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**Deposition and characterization of sulfide
chalcogenide glass thin films prepared by spin-coating
technique**

Annotation of dissertation thesis

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CONTENTS

| | | |
|----|-----------------------------|----|
| 1. | INTRODUCTION | 3 |
| 2. | THEORY | 4 |
| 3. | EXPERIMENTAL PART | 5 |
| 4. | RESULTS | 7 |
| 5. | CONCLUSION | 18 |
| 6. | REFERENCES | 20 |
| 7. | AUTHOR'S BIBLIOGRAPHY | 21 |

1. INTRODUCTION

Chalcogenide glasses are compounds of 16. group elements (S, Se, Te) with the elements of 13., 14. and 15. group (notably Ge, Ga, As, Sb or In). The first synthesized glass in 1950 was stoichiometric As_2S_3 and since then the countless others stoichiometric and non-stoichiometric chalcogenide glasses were successfully prepared. The chalcogenide glasses differ from commonly used oxide glasses in good ion conductivity, higher refractive index, significantly lower glass transformation temperatures and higher IR transparency. The important property of chalcogenide glasses is also their sensitivity to various kinds of radiation (mainly electro-magnetic). The exposure of these materials can induce changes of structure, optical properties or even induce their crystallization.

Chalcogenide glasses, their synthesis, characterization and material research are being studied on Department of General and Inorganic chemistry at University of Pardubice for many years.

For many applications of chalcogenide glasses, it is necessary to deposit them in thin film form. Chalcogenide glass thin films are usually deposited by vacuum deposition techniques – such as vacuum thermal evaporation, sputtering or laser ablation. But these techniques are less accessible due to their energetical consumption and necessity of expensive vacuum equipment. Thus, the solution based deposition techniques (spin-coating, dip-coating or spiral bar-coating) are currently gaining attention. Due to the content of organic residuals in the structure of as-prepared thin films, it is necessary to perform their thermal stabilization. The study of chalcogenide glass dissolution processes, the deposition of thin films by spin-coating technique and their thermal stabilization are the main aims of this work.

2. THEORY

The chalcogenide glass dissolution is the first and the most important step for deposition of thin films from their solutions. Chalcogenide glasses possess good resistivity to acids, but they can be relatively easily dissolved in inorganic or organic alkaline solvents. Previous experiments have confirmed good solubility of chalcogenide glasses in aqueous solutions of inorganic hydroxides or ammonia [1], but aqueous glass solutions cannot be used for thin film deposition due to the low volatility of water solvent and possibility of chalcogenide glass hydrolysis.

The Chern and Lauks have found, that organic alkaline aliphatic amines are suitable for chalcogenide glass dissolution and also for spin-coating deposition due to their high volatility [2, 3]. They have proposed that the aliphatic amine molecules disrupt the bonds of chalcogenide glasses mainly in the defect centers of material. The dissolution processes for both organic and inorganic solvents include two steps: the absorption of nucleophile (hydroxyl or amine group) atop the surface of chalcogenide glass followed by nucleophile substitution of sulfur in M-S (M = As, Ge, ...) bonds with molecules of used nucleophile. In case of aliphatic amines, the free electron pair on nitrogen atom is offered to M glass net-forming atom resulting in disruption of M-S bond. The dissolution of As-S chalcogenide glasses produces planar ionic nano-clusters compensated with ammonium groups of aliphatic amine solvent (Figure 1).

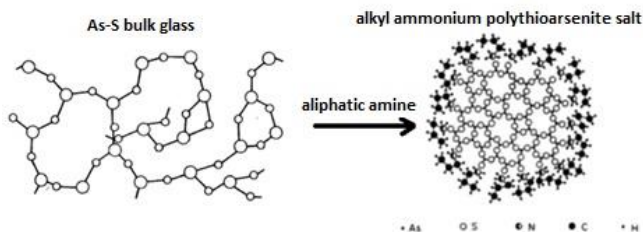


Figure 1: The dissolution mechanism of As-S chalcogenide glasses in aliphatic amines [1, 4].

The chalcogenide glass solutions of ionic dissolution products in organic amines are used for thin film deposition. During thin film formation, the volatile organic solvent is evaporated and chalcogenide salts are deposited in form of bulk material. The volume of as-prepared thin films contains high quantities of organic solvent residuals, either in form of chemically bonded ionic molecules compensating chalcogenide salts or as a free non-bonded fraction in cavities of deposited thin films. Thus, the thermal stabilization process is necessary to remove organic residuals and consequently increase compactness and optical quality of solution processed thin films.

3. EXPERIMENTAL PART

Preparation of chalcogenide glasses and solutions

Source bulk $As_{30}S_{70}$, $As_{30}S_{70-x}Se_x$ ($x = 5, 15, 25, 35$), $Ge_{25}S_{75}$ a $Ge_{20}Sb_5S_{75}$ chalcogenide glasses (ChGs) were prepared by melt-quenching method. High purity (5 N) elements were loaded into a cleaned quartz ampule in calculated amounts. The ampule was evacuated ($\sim 10^{-3}$ Pa) and sealed. The reagents were melted in a rocking tube furnace at $800\text{ }^\circ\text{C}$ for 48 h. Subsequently the ampule with melted glass was quenched in cold water. Bulk glass was powdered in agate bowl and dissolved in n-butylamine (BA) solvent at various concentrations (0,1 g / 1 ml BA for arsenic ChGs and 0,075 g / 1 ml BA for germanium ChGs). The ChGs were dissolved using magnetic stirrer when the whole glass material was dissolved within 24 hours.

