

# Solution processed As<sub>30</sub>Se<sub>70</sub> chalcogenide glass thin films with specular optical quality: multi-component solvent approach

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**Abstract:** We present the study of volatile amine-based single or multi-component solvent formulations and their influence on As<sub>30</sub>Se<sub>70</sub> chalcogenide glass solubility and dissolution mechanism. The source As<sub>30</sub>Se<sub>70</sub> bulk glass was dissolved in various amine based solvents and solutions of quantitatively dissolved bulk glass were used for thin films deposition by spin-coating technique. The methanol – n-propylamine solvent mixture proved to be suitable for preparation of thin films in specular optical quality, low surface roughness and targeted composition. The post-deposition thermal treatment has high impact on thickness, optical properties and structure of studied thin films. The content of organic residuals was also significantly reduced.

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**OCIS codes:** (160.2750) Glass and other amorphous materials; (310.6860) Thin films, optical properties; (310.6870) Thin films, other properties; (240.2130) Ellipsometry and polarimetry.

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## 1. Introduction

Chalcogenide glasses (ChGs) are semiconducting materials with high refractive index and wide IR transparency region [1, 2]. Due to their unique properties, they have found many applications in optics, optoelectronics and photonics [1–5]. ChGs can be used in a form of bulk material (e.g. lenses, windows, fibers, etc. [1, 2, 6, 7]) or as an amorphous thin film deposited on appropriate substrate (e.g. optical recording discs, diffractive optical elements, planar waveguides, high resolution photoresists, etc. [8–12]). The thin films are frequently deposited by physical vapor deposition techniques (e.g. thermal evaporation, laser ablation, etc. [8–14]) but solution based techniques (e.g. spin-coating, dip-coating, spiral bar-coating, electrospray, etc. [15–22]) which exploit solubility of ChGs in volatile alkaline amines are also gaining attention. The solution-based deposition route can be also used for preparation of ChG thin films with embedded luminescent nanoparticles [23–25]. The main advantage of solution based deposition techniques lies in simplicity of thin films deposition and thus in low cost instrumentation. The major disadvantage of ChG thin films deposited from solutions is presence of organic residuals in deposited thin films, which can be limiting for some IR optical applications. However, organic residuals content can be significantly reduced by proper post-deposition thermal treatment [15, 16, 19, 26].

The poor solubility of selenide ChGs in pure volatile amine solvents limits the variety of glass compositions suitable for solution processing. Previously, the arsenic-selenide thin films were deposited from ethylenediamine [27] or ethanolamine [28] solutions but their optical quality, roughness or targeted composition were highly affected. Moreover, the high boiling points and low volatility of used ethylenediamine (b.p. 116 °C [29]) and ethanolamine (b.p. 172 °C [30]) solvents dampen the possibility of successful organic residuals removal from deposited thin films. The presence of residual particles or precipitate in prepared ChG solutions was also reported, and it is usually removed by filtration, centrifugation or sedimentation [15, 27, 28, 31]. However, the precipitation and filtration procedures can consequently influence the composition of used ChG solution and in extension the composition of deposited thin films. To overcome these problems new solvents with suitable physical and chemical properties should be found.

In this work, the study of volatile amine-based solvent mixtures and their influence on  $As_{30}Se_{70}$  ChG solubility and dissolution mechanism is presented. The main aim of our research is focused on finding of volatile solvent or multi-component solvent mixture, which would be able to quantitatively dissolve  $As_{30}Se_{70}$  bulk ChG, deposit thin films with specular optical quality and maintain glass composition. The thermal stabilization treatment is used to reduce organic residuals content and subsequently enhance the optical properties of studied thin films. The  $As_{30}Se_{70}$  thin films are deposited as well to compare the organic residuals content between arsenic selenide and arsenic sulfide solution processed ChG thin films.

## 2. Experimental

The source bulk  $\text{As}_{30}\text{Se}_{70}$  and  $\text{As}_{30}\text{S}_{70}$  chalcogenide glasses (ChGs) were prepared by standard melt-quenching method. High purity (5N) elements were loaded into cleaned quartz ampules in calculated amounts. The ampules were evacuated ( $\sim 10^{-3}$  Pa) and sealed. The reagents were melted in a rocking tube furnace at 800 °C for 48 hours. Subsequently the ampules with melted glass were quenched in a cold water.

