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Selective etching of spin-coated and thermally evaporated $As_{30}S_{45}Se_{25}$ thin films

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ABSTRACT

Chalcogenide glasses are intensively studied materials due to their interesting optical properties such as high values of refractive index, wide transparency in IR, photosensitivity, etc. We report on the comparison of photo and thermo-induced changes in optical properties and chemical resistance of thermally evaporated and spin-coated $As_{30}S_{45}Se_{25}$ thin films. Significantly different trends of photo-induced changes in chemical resistance in both types of thin films such as negative etching of thermally evaporated thin films and positive etching of spin-coated thin films were observed. The structural changes responsible for the observed phenomena were investigated as well.

1. Introduction

Chalcogenide glasses (ChGs) are promising materials for many applications (especially in IR optics) due to their interesting physical and chemical properties such as high values of refractive index, wide transmission window in IR spectral range, frequent photosensitivity which together with good solubility in alkaline solutions often results in selective etching of ChGs, etc. [1]. Particular attention has been paid to ChGs of As-S-Se system. ChGs of this system can be prepared in wide range of glass compositions due to the broad glass forming region [2], which allows tailoring of physical and chemical properties. ChGs of As-S-Se system have been thoroughly studied as materials suitable for holography and lithography because of their significant photosensitivity resulting in selective etching in both organic and inorganic alkaline solutions [3–6]. Further interest in ChGs of this system was attracted because of their significant non-linear optical properties [7–9] and the possibility of photo-doping with Ag [10,11].

Many applications of ChGs require the glass to be in a thin film (TF) form. The traditional methods of the TF deposition such as vacuum thermal evaporation, sputtering and PLD form the TF from the gaseous phase [12,13]. Alternatively the TFs can be prepared from the solution of ChG in volatile alkaline solvent. Methods such as spin-coating [14] and spiral bar coating [15] can be used for a TF deposition. The advantages of solution based deposition methods lie in the simplicity of the techniques (no need for high vacuum) and in the possibility to use well managed coating techniques for TF deposition [15]. On the other hand the TFs prepared via solution contain residual amount of the solvent captured in their structure, which can alter the physical and chemical properties of the glass [16].

We report on the comparison of $As_{30}S_{45}Se_{25}$ TFs prepared using thermal evaporation and spin-coating. The optical properties, chemical resistance, structure and their photo and thermo-induced changes were investigated and discussed in dependence on the method of the TF deposition.

2. Experimental details

The source bulk glass was prepared by standard melt quenching method. The high purity (5 N) elements were loaded into cleaned quartz ampoule in appropriate amounts. The ampoule was consequently evacuated ($\sim 10^{-3}$ Pa) and sealed. The synthesis was performed in rocking tube furnace at 850 °C. Quenching was done in cold water. Obtained bulk glass was used for TF deposition using thermal evaporation and spin-coating.

Thermal evaporation was carried out using device UP-858 (Tesla, Czech Republic). The residual pressure during TF deposition was $\sim 10^{-3}$ Pa. Evaporation rate as well as the thickness of deposited TF was measured in situ during deposition by quartz crystal microbalance method. The evaporation rate was $\sim 1\ nm \cdot s^{-1}$. Thickness of deposited TF was ~185 nm in order to be similar to the thickness of as-prepared spin-coated TFs.

Source bulk glass was manually powdered and dissolved in n-butylamine (BA) for purposes of spin-coating. TFs were prepared using spin-coater SC110 (Best Tools, USA) onto cleaned silicate glass substrates. Freshly prepared TFs were stabilized by annealing at 60 °C for 20 min in order to remove the excess solvent.

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TFs prepared by both used methods were stored in dark dry environment at laboratory temperature.

Annealing of TFs was performed using annealing table (Conbrio, Czech Republic) providing homogeneous thermal field over the whole surface of the samples. Annealing at temperatures 80 and 100 °C was performed for 60 min in protective Ar atmosphere in order to prevent surface oxidation. The annealing temperatures were chosen with respect to the decomposition temperatures of salts (glass dissolving products) inside the matrix of spin-coated TFs (70–90 °C) and still below the T_g of ChGs with the similar compositions [14,16]. As-prepared and annealed TFs were exposed to the solid state green laser beam (532 nm–2.33 eV, 380 mW·cm^{-2}; Roithner Lasertechnik, Austria) for 60 min in protective Ar atmosphere.

Transmission spectra of studied TFs were measured using spectrometer UV-3600 (Shimadzu, Japan). Structure of the TFs was investigated by Raman spectroscopy using FTIR spectrometer IFS 55 with Raman accessory FRA 106 (Bruker, Germany). Nd:YAG laser ($\lambda = 1064$ nm) was used as an excitation beam. Presented Raman spectra were normalized by the intensity of the most intensive band in the spectrum.

The kinetics of TFs dissolution in BA based solution in aprotic solvent were measured and evaluated by procedure described in [17].

3. Results and discussion

3.1. Methodology of transmission spectra evaluation

Optical parameters of TFs were determined from measured transmission spectra. Thickness (d) and spectral dependence of refractive index (n) were calculated from transparent region (extinction coefficient $k \to 0$) of measured transmission spectra by fitting a model of transmission spectrum (Fig. 1) presented by Swanepoel [18] where absorption in the TF is neglected ($k = 0$) and dispersion of refractive index n is expressed by Wemple-DiDomenico's equation [19]:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2}, \tag{1}$$

where E_d is parameter of dispersion energy, E_0 is single oscillator energy and $h\nu$ is photon energy. Described evaluation method is suitable for very thin films of dielectric materials [15] when the measured transmission spectra exhibit insufficient number of interference fringes for classical Swanepoel's method to be used.

