of refraction of prepared film increases.

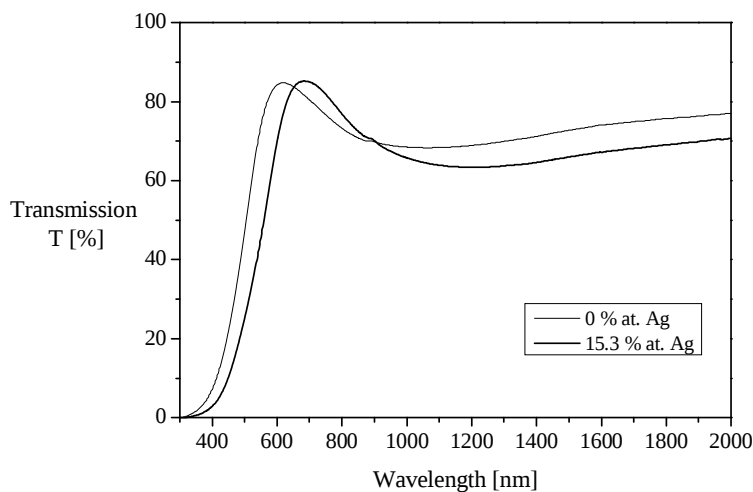


Fig. 2. Optical transmission curves of prepared binary Sb-S and ternary Ag-Sb-S films.

The Raman spectra measured in Sb-S and Ag-Sb-S films and source $\text{Sb}_{33}\text{S}_{67}$ bulk sample are shown in Fig. 3. The spectra were interpreted using reference [11]. The bulk $\text{Sb}_{33}\text{S}_{67}$ sample contains two strong bands at 287 cm^{-1} and 308 cm^{-1} (units $\text{SbS}_{2/3}$), which are hidden in broad band vibration of Sb-S spin coated film. There is in binary Sb-S bulk sample and Sb-S film band at 170 cm^{-1} due to an Sb-Sb vibration in $\text{S}_2\text{Sb-SbS}_2$ units and also bands at 140 and 475 cm^{-1} (S rings fragments), respectively. The consequent OIDD process of silver leads to a decrease of intensities of S units bands and increase of intensity of band at 170 cm^{-1} and shift of the main band at 290 cm^{-1} to lower frequencies. After silver is photodissolved in spin coated film maximum main vibration band is found at 323 cm^{-1} , which could be attributed in analogy with Ag-As-S system [12, 13] to SbS_3 pyramids or Sb_3S_6 unit [13] connected by S-Ag-S linkage or AgS_3 pyramids.

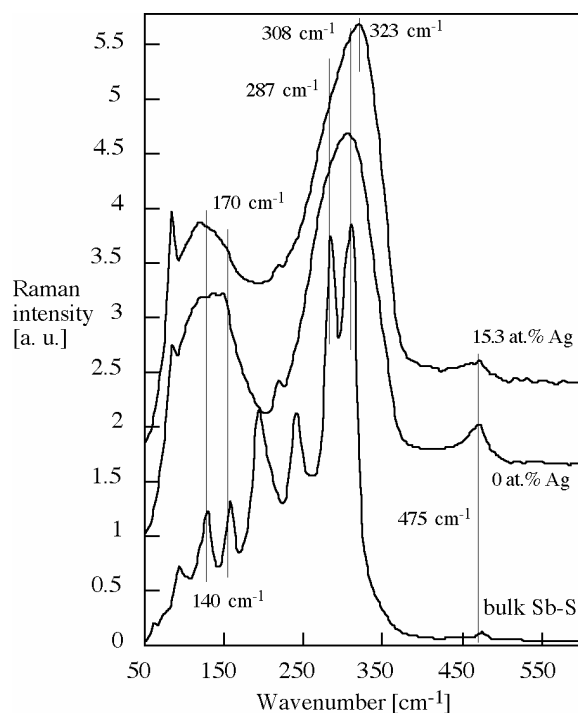


Fig. 3. Raman spectra of the source bulk sample and prepared spin coated films.