Synthesized  $\text{As}_{30}\text{Se}_{70}$  bulk glass was powdered in agate bowl and weighted into glass vials to planned concentration of 0.075 g of glass powder per 1 ml of solvent. The three different solvents were chosen in total: pure n-propylamine ( $\text{PrNH}_2$ ), 10 % vol. solution of 1-propanethiol ( $\text{PrSH}$ ) in  $\text{PrNH}_2$  and 10 % vol. solution of methanol ( $\text{MeOH}$ ) in  $\text{PrNH}_2$ . All solvents were miscible without any phase separation. The  $\text{As}_{30}\text{Se}_{70}$  ChG was dissolved under rigorous stirring using a magnetic stirrer. The glass solutions were pipetted onto rotating soda-lime glass substrates and spin-coated (spin-coater Best Tools SC110-B) in argon atmosphere at 2000 rpm for 120 s. Immediately after the deposition the films were stabilized by annealing (soft baking) at 60 °C on a hot plate (stabilized thin films are hereafter referred as as-prepared thin film). In order to compare the content of organic residuals between sulfide and selenide thin films the  $\text{As}_{30}\text{S}_{70}$  ChG was dissolved in the  $\text{PrNH}_2$ - $\text{MeOH}$  solvent with the same concentration and spin-coated at 8000 rpm for 120 s to reach similar thickness as  $\text{As}_{30}\text{Se}_{70}$  thin films. All annealed samples were stored in dry, dark environment at laboratory temperature.

The samples of  $\text{As}_{30}\text{Se}_{70}$  and  $\text{As}_{30}\text{S}_{70}$  thin films prepared from  $\text{PrNH}_2$ - $\text{MeOH}$  solution were annealed at 70, 80, 90, 100, 110, 120 and 130 °C for 60 min on the hot plate (Conbrio, Czech Republic) in argon-filled annealing chamber.

Variable angle spectroscopic ellipsometer (VASE J. A. Woollam Co.) was used for the optical properties characterization of the prepared  $\text{As}_{30}\text{Se}_{70}$  samples. The ellipsometer was equipped with an automatic rotating analyzer over the spectral range 210 nm – 1700 nm (UV-VIS-NIR), measuring 30 revolutions with photon energy steps of 0.05 eV at three selected angles of incidence (AOI) (50°, 60° and 70°). Near normal incidence optical reflectance was measured by the same instrument. Optical spectrometer (Shimadzu UV3600) was used for transmission spectra measurements in the spectral region 190 – 2000 nm. The evaluation of the measured data was performed in WVASE32 software.

Surface topography of spin-coated  $\text{As}_{30}\text{Se}_{70}$  thin films was studied by atomic force microscopy method (Solver NEXT, NT-MDT). Surface roughness was determined from measured data as a root mean square value (RMS) according to the ISO 4287/1 norm. The measurements were performed on four 10 x 10  $\mu\text{m}$  spots of the same thin film and obtained RMS values were averaged.

The SEM scans and elemental concentration of studied samples were obtained using scanning electron microscope LYRA 3 (Tescan) equipped with EDS analyzer AZtec X-Max 20 (Oxford Instruments). The EDS measurements were performed at 5 kV (thin films) and 20 kV (bulk glass) acceleration voltage on four 400x400  $\mu\text{m}$  spots for each sample.

The structure of the source  $\text{As}_{30}\text{Se}_{70}$  bulk glass and spin-coated thin films was determined using FT-IR spectrometer IFS55 with Raman module FRA106 (Bruker) utilizing excitation by Nd:YAG laser (1064 nm). The Raman spectra were measured with laser beam intensity of 50 mW (2  $\text{cm}^{-1}$  resolution, 200 scans). Presented spectra were normalized by the intensity of the most intense band in the spectrum.