Thin film deposition

ChG thin films were deposited from their BA solutions using spin-coating technique (spin-coater Best Tools SC110-B). The glass solution was pipetted and deposited onto rotating soda-lime glass substrates and spin-coated in ambient or argon atmosphere to yield thin films of optical quality. The arsenic ChGs were spin-coated at 4000 rpm for 40 s and germanium ChGs at 2000 rpm for 120 s. Immediately after the deposition the films were stabilized by annealing (soft baking) at $60\text{ }^\circ\text{C}$ on a hot plate (hereafter referred as as-prepared thin film). Baked samples were stored in dry, dark environment.

For comparison of optical parameters, the thin films were also deposited by vacuum thermal evaporation technique (device UP-858, Tesla corp.). The films were prepared in conventional manner from source ChG bulk glass by evaporation from a molybdenum boat with the evaporation rate of $1\text{--}2\text{ nm}\cdot\text{s}^{-1}$ at a pressure of $\sim 10^{-3}$ Pa ($\sim 10^{-5}$ Torr), and deposited onto soda-lime glass substrates. The resulting film's final thickness was corresponding to the thicknesses of spin-coated thin films. The thickness of vacuum deposited thin films and evaporation rate were measured using quartz crystal microbalance.

Thin film annealing and exposure

Deposited ChG thin films were annealed at various temperatures for 60 min on an annealing table (Conbrio, Czech Republic) in argon atmosphere or in vacuum oven (Vacucell 22, BMT Medical Technology) with residual pressure 0.3 bar. To examine the effect of irradiation on studied thin films the samples were exposed to UV lamp light (365 nm , $156\text{ mW}\cdot\text{cm}^{-2}$) or to laser beam (532 nm , $380\text{ mW}\cdot\text{cm}^{-2}$) in argon atmosphere for 60 min.

Transmission spectra measurement

The transmission spectra of as-prepared, annealed and irradiated thin films were measured using optical spectrometer (Shimadzu UV3600) in the spectral region $190\text{--}2500\text{ nm}$.

Determination of thin films geometrical and optical parameters

The thicknesses and refractive index values of spin-coated and vacuum thermally deposited as-prepared and annealed thin films were determined using the fitting procedure described in [5] based on Wemple-DiDomenico's equation [6] and the model presented by Swanepoel [7]. The parameters of thin films deposited by both techniques and were obtained from transparent region of measured transmission spectra by fitting modeled transmission spectrum (Swanepoel's model) using refractive index dispersion expressed by Wemple-DiDomenico's equation. The optical bandgap values were calculated using Tauc's method for semiconductors [8]. The optical parameters of germanium ChG thin films were determined using optical ellipsometry with two variable angle spectroscopic ellipsometers (VASE and IR-VASE J. A. Woollam Co.).

SEM microscopy and elemental analysis

The as-prepared and annealed thin films were analyzed by energy dispersion x-ray microanalysis method using scanning electron microscope (LYRA 3, Tescan) equipped with EDS analyzer Aztec X-Max 20 (Oxford Instruments) at acceleration voltage 5 kV.

Wet etching

The etching kinetics of as-prepared and annealed thin film samples were studied by procedure presented in [9] in various BA solutions (0,01-50 vol. %) in aprotic solvent (N,N-dimethylformamide). The etching curves were evaluated at two wavelengths corresponding to the first interference maximum and the first minimum of measured transmission spectra.

Structural analysis

The structure of source bulk glasses, spin-coated thin films and pure BA solvent was determined using FT IR spectrometer IFS55 equipped with Raman module FRA106 (Bruker) with excitation by Nd:YAG laser (1064 nm).

The elemental profile and XPS surface analysis

The As-S depth concentration profile of As₃₀S₇₀ thin film annealed at 120 °C in argon atmosphere was recorded using high sensitivity-low energy ion scattering (HS-LEIS) spectrometer (Qtac 100) with ⁴He⁺ probe beam (3000 eV, measured area 750 × 750 μm), and ³⁶Ar⁺ sputtering beam (2000 eV, sputtered area 1500 × 1500 μm).

High-resolution XPS spectra were recorded with a Scienta ESCA-300 spectrometer using monochromatic Al K α X-rays (1486.6 eV) under a vacuum of 2×10^{-8} Torr or better. For all measurements the angle between the surface and the detector was 90°. The instrument was operated in a mode that yielded a Fermi level width of 0.4 eV for Ag metal and at a full width at half maximum (FWHM) of 0.54 eV for Ag 3d_{5/2} core level peak.

4. RESULTS

Thin films of As₃₀S₇₀ composition

The As₃₀S₇₀ ChG composition was chosen with respect to the high over-stoichiometry of sulfur which allowed to fasten its dissolution. The As₃₀S₇₀ thin films were deposited from their solution in specular optical quality using spin-coating technique (Figure 2).



Figure 2: The As₃₀S₇₀ source bulk glass (left) and as-prepared spin-coated thin film (right).

The transmission spectra of as-prepared and annealed spin-coated As₃₀S₇₀ chalcogenide thin films were evaluated according to the procedure described in [10]. The thickness values were normalized to the thicknesses of the as-prepared (i.e. pre-annealed, $d \sim 260$ nm) thin film in order to eliminate the minor variation of spin-coating conditions (Fig. 3). As described previously in [2, 3, 11], the as-prepared spin-coated As-S ChG thin films contain molecules of residual solvent and alkyl ammonium arsenic sulfide (AAAS) salts, which were already formed in glass solution during dissolution of source chalcogenide bulk glass. These compounds subsequently decompose during annealing and leave the volume of annealed film, which then decrease its thickness. Contrary, the thin films annealed at low residual pressure (LRP) exhibited another large thickness loss at temperatures above 100 °C due to low molecular glass fragments evaporation or due to the release of additional residual molecules supported by LRP at temperature close to the T_g (~ 132 °C [1]) of annealed material.