There were prepared holographic gratings making use of OIDD process of silver in Sb-S spin coated film. It was found an optimum exposure time (65 s) for present holographic set-up as maximum intensity of light which was diffracted into 1st diffraction order (+T1) as it is shown in Fig. 4. The diffraction efficiency of prepared grating was around 2 % measured in TM mode. Produced diffraction grating is presented in Fig. 5. Optical microscopy in transmitted light (Fig. 5) - indicates the presence of two phases, probably with sinusoidal distribution of Ag concentration, or at least sinusoidal-like distribution of it. It is expected that holographic exposure leads to such redistribution of Ag as the OIDD process is sensitive to light intensity modulation. Two phases are seen in the optical microscope as bright and dark stripes. The surface of the grating was measured by AFM which revealed the surface structure of the grating. The silver-rich stripes of the grating had an excursion amplitude 5 nm above the original layer surface.

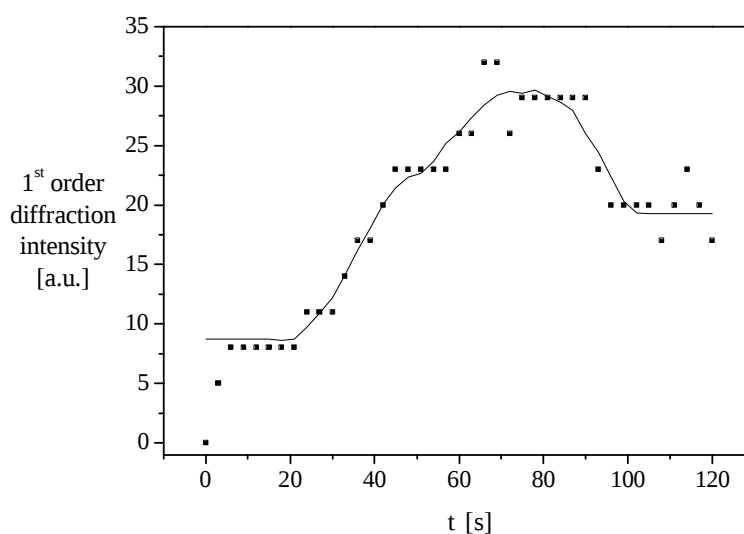


Fig. 4. Time dependence of intensity of the 1st diffraction order (+T1) during a holographic.

There was studied influence of argon ion laser laser focused to a 1 mm in diameter spot with intensity of 89 W/cm^2 on studied spin coated films. Exposure to light with such energy leads to photodarkening and photocrystallization of films in exposed spot as it is documented in Fig. 6. The kinetics of photodarkening of spin-coated binary and ternary films is presented in Fig. 7.

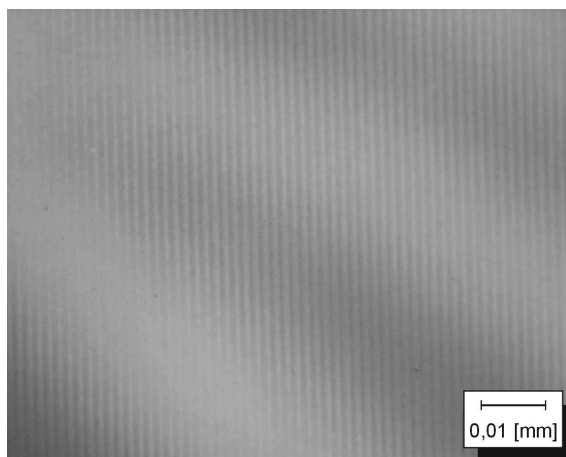


Fig. 5. A typical example of diffraction grating prepared by holographic exposure of Ar ion laser.

4. Discussion

Measured thermal properties of spin coated films are characterized by the decrease of weight in TGA curves in the region between 30 and 80 °C, which effect could be attributed to release of residual solvent present in films in agreement with [7]. The prepared spin-coated films have clearly amorphous character. The glass transition region is observable on heat flow curves (Fig. 1) in both binary Sb-S and ternary Ag-Sb-S film.

Optical properties, i.e. increase of refraction index, n , and the decrease of $E_{g, opt}$ value with Ag content increasing is clearly explained by the fact that the binding energies of Ag-S and Sb-Sb bonds, 217 and 175 kJ mol⁻¹, respectively, is much smaller than those of the Sb-S and S-S bonds, 260 and 280 kJ.mol⁻¹, respectively. Therefore, this leads to significantly smaller energy splitting between the states of the valence and conduction bands. Silver can create either one bond at the S-chain end or can break S-S bond in sulphur chains and rings. Their disappearance is clearly seen in Raman spectra (Fig. 3, curves $x = 0$ to $x = 15.3$). Optical transmission and Raman spectra of Ag-Sb-S films show also the homogenous OIRD reaction products between silver and spin-coated film.