## 3. Results and discussion

Previous research has confirmed, that As-S ChGs can be successfully dissolved in volatile amines with short aliphatic chain (such as n-propylamine or n-butylamine) [15, 16, 19, 20]. In this work, we have also used the n-propylamine ( $\text{PrNH}_2$ ) solvent for  $\text{As}_{30}\text{Se}_{70}$  ChG dissolution. However, the experiments proved that  $\text{As}_{30}\text{Se}_{70}$  bulk glass has a poor solubility in pure  $\text{PrNH}_2$  and the dissolution process is accompanied by formation of substantial amounts of precipitate

(Fig. 1 (A)). Therefore, the  $As_{30}Se_{70}$  solution in  $PrNH_2$  was not used for thin film deposition. The solid particles would spoil the optical quality of spin-coated thin films and the precipitation could significantly change the composition of ChG solution. The poor solubility of  $As_{30}Se_{70}$  ChG in  $PrNH_2$  can be partially explained by presence of Se-Se homopolar bonds due to the high Se overstoichiometry. The selenium (with Se-Se homopolar bonds) is notoriously insoluble in most common solvents under ambient conditions [32–34] and XPS measurements of  $As_{30}Se_{70}$  bulk glass have confirmed, that nearly 70% of Se atoms are present in form of Se-Se-As or Se-Se-Se fragments [35].

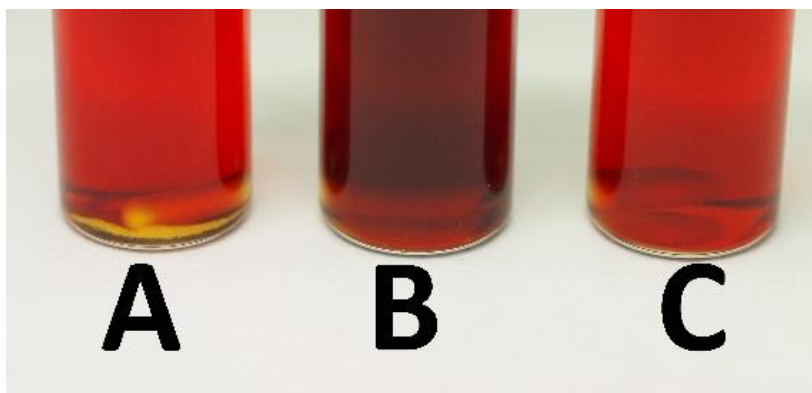


Fig. 1. The  $As_{30}Se_{70}$  solutions in pure n-propylamine (A) and in 10 vol. % solutions of 1-propanethiol (B) and methanol (C) in n-propylamine.

The elemental selenium and compounds of selenium with 15. group elements can be dissolved at room temperature and ambient pressure in solution formed by mixing amines with thiols [33, 34, 36]. The thiols are responsible for cleavage of Se-Se bonds and the amines actively participate in stabilization of Se ions (probably by hydrogen bonding). To ensure the formation of thin film by solution-based coating techniques and easier removal of organic residual from the volume of deposited thin films, the amine and thiol solvents must be volatile and be of low molar mass. Thus, the  $As_{30}Se_{70}$  ChG powder was mixed with 10 vol. % solution of 1-propanethiol ( $PrSH$ ) in  $PrNH_2$ . In this case, the ChG was quantitatively dissolved without any precipitation (Fig. 1 (B)). The clear solution of  $As_{30}Se_{70}$  ChG was used for thin film deposition. However, despite using the inert argon atmosphere the as-prepared spin-coated thin films were opaque with poor optical quality (Fig. 2, red line). The deposited thin films would be also contaminated with disulfides which are formed from thiols as a part of proposed dissolution mechanism [33].