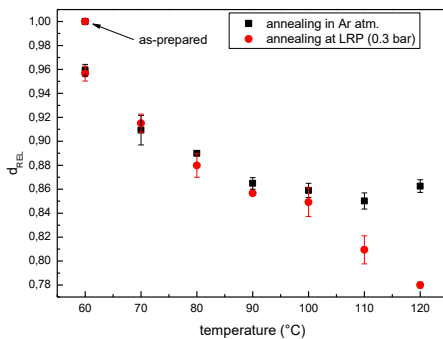


Figure 3: The dependence of normalized thicknesses of As₃₀S₇₀ thin films on annealing temperatures (60 minutes annealing, argon atmosphere and low residual pressure – LRP).

The refractive index and optical bandgap of studied samples are presented in Table 1. The refractive index increases with increasing annealing temperature for both annealing conditions (argon atmosphere and LRP). The corresponding values for the two annealing methods are almost identical within the whole temperature range and saturate at ~ 110 °C with $n_{1550} = 2,17$. Its value for vacuum thermally deposited thin film with the same thermal treatment (annealing at 60 °C for 20 minutes followed by annealing at 110 °C for 60 minutes in argon atmosphere) yielded $n_{1550} = 2,29$. That is, the refractive index of thermally stabilized spin-coated $As_{30}S_{70}$ thin films is significantly lower than that of vacuum thermally deposited thin films of the same composition.

Similar to the refractive index, the E_g^{opt} is almost identical for both annealing methods. The E_g^{opt} results exhibit two significant step-like drops at 60 °C and at 100-110 °C. The first decrease at 60 °C is attributed to the intensive loss of free (chemically non-bonded) residual solvent molecules. The second decrease at 100-110 °C is attributed to the complete decomposition of AAAS salts and expected distinctly higher release of organic residuals due to the relaxation of glass structure during annealing close to the T_g of material.

The refractive index of $As_{30}S_{70}$ thin films slightly increased upon UV exposure. However, the optical bandgap and thickness did not change after the exposure; also no photo-bleaching or photo-darkening was observed. Thus, the studied spin-coated thin films are photo-sensitive

Table 1: The refractive index $n_{1550}(\lambda = 1550 \text{ nm})$ and optical bandgap E_g^{opt} of spin-coated $As_{30}S_{70}$ thin films.

| Thin films annealed in Ar | | |
|---------------------------------------|--------------------------------|--------------------------------------|
| Sample | n_{1550} unexp. / UV exp. | E_g^{opt} (eV) unexp. / UV exp. |
| as-prepared | 2.04 / 2.08 | 2.32(1) / 2.32(1) |
| T-60 °C | 2.07 | 2.31(5) |
| T-70 °C | 2.09 | 2.31(5) |
| T-80 °C | 2.13 / 2.15 | 2.31(4) / 2.31(4) |
| T-90 °C | 2.15 | 2.31(4) |
| T-100 °C | 2.14 / 2.18 | 2.31(6) / 2.31(4) |
| T-110 °C | 2.17 | 2.29(4) |
| T-120 °C | 2.17 / 2.19 | 2.29(5) / 2.29(9) |
| Thin films annealed at 0,3 bar | | |
| Sample | n_{1550} | E_g^{opt} (eV) |
| as-prepared | 2.04 | 2.32(1) |
| T-60 °C | 2.06 | 2.31(5) |
| T-70 °C | 2.08 | 2.31(4) |
| T-80 °C | 2.14 | 2.31(5) |
| T-90 °C | 2.15 | 2.31(5) |
| T-100 °C | 2.16 | 2.29(7) |
| T-110 °C | 2.17 | 2.29(6) |
| T-120 °C | 2.19 | 2.29(6) |

The unexposed and UV light exposed spin-coated thin films were etched in aprotic solvent containing 0,01 vol.% of BA. The etching curves are presented in Fig. 4; the insets show the dependence of transmittance at the wavelength of the first interference maximum in the transmission spectrum on the etching time. The data show that the annealing process considerably increases chemical stability of spin-coated thin films. The etching rates significantly decrease with increasing annealing temperature. For example, the etching of the sample annealed at 120 °C is 18 times slower than the etching of the as-prepared thin film.

The exposure of as-prepared thin film to UV lamp light slightly increases a film's chemical stability. The UV exposure of annealed samples increases the etching rates, resulting in positive etching (exposed areas dissolve faster in comparison to the non-exposed areas). The highest etching selectivity (ratio between the etching rates of exposed and unexposed thin films) is achieved for samples annealed at 120 °C when the etching of exposed thin films is 1,8 times higher than the etching of unexposed sample.

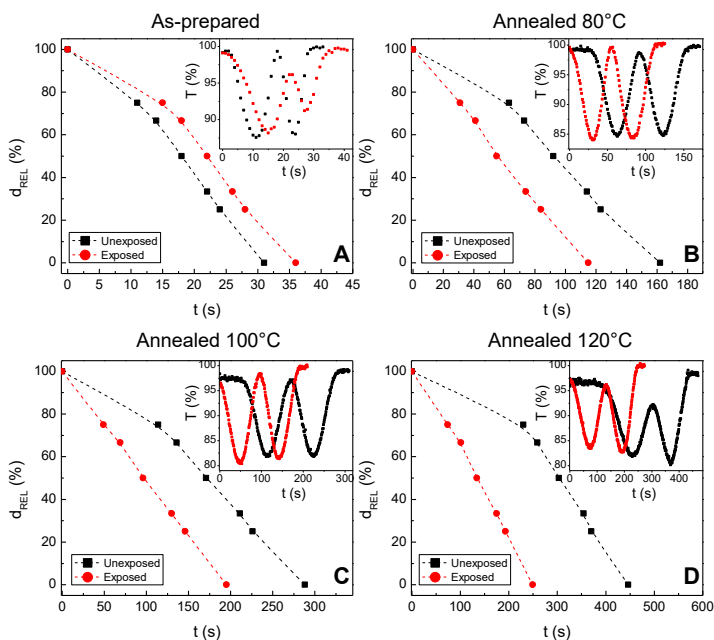


Figure 4: Etching curves of spin-coated $As_{30}S_{70}$ thin films. Insets show the dependence of transmittance related to the wavelength of the first interference maximum in the transmission spectrum on the etching time. A – as-prepared thin film, B – annealed at 80°C, C – annealed at 100°C, D – annealed at 120°C.