The values of absorption coefficients α were calculated from measured transmission spectra using procedure described in [18]. The optical bandgap values E_g^{opt} of TFs were determined by Tauc's method for semiconductors [20].

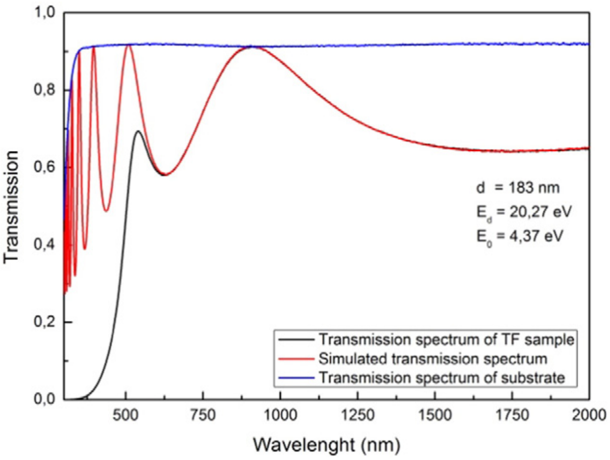

Fig. 1. The transmission spectrum of thermally evaporated $As_{30}S_{45}Se_{25}$ TF (black) and silicate glass substrate (blue) together with the fitted transmission spectrum (red).

Optical properties of both thermally evaporated and spin-coated TFs were measured on four separate samples for each treatment in order to increase the accuracy of the measurements. The error bars presented in the following plots represent the standard deviation of measured values.

3.2. Optical properties

Refractive index of as-prepared thermally evaporated TFs was 2.44 at 1064 nm (Fig. 2A). Annealing of the samples at 80 and 100 °C for 1 h did not influence this value significantly. Exposure to the beam of 532 nm laser (380 mW·cm^{-2}) for 1 h caused increase of the refractive index to the value 2.51. This value did not differ for any of the annealed samples. The optical band gap (E_g^{opt}) of as-prepared thermally evaporated TFs was 2.00 eV (Fig. 2B). Annealed samples exhibited increase of E_g^{opt} to the value 2.03 eV for the sample annealed at 80 °C and 2.04 eV for the sample annealed at 100 °C. Exposure of the as-prepared thermally evaporated TFs did not cause any change of the E_g^{opt}. Both annealed samples exhibited photo-darkening (red shift) after exposure to the laser beam dropping the value of the E_g^{opt} to 2.00 eV. The thicknesses of the annealed thermally evaporated samples increased slightly with increasing temperature of the annealing (Fig. 2C). Exposure of the as-prepared and annealed samples to the laser beam resulted in slight compression (~3 nm) of the TFs (Fig. 2C). All of the changes in the thicknesses of the evaporated TFs are on the verge of the evaluation method's preciseness; nevertheless the trend is apparent (Fig. 2C).

Refractive index of as-prepared spin-coated TFs was 2.13 at 1064 nm (Fig. 2D), which is significantly lower value in comparison with the TFs prepared by thermal evaporation (Fig. 2A). The difference in the values of refractive index is most likely caused by residual amount of BA enclosed in the structure of the spin-coated samples [16]. Annealing of the as-prepared spin-coated TFs at 80 and 100 °C respectively caused partial release of the solvent from the TF resulting in the increase of refractive index up to the value 2.26 for the sample annealed at 100 °C. The exposure of the samples prepared by spin-coating to the 532 nm laser beam does not cause any significant change in the values of refractive index in as-prepared and 80 °C annealed TF. Sample annealed at 100 °C exhibits photo-induced increase of the refractive index to the value 2.29 (at 1064 nm).

The E_g^{opt} of the as-prepared spin-coated TFs was 1.91 eV (Fig. 2E). This value is slightly lower that E_g^{opt} of thermally evaporated samples. Annealing of the as-prepared spin-coated TFs at 80 and 100 °C increased the value of the E_g^{opt} to 1.97 eV, which is comparable with the values of thermally evaporated TFs' E_g^{opt} (Fig. 2B). Exposure to the 532 nm laser beam caused photo-bleaching (blue shift) of the as-prepared spin-coated samples increasing the value of E_g^{opt} to 1.94 eV. Contrary to the exposure of as-prepared TFs the exposures of annealed samples (both 80 and 100 °C) caused photo-darkening. In case of the sample annealed at 80 °C the optical band gap decreased to 1.91 eV and 1.94 eV for the sample annealed at 100 °C.

The thickness (d) of spin-coated TFs depends significantly on the thermal history of the sample (Fig. 2F). The thickness of as-prepared spin-coated TFs was ~185 nm. The thickness of annealed samples decreased significantly - $d = 160$ nm in case of the TFs annealed at 80 °C and $d = 155$ nm in case of the samples annealed at 100 °C. With increasing temperature of annealing the thickness decreases due to the release of solvent molecules bonded within the structure of TF [16,21]. Exposure to the 532 nm laser beam induces no significant changes in the thickness of any studied spin-coated TF.

3.3. Etching kinetics

Both thermally evaporated and spin-coated TFs were etched in solution of BA in aprotic solvent. Thermally evaporated TFs proved to be