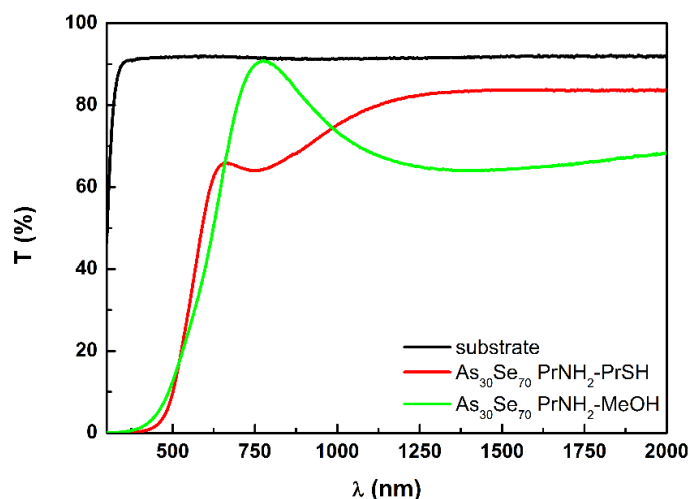


Fig. 2. The transmission spectra of clean substrate and as-prepared spin-coated  $\text{As}_{30}\text{Se}_{70}$  thin films deposited from 10 vol. % solutions of 1-propanethiol (PrSH) and methanol (MeOH) in n-propylamine (PrNH<sub>2</sub>).

To overcome the possible sulfur contamination and to increase the optical quality of deposited thin films, we have replaced the 10 vol. % of PrSH by 10 vol. % of methanol (MeOH). The  $\text{As}_{30}\text{Se}_{70}$  ChG was quantitatively dissolved without any precipitation (Fig. 1 (C)). Thus, the mixture of PrNH<sub>2</sub> and MeOH is suitable for  $\text{As}_{30}\text{Se}_{70}$  ChG dissolution, but reaction mechanism is still yet to be explained. We assume that the MeOH can either participate in Se-Se bond cleavage or more probably it can help to disperse the  $\text{As}_{30}\text{Se}_{70}$  ionic dissolution products, which proved to have only limited solubility in pure PrNH<sub>2</sub> (Fig. 1 (A)). Dielectric constant (which can be interpreted as a measure of polarity [37]) of MeOH ( $\epsilon = 33.30$  [38]) is significantly higher than dielectric constant of PrNH<sub>2</sub> ( $\epsilon = 5.42$  [39]). The more polar MeOH molecules probably solvate some of the  $\text{As}_{30}\text{Se}_{70}$  ionic dissolution products, which are otherwise insoluble or only partially soluble in pure PrNH<sub>2</sub>.

The thin films were spin-coated in inert argon atmosphere from the clear  $\text{As}_{30}\text{Se}_{70}$  solution in binary PrNH<sub>2</sub>-MeOH solvent. The transmission spectra proved that the deposited thin films have high optical quality (Fig. 2, green line) and thus the new PrNH<sub>2</sub>-MeOH solvent mixture is superior to PrNH<sub>2</sub>-PrSH mixture from the point of view of optical quality of deposited thin films. The content of residual solvent molecules was reduced by subsequent thermal treatment. The as-prepared  $\text{As}_{30}\text{Se}_{70}$  thin films were annealed under Ar atmosphere at 70 - 130 °C with 10 °C increment. The maximum annealing temperature was chosen with respect to the  $T_g$  of source bulk glass ( $T_g = 115\text{-}120$  °C [40, 41]). However, the thin films annealed at 120 and 130 °C were significantly degraded (Fig. 3). Their surface was covered by “droplets” with several  $\mu\text{m}$  in diameter resulting in only partially transparent thin film with low optical quality. The droplets were probably formed due to the influence of annealing at (or above) the  $T_g$  of material and thus the thermal stabilization at higher temperatures cannot be performed without spoiling of samples optical quality.

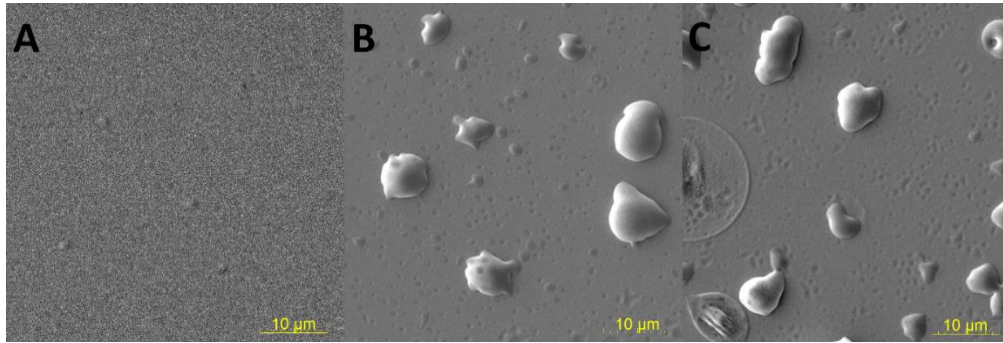


Fig. 3. The SEM scans of spin-coated  $\text{As}_{30}\text{Se}_{70}$  thin films annealed at 110 °C (A), 120 °C (B) and 130 °C (C).