The Raman spectra of thin films annealed in argon atmosphere (Figure 5) show that thermal treatment has also strong influence on the structure of films. In particular, thermal treatment induces structural polymerization. The intensities of S_8 (151, 218 and 475 cm^{-1}) and As_4S_4 (369 cm^{-1}) bands decrease and the intensity of $AsS_{3/2}$ (344 cm^{-1}) band proportionally increases with increasing annealing temperature. Observed structural polymerization is accompanied by the decomposition of AAAS salts (415 cm^{-1} band decreases) and release of organic residuals (2800-3000 cm^{-1} bands decrease). Generally, the structure of annealed thin films shifts towards the structure of source bulk glass. The same observed structural changes occur in thin films annealed at LRP (Figure 5-B). Unfortunately, high intensity fluorescence band (appearing in the spectra of thin films annealed above 110 $^{\circ}\text{C}$) interferes with the Raman bands and makes the spectra difficult to evaluate.

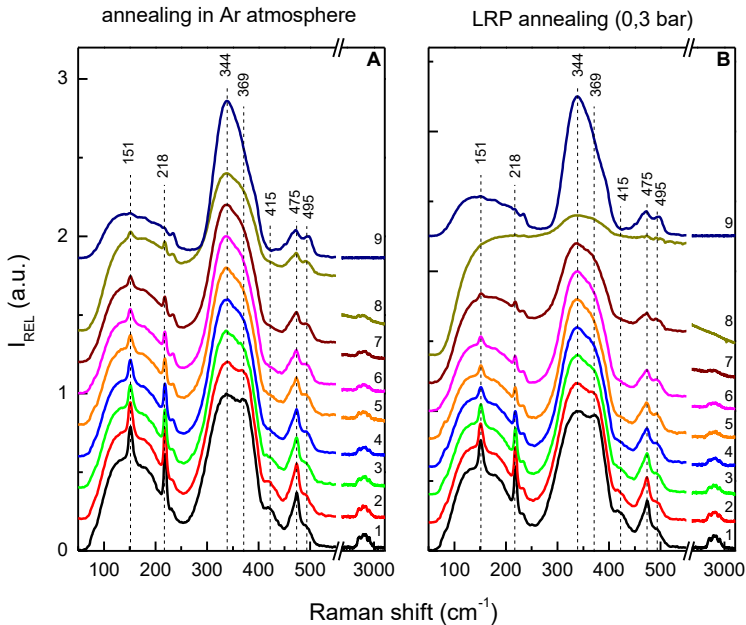


Figure 5: Raman spectra of $As_{30}S_{70}$ thin films annealed in argon atmosphere (A) and at low residual pressure – LRP (B). 1: as-prepared; 2: annealed at 60 $^{\circ}\text{C}$; 3: annealed at 70 $^{\circ}\text{C}$; 4: annealed at 80 $^{\circ}\text{C}$; 5: annealed at 90 $^{\circ}\text{C}$; 6: annealed at 100 $^{\circ}\text{C}$; 7: annealed at 110 $^{\circ}\text{C}$; 8: annealed at 120 $^{\circ}\text{C}$; 9: source bulk glass.

In order to determine the depth profile of As/S concentration ratio within $As_{30}S_{70}$ spin-coated thin film annealed at 120 $^{\circ}\text{C}$ (argon atmosphere) the HS-LEIS spectroscopy was used (Figure 6). The results are presented as the variation of S:As atomic ratio as a function of sputtered depth of the measured film. Clearly, the surface of annealed thin film is arsenic deficient with the composition being $As_{25,1}S_{74,9}$. Then the arsenic content quickly increases and stabilizes at the $As_{29,1}S_{70,9}$ composition.

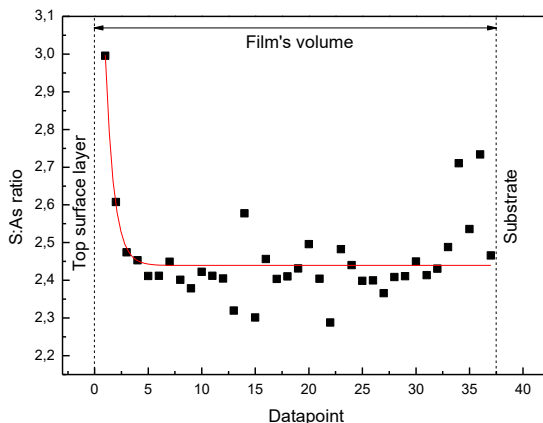


Figure 6: The S:As atomic ratio depth profile of $As_{30}S_{70}$ spin-coated thin film (annealed in argon atmosphere at $120\text{ }^{\circ}C$) measured by HS-LEIS spectroscopy. The red curve is drawn to guide the eye.