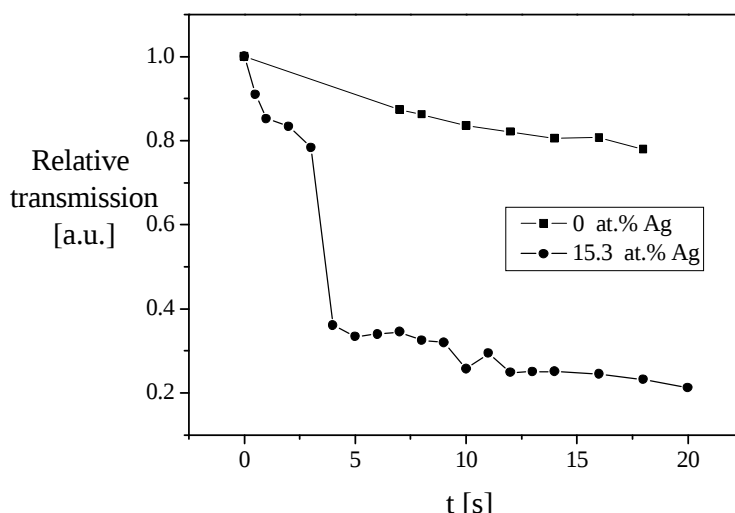


Fig. 6. Kinetics of photodarkening (photocrystallization) in spin coated Sb-S and Ag-Sb-S films during exposure by Ar ion laser with intensity $I = 89\text{W/cm}^2$.

The diffraction efficiency, optical microscopy and AFM examination demonstrate that for holographic exposure photo-dissolution of silver creates a phase grating while the attendant photo-expansion effects induces a shallow surface relief grating. Higher concentration of silver in light exposed areas compared to unexposed ones is a result of silver diffusion from unexposed parts. Silver-doped regions in exposed areas of the grating are conductively connected with the silver layer in unexposed part, so that elemental silver present there can provide a source of Ag ions from surface. As a result silver source in unexposed area depletes, which has been previously reported by Ong [14] and by Wagner [15]. The difference between photo-induced dissolution and photo-expansion is resolved by considering the process of surface dilatation which was discussed in details in [16]. The resulting diffraction efficiency of about 2% should be mainly due to the alteration in refractive index, i.e. the phase grating, although the surface relief structure does slightly contribute. It is important to note that altering the refractive index of the material using OIDD offers also a potential technique for the fabrication of artificial photonic crystals, if the effect is strengthened by selective dry or wet etching of photodoped films.

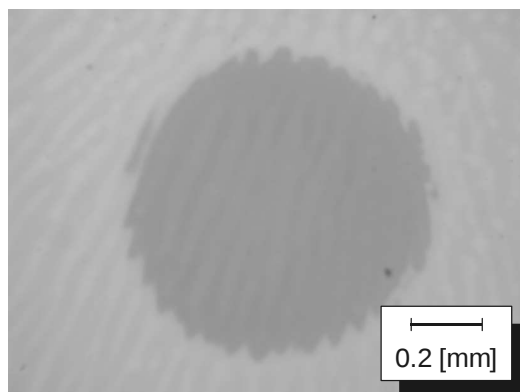


Fig. 7. A typical example of Ag-Sb-S spin coated film with Ar ion laser exposed spot (exposure time $t = 7\text{s}$).

Photodarkening (crystallization) induced in spin coated Sb-S and Ag-Sb-S films induced by continuous wave argon laser is clearly visible in Figs. 6 and 7. The percolation type of kinetic curve in case of Ag-Sb-S film could be explained by photocrystallization even though exposed spots remain optically homogeneous. Structural origin of the abrupt change in kinetic curve is currently under investigation. The potential application of such effect is in optical storage media.

5. Summary

There were prepared binary Sb-S and ternary Ag-Sb-S films by spin coating method combined with optically induced silver diffusion and dissolution in spin coated Sb-S films. Thermal, optical and structural properties of prepared film documented amorphous origin of prepared films, with good optical quality. We have demonstrated the possibility to alter the refractive index of the material by using the optically induced dissolution and diffusion (of silver) (OIDD) effect, thus opening the way towards the fabrication of artificial photonic crystals.

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