The thickness and optical parameters of studied samples were studied by spectroscopic ellipsometry, but optical parameters of samples annealed at 120 and 130 °C were not evaluated due to their low optical quality. For evaluation of measured ellipsometry spectra the sample model consists of 1) a semi-infinite glass substrate (with optical constants obtained previously on a blank sample of uncoated microscopic soda-lime glass slide), 2) a homogenous and isotropic thin film, 3) surface roughness modeled by a Bruggeman type effective medium approximation of the voids and layers [42], and 4) air as the ambient medium was used. Minimization procedure using the mean square error (MSE) values was conducted to calculate geometrical and optical parameters of studied samples. The Tauc-Lorentz oscillator has been used for description of the short wavelength absorption edge which is present in the measured part of the spectra because of amorphous semiconducting nature of the samples [43]. The data from transmission and reflection have been used in the fit using MSE minimization together with the ellipsometry data to ensure validity of short wavelength absorption edge determination and determination of the thickness. Overall MSE was less than 6.6 for all samples. Four samples for each treatment were analyzed and the averaged values of thickness, surface roughness, refractive index at 1550 nm and optical bandgap together with their standard deviations are presented in Table 1. The surface roughness of studied thin films was also determined using AFM technique as root mean square (RMS) and their values are presented in Table 1 as well. Obtained spectroscopic and roughness data confirmed that  $\text{As}_{30}\text{Se}_{70}$  thin films deposited from chalcogenide glass solution in 10 vol. % of MeOH in  $\text{PrNH}_2$  had a specular optical quality.

**Table 1. Values of  $\text{As}_{30}\text{Se}_{70}$  thin film's thickness, refractive index at 1550 nm ( $n_{1550}$ ) and optical bandgap ( $E_g^{opt}$ ) determined by spectroscopic ellipsometry and surface roughness determined by spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).**

Sample	Thickness (nm)	SE roughness (nm)	AFM roughness (nm)	$E_g^{opt}$ (eV)	$n_{1550}$
as-prepared	$139 \pm 3$	$0.1 \pm 0.1$	$0.61 \pm 0.03$	$1.80 \pm 0.01$	$2.42 \pm 0.01$
T – 70 °C	$134 \pm 2$	$0.0 \pm 0.1$	$0.50 \pm 0.02$	$1.79 \pm 0.01$	$2.47 \pm 0.01$
T – 80 °C	$132 \pm 2$	$0.0 \pm 0.1$	$0.55 \pm 0.02$	$1.80 \pm 0.01$	$2.49 \pm 0.01$
T – 90 °C	$133 \pm 1$	$0.0 \pm 0.1$	$0.49 \pm 0.02$	$1.82 \pm 0.01$	$2.51 \pm 0.01$
T – 100 °C	$134 \pm 1$	$0.1 \pm 0.2$	$1.31 \pm 0.14$	$1.86 \pm 0.01$	$2.54 \pm 0.01$
T – 110 °C	$123 \pm 1$	$0.1 \pm 0.2$	$1.25 \pm 0.10$	$1.81 \pm 0.01$	$2.55 \pm 0.01$