The XPS technique have also confirmed that the surface of annealed As-S spin-coated thin films is slightly As-depleted due to sublimation of arsenic oxides in UHV atmosphere in machine (10^{-9} Pa). The As 3d XPS spectra proved that the As in surface of studied samples is bonded in form of $S-As<(S)_2$ as trigonal pyramidal units $AsS_{3/2}$. The S 2p XPS spectra proves existence of four bonding surrounding of S atoms. S $2p_{3/2}$ band at $\sim 162,1$ eV belong to $As-S-As$ fragments, which serves as bridges between trigonal pyramidal units $AsS_{3/2}$. The second band at $\sim 163,0$ eV is connected with presence of $S-S-As$ units and the third band at $\sim 161,0$ eV can be attributed to the one-coordinate sulfur units in form of non-bridging atoms (dangling bonds). This band can be also attributed to the presence of S^- ions from AAAS thermal decomposition. The fourth band at $163,70$ eV belong to the $S-S-S$ sulfur structural fragments which presence can be explained by significant S overstoichiometry.

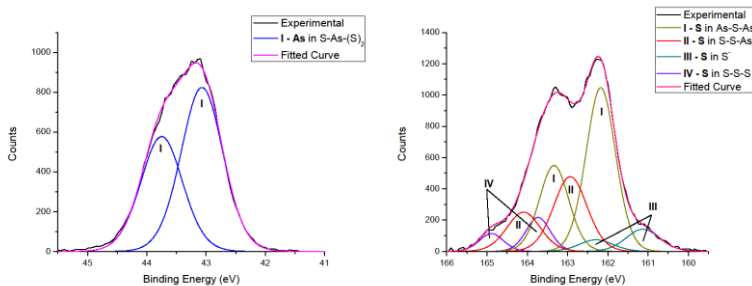


Figure 7: The As 3d (left) and S 2p (right) XPS core level spectra of $As_{30}S_{70}$ spin-coated thin films.

Thin films of As₃₀S₄₅Se₂₅ composition

The As₃₀S₄₅Se₂₅ thin films were deposited by both spin-coating and vacuum thermal evaporation techniques. The evaluated thickness and optical parameters are presented in Table 2. Refractive index of as-prepared thermally evaporated thin films was 2.41 at 1550 nm. Annealing of the samples at 80 and 100°C for 60 min did not influence this value significantly. Exposure to the beam of 532 nm laser (380 mW.cm⁻²) for 60 min caused increase of the refractive index to the value 2.47(8). This value did not differ for any of the annealed samples. The optical band gap (E_g^{opt}) of as-prepared thermally evaporated thin films was 2.01(9) eV. Annealed samples exhibited increase of E_g^{opt} to the value 2.04(7) eV for the sample annealed at 80°C and 2.06(5) eV for the sample annealed at 100°C. Exposure of the as-prepared thermally evaporated thin films did not cause any significant 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} .

Refractive index of as-prepared spin-coated thin films was 2.11 at 1550 nm, which is significantly lower value in comparison with the thin films prepared by thermal evaporation. 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. Annealing of the as-prepared spin-coated thin films at 80 and 100°C respectively caused partial release of the solvent from the thin film resulting in the increase of refractive index up to the value 2.23 for the sample annealed at 100°C. The E_g^{opt} of the as-prepared spin-coated was slightly lower than E_g^{opt} of thermally evaporated samples. Annealing of the as-prepared spin-coated thin films at 80 and 100°C increased the value of the E_g^{opt} . Exposure to the 532 nm laser beam caused photo-bleaching (blue shift) of the as-prepared spin-coated samples. Contrary, the exposures of annealed samples (both 80 and 100°C) caused photo-darkening. In case of the sample annealed at 80°C the optical bandgap decreased to 1.91 eV and 1.92 eV for the sample annealed at 100°C.

Table 2: The thickness and optical properties of As₃₀S₄₅Se₂₅ thin films deposited by spin-coating and vacuum thermal evaporation.

| Spin-coated As₃₀S₄₅Se₂₅ thin films | | | |
|---|---------------------------------|------------------------------------|-----------------------------------|
| sample | thickness (nm) unexp. / exp. | n ₁₅₅₀ unexp. / exp. | E_g^{opt} (eV) unexp. / exp. |
| as-prepared | 185 / 183 | 2.11 / 2.11 | 1.94(7) / 1.90(0) |
| T-80 °C | 160 / 159 | 2.19 / 2.19 | 1.94(9) / 1.91(1) |
| T-100 °C | 156 / 154 | 2.23 / 2.26 | 1.95(3) / 1.92(1) |
| Vacuum thermally deposited As₃₀S₄₅Se₂₅ thin films | | | |
| sample | thickness (nm) unexp. / exp. | n ₁₅₅₀ unexp. / exp. | E_g^{opt} (eV) unexp. / exp. |
| as-prepared | 181 / 178 | 2.41 / 2.47 | 2.01(9) / 2.02(1) |
| T-80 °C | 185 / 181 | 2.41 / 2.48 | 2.04(7) / 2.03(3) |
| T-100 °C | 187 / 184 | 2.43 / 2.48 | 2.06(5) / 2.04(1) |

Both thermally evaporated and spin-coated thin films were etched in solution of BA in aprotic solvent. Thermally evaporated thin films proved to be significantly more resistant in comparison with spin-coated ones. Thus, concentration of BA in solutions used for etching of thermally evaporated samples was 1 vol.% and 0.1 vol.% concentration was used for etching of spin-coated thin films. The etching rates of the samples prepared by vacuum thermal evaporation (Figure 8-A) show that as-prepared and 80°C annealed sample dissolve at similar rate. Sample annealed at 100°C exhibits significantly lower etching rate due to the partial relaxation of the glass structure caused by annealing.