The results proved that the as-prepared spin-coated thin films have relatively low thickness (below 142 nm, Fig. 4 (A)). The thermal stabilization of studied  $\text{As}_{30}\text{Se}_{70}$  thin films up to 100 °C induced only minor thickness decrease ( $\sim 4\%$ ). It indicates that solution processed as-prepared arsenic selenide thin films have lower content of organic residuals (either in a form of

chemically bonded molecules or as inclusions) in comparison with more frequently studied arsenic sulfide thin films prepared from different volatile amine-based solvents ( $\sim 15\%$  thickness contraction [26]). However, annealing of deposited  $\text{As}_{30}\text{Se}_{70}$  thin films at  $110\text{ }^\circ\text{C}$  induced higher thickness contraction ( $\sim 11\%$ ) which was at  $120$  and  $130\text{ }^\circ\text{C}$  also accompanied by surface degradation (see Figure 3). The roughness of studied samples was also very low which is beneficial for potential optical applications (Figure 4 – B). The thin films annealed at  $100$  and  $110\text{ }^\circ\text{C}$  exhibited slight roughness increase, but its RMS values have not exceeded  $1.31 \pm 0.14\text{ nm}$ . The difference between AFM and SE roughness values can be explained by significantly different evaluation technique and by different measurement area.

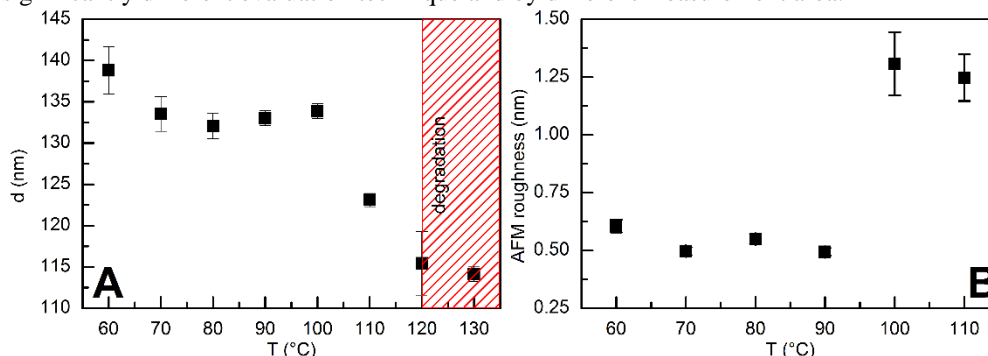


Fig. 4. The thickness (A) and AFM surface roughness (B) of studied  $\text{As}_{30}\text{Se}_{70}$  thin films in dependence on the annealing temperature.

The optical parameters of solution processed  $\text{As}_{30}\text{Se}_{70}$  thin films with specular optical quality (i.e. without surface degradation) proved that refractive index is steadily increasing with increasing annealing temperature (Fig. 5) but optical bandgap is changing only negligibly. The refractive index at  $1550\text{ nm}$  and optical bandgap of thin film annealed at  $110\text{ }^\circ\text{C}$  was  $n_{1550} = 2.55$  and  $E_g^{\text{opt}} = 1.81\text{ eV}$ , respectively. The refractive index of thermally stabilized  $\text{As}_{30}\text{Se}_{70}$  sample is one of the highest observed for solution processed chalcogenide glass thin films. The thermally evaporated thin films of the same  $\text{As}_{30}\text{Se}_{70}$  composition have only slightly higher refractive index ( $n_{1550} = 2.57$  [44]) and slightly lower optical bandgap ( $E_g^{\text{opt}} = 1.79\text{ eV}$  [41, 44]). Thus, despite using the solution-based deposition technique it is possible to prepare thin films in specular optical quality with optical properties very similar to those of thermally evaporated thin films.

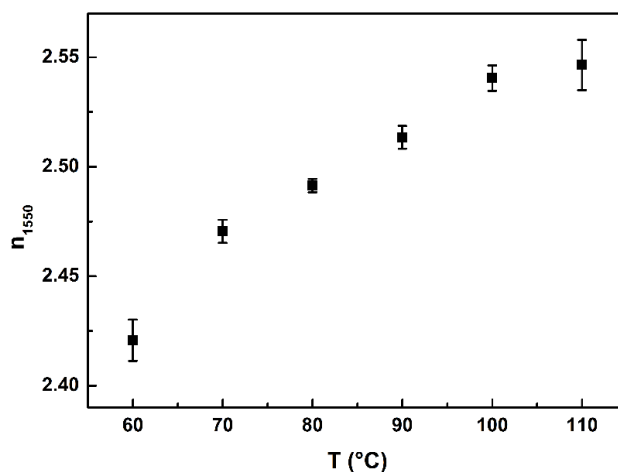


Fig. 5. The refractive index of studied  $\text{As}_{30}\text{Se}_{70}$  thin films at  $\lambda = 1550\text{ nm}$  in dependence on the annealing temperature.