Figure 8-B gives evidence of very high etching rates for both unexposed and exposed as-prepared spin-coated samples. The etching rate of exposed thin films is slightly lower than etching rate of unexposed ones. The thermal stabilization induced increase of their chemical stability, which was reflected in dramatical decrease of etching rates. Exposure to the 532 nm laser beam induces significant increase in the etching rate of annealed spin-coated samples. The photo-induced increase of the etching rate is completely opposite to the observed photo-induced changes of the chemical resistance of thermally evaporated thin films.

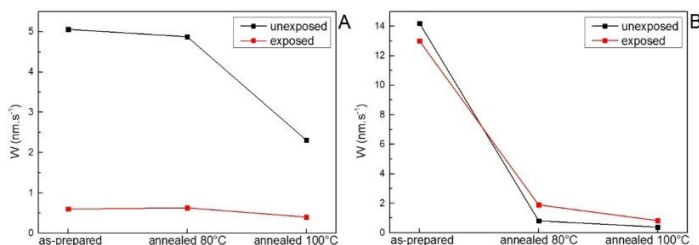


Figure 8: The average etching rates W of thermally evaporated (A) and spin-coated (B) thin films in BA based solution.

In order to demonstrate the selectivity of the etching process in the spin-coated thin films a diffraction grating with period $20\ \mu\text{m}$ was prepared using selective etching method. The exposure of the grating motive was done through the chromium mask by contact method (Figure 9).

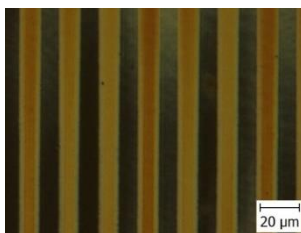


Figure 9: Diffraction grating prepared in spin-coated pre-annealed $\text{As}_{30}\text{S}_{45}\text{Se}_{25}$ thin film by selective etching.

Thin films of $Ge_{25}S_{75}$ composition

The $Ge_{25}S_{75}$ chalcogenide glass powder was weighted to reach 0,1 g / 1 ml BA concentration (similarly to $As_{30}S_{70}$ and $As_{30}S_{45}Se_{25}$ solutions). However, the bulk glass was not quantitatively dissolved within 24 hours and in following days the solution proved to be unstable (Figure 10). Thus, the concentration was lowered to 0,075 g / 1 ml BA, which was dissolved within 24 hours and allowed to immediately process it for thin films deposition.

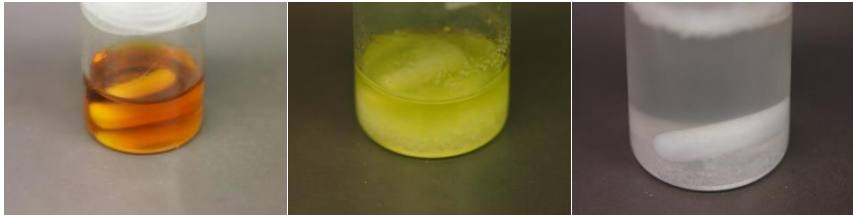


Figure 10: Fresh $Ge_{25}S_{75}$ solution (left) together with solutions at 48 hours (middle) and week (right) after dissolution.

The $Ge_{25}S_{75}$ thin films were spin-coated at 2000 rpm. The spin-coating speed was chosen with respect to the best obtained optical quality. Geometrical and optical parameters (thickness of the films and surface roughness, optical bandgap and refractive index values at 1550 nm) obtained using this model, are summarized in Table 1. Values of surface roughness determined by SE are in good agreement with AFM data reported in Table 1 as well.

Table 3: Values of thin film's thickness, surface roughness (spectroscopic ellipsometry – SE, atomic force microscopy – AFM), optical bandgap (E_g^{opt}) and refractive index values (n_{1550}) for 1550 nm determined by spectroscopic ellipsometry.

| sample | thickness (nm) | roughness (OE) (nm) | roughness (AFM) (nm) | E_g^{opt} (eV) | n_{1550} |
|-------------|----------------|---------------------|----------------------|------------------|------------|
| as-prepared | 396 | 0.3 | 0.40 | 3.45 | 1.70 |
| T-90 °C | 378 | 0.9 | 0.69 | 3.33 | 1.70 |
| T-120 °C | 345 | 2.3 | 0.83 | 3.17 | 1.71 |
| T-150 °C | 260 | 5.5 | 7.64 | 3.06 | 1.81 |
| T-180 °C | 220 | 5.1 | 5.36 | 3.05 | 1.88 |
| T-210 °C | 197 | 11.2 | 13.68 | 3.04 | 1.94 |

The refractive index in the transparent region of spin-coated $Ge_{25}S_{75}$ thin films is monotonously increasing with the increasing annealing temperature. Observed increase could be explained by increasing compactness of the film (densification). The as-prepared spin-coated thin films of As-S system consist of glass clusters separated by voids and organic molecules used in the solution. The organic molecules are ionically bonded to the ChG clusters in form of alkyl ammonium chalcogenide salt. When annealing process

decomposes these salts and subsequently evaporates organics molecules, the glass particles are forming more compact film. Similar mechanism can be expected for ChGs of Ge-S system as well, which would be in a good agreement with observed significant decrease of the thin films thickness during the annealing process. However, observed thickness decrease of Ge₂₅S₇₅ thin films is more significant (~50%) in comparison with As-based ones (~15%), which suggest higher content of organic residuals.

Thin films of Ge₂₀Sb₅S₇₅ composition

The Ge₂₀Sb₅S₇₅ thin films were deposited at same conditions as Ge₂₅S₇₅ thin films. The thin films of same composition were also deposited by vacuum thermal deposition and all samples were exposed to UV lamp light in order to study the photo-induced changes. The results proved similar thermally-induced behavior of studied spin-coated samples as Ge₂₅S₇₅ thin films. The data also proved that the spin-coated Ge₂₀Sb₅S₇₅ thin films are photo-sensitive and comparing all studied materials, they exhibit the most significant photo-induced changes of optical parameters.

Table 4: The optical and geometrical parameters of spin-coated and thermally evaporated Ge₂₀Sb₅S₇₅ thin films.

| Spin-coated Ge₂₀Sb₅S₇₅ thin films | | | | |
|--|---------------------------------|---------------------------------|------------------------------------|---|
| sample | thickness (nm) unexp. / exp. | roughness (nm) unexp. / exp. | n ₁₅₅₀ unexp. / exp. | E _g ^{opt} (eV) unexp. / exp. |
| as-prepared | 388 / 373 ± 0.2 / ± 0.2 | 0.5 / 4.0 ± 0.1 / ± 0.1 | 1.74 / 1.70 | 2.34 / 2.32 |
| T-110 °C | 359 / 355 ± 0.2 / ± 0.4 | 1.0 / 3.2 ± 0.1 / ± 0.2 | 1.75 / 1.72 | 2.42 / 2.52 |
| T-160 °C | 260 / 257 ± 0.2 / ± 0.6 | 5.4 / 8.3 ± 0.1 / ± 0.4 | 1.86 / 1.81 | 2.62 / 2.66 |
| T-210 °C | 192 / 200 ± 0.1 / ± 0.1 | 7.9 / 9.8 ± 0.1 / ± 0.1 | 2.01 / 1.99 | 2.63 / 2.63 |
| Vacuum thermally deposited Ge₂₀Sb₅S₇₅ thin films | | | | |
| sample | thickness (nm) unexp. / exp. | roughness (nm) unexp. / exp. | n ₁₅₅₀ unexp. / exp. | E _g ^{opt} (eV) unexp. / exp. |
| as-prepared | 175 / 184 ± 0.2 / ± 0.2 | 4.2 / 3.7 ± 0.1 / ± 0.1 | 2.11 / 2.05 | 2.61 / 2.79 |
| T-110 °C | 174 / 177 ± 0.2 / ± 0.2 | 3.8 / 4.7 ± 0.1 / ± 0.1 | 2.10 / 2.06 | 2.65 / 2.76 |
| T-160 °C | 169 / 178 ± 0.2 / ± 0.2 | 10.3 / 3.9 ± 0.1 / ± 0.1 | 2.09 / 2.05 | 2.65 / 2.74 |
| T-210 °C | 169 / 179 ± 0.1 / ± 0.1 | 5.6 / 5.5 ± 0.1 / ± 0.1 | 2.10 / 2.05 | 2.72 / 2.74 |

In order to study the effect of annealing and exposure on chemical resistance of studied thin films, the $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ samples were etched in BA based solution. Based on the obtained data of films thicknesses and etching times, the etching selectivity (ratio between the etching rate of exposed and un-exposed thin film) were calculated (Figure 11). As-prepared spin-coated samples were dissolved immediately after their immersion into etching solution and thus they are not presented in our results. Both, the thermally evaporated and spin-coated thin films increase their chemical stability with increasing annealing temperature. This effect is even more eminent on spin-coated thin films due to the content of organic residuals which significantly decreases their chemical stability. The annealing temperature additionally affected the etching selectivity as well. The as-prepared thermally evaporated sample and spin-coated sample annealed at 110 °C are etched faster than their UV exposed counterparts (negative etching). With increasing annealing temperature, the difference between etching rates of unexposed and exposed samples decreases and eventually the selectivity is inverted. The spin-coated and thermally evaporated thin films annealed at 210 °C are etched slower than exposed samples (positive etching).

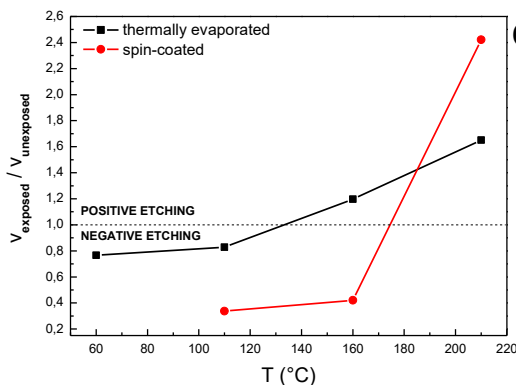


Figure 11: The calculated etching selectivity of spin-coated and thermally evaporated $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ thin films.

Selected spin-coated and thermally evaporated $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ thin films were structured using UV photolithography. Obtained gratings were studied by AFM and SEM techniques. The SEM scans and AFM cross-sections of spin-coated thin films (Figure 12) prove that prepared gratings have regular nearly sinusoidal profile with 20 μm grating period. The depth of grating in surface of spin-coated samples annealed at 160 °C is ~105 nm and annealed at 210 °C is ~75 nm. The positively etched and chemically more stable spin-coated sample annealed at 210 °C have significantly smoother surface than negatively etched SC sample annealed at 160 °C. Obtained gratings prepared by photolithography have a very low quality with high surface roughness.