The elemental composition of prepared bulk glass and spin-coated  $\text{As}_{30}\text{Se}_{70}$  thin films was studied by EDS technique. The measurements confirmed that the bulk glass has  $\text{As}_{29.5}\text{Se}_{70.5}$  composition which is close to the planned  $\text{As}_{30}\text{Se}_{70}$  composition and still well within the experimental error of EDS technique. Prepared thin films have stable  $\text{As}_{29.1}\text{Se}_{70.9}$  composition which is practically the same as the source bulk glass. The elemental composition of studied samples did not change with increasing annealing temperature, even for surface degraded samples annealed at 120 and 130 °C.

The content of organic residuals was also studied by EDS using the nitrogen content. The  $\text{PrNH}_2$  molecules contains one nitrogen atom and there is no other possible source of nitrogen in the studied thin films due to the inert Ar atmosphere used during thin films deposition and their annealing. Thus, the nitrogen content should be equivalent to the residual  $\text{Pr-NH}_2$  organic molecules inside the glass matrix. The nitrogen content is presented relative to the content of arsenic in Fig. 6. In order to compare the content of organic residuals between arsenic selenide and arsenic sulfide thin films, the  $\text{As}_{30}\text{S}_{70}$  thin films were also deposited from the solution of the same formulation (10 vol. % of MeOH in  $\text{PrNH}_2$ ) and concentration (0.075 g of glass powder per 1 ml of solvent). The spin-coating rotation speed was adjusted to yield thin films of the similar thickness ( $d \sim 142$  nm) as the  $\text{As}_{30}\text{Se}_{70}$  thin films. The relative nitrogen content for both spin-coated  $\text{As}_{30}\text{S}_{70}$  and  $\text{As}_{30}\text{Se}_{70}$  thin films is given in Fig. 6. The data confirm that the content of organic residuals in  $\text{As}_{30}\text{Se}_{70}$  thin films as well as in  $\text{As}_{30}\text{S}_{70}$  thin films is gradually decreasing with increasing annealing temperature. However, the organic residuals in  $\text{As}_{30}\text{Se}_{70}$  thin films can be almost completely removed at temperatures close to the  $T_g$  but at cost of observed surface degradation.

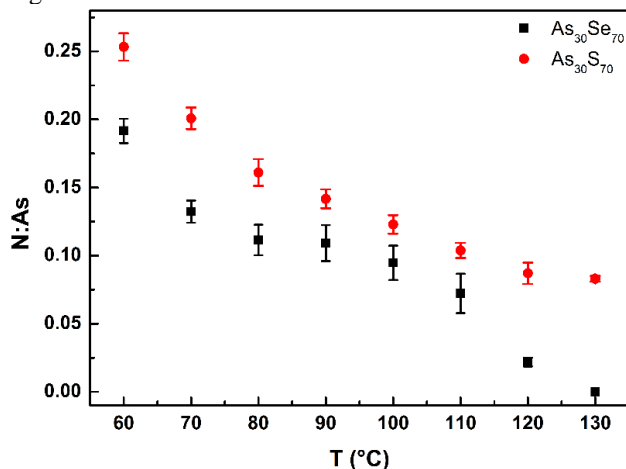


Fig. 6. The dependence of the nitrogen/arsenic ratio on the annealing temperature in spin-coated  $\text{As}_{30}\text{Se}_{70}$  and  $\text{As}_{30}\text{S}_{70}$  thin films prepared from  $\text{PrNH}_2$ -MeOH solutions.

The data show that the  $\text{As}_{30}\text{S}_{70}$  thin films have significantly higher content of organic residuals in comparison with  $\text{As}_{30}\text{Se}_{70}$  thin films. We assume that observed difference