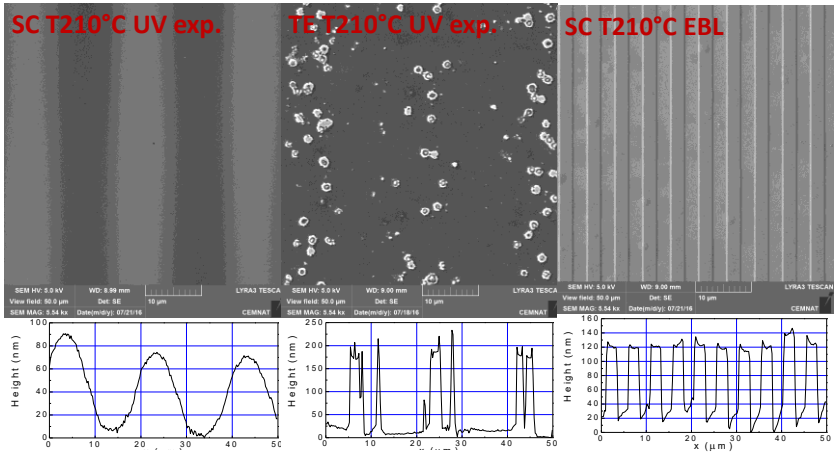


Figure 12: SEM scans with AFM cross-sections of chosen gratings prepared by UV photolithography (UV exp.) and EBL in surface of $Ge_{20}Sb_5S_{75}$ thin films.

To study the sensitivity of well-stabilized and chemically resistant thin films to electron beam, the spin-coated and thermally evaporated $Ge_{20}Sb_5S_{75}$ thin films annealed at 210 °C were structured by electron beam lithography (EBL). The used recorded pattern was 250x250 μm grating with 5 μm period and 1000 $\mu\text{C}\cdot\text{cm}^{-2}$ dose. Thin films with latent images were etched in the BA based solution for the same time as was used for etching of samples with corresponding thermal treatment structured by UV photolithography. The data proved that electron beam exposure of spin-coated samples induces structural changes resulting in different chemical resistivity. Obtained linear grating (Figure 12 - right) has regular rectangular profile with 5 μm period and relatively low surface roughness. However, the material of thermally evaporated thin film annealed at 210 °C was practically inert to electron beam exposure and no surface structures were obtained. Thus, the $Ge_{20}Sb_5S_{75}$ thin films prepared by spin-coating can be successfully used for fabrication of optical micro-elements by EBL technique.

5. CONCLUSION

The dissertation thesis is focused on preparation, study and characterization of $As_{30}S_{70}$, $As_{30}S_{45}Se_{25}$, $Ge_{25}S_{75}$ and $Ge_{20}Sb_5S_{75}$ sulfide chalcogenide glass thin films deposited from their solutions by spin-coating technique. The changes of physical and chemical properties induced by thermal stabilization and electro-magnetic beam exposure were also studied. The properties of chosen spin-coated chalcogenide glass thin films were compared to properties and behavior of thin films deposited by more conventional vacuum thermal deposition technique.

The dissolution experiments with used chalcogenide bulk glasses confirmed, that the content and over-stoichiometry of sulfur atoms have a major impact on feasibility and rate of dissolution processes; and bulk glass dissolution reaction is fastest on homopolar S-S bonds. Dissolution rate was also influenced by bonding conditions on central glass forming element, when arsenic atoms with non-bonding electron pairs allowed to fasten dissolution process. Experiments also confirmed high sensitivity of germanium chalcogenide glass solutions to hydrolysis and oxidation.

Prepared solutions were used for thin film deposition by dynamic spin-coating technique. The inert argon atmosphere was used during spin-coating, due to the high sensitivity of germanium chalcogenide glass solutions. The thickness comparison of prepared thin films and the data from elemental EDS analysis confirmed, that as-prepared germanium thin films contained higher content of organic residuals, which was reflected in their higher thickness in comparison with arsenic thin films.

Thermal stabilization of as-prepared thin films of all used compositions induced significant thickness decrease and changes of their optical parameters. Annealing process induced ~15 % thickness decrease of $As_{30}S_{70}$ and $As_{30}S_{45}Se_{25}$ thin films and ~50 % thickness decrease of $Ge_{25}S_{75}$ and $Ge_{20}Sb_5S_{75}$ thin films. Observed changes were explained by annealing induced structural changes connected with thermal decomposition of present alkylammonium polythioarsenite and polythiogermanate salts, release of organic residuals and polymerization of glass matrix resulting in material with structure close to the source bulk glass. The HS-LEIS technique confirmed that spin-coated thin films with thickness ~200 nm have stable atomic ration within the films volume without the gradient of composition.

Thermal stabilization induced significant changes in refractive index and optical bandgap of studied thin films deposited by spin-coating technique. The annealing induced increase in refractive index was observed in all thin films of all studied compositions and with exception of $Ge_{20}Sb_5S_{75}$ thin films the annealing induced darkening (shift of short wavelength absorption edge towards IR) was also confirmed.

Experiments also confirmed, that spin-coated thin films are photo-sensitive. Electro-magnetic radiation exposure in argon atmosphere induced significant changes of their

optical properties. Based on obtained data, the most photo-sensitive studied materials were $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ thin films.

The influence of thermal stabilization and exposure on chemical resistance of prepared thin films was studied by wet-etching. It was confirmed that with increasing of annealing temperature, the chemical resistance was also dramatically increasing. The photo-induced structural changes also influenced the chemical resistance of studied thin films – the samples annealed at lower temperatures exhibited exposure induced increase of chemical resistance (negative etching) and contrary the samples annealed at higher temperatures exhibited exposure induced decrease of chemical resistance (positive etching).

Exposure induced changes of chemical resistance were exploited for surface structuring of prepared thin films by contact UV lithography and electron beam lithography EBL. These techniques confirmed, that spin-coated chalcogenide glass thin films can be successfully used as inorganic resists, which are in some cases more suitable and have higher quality than the resists of same composition prepared by thermal vacuum evaporation. That opens the variety of other potential application possibilities and research directions for solution-deposited chalcogenide glass thin films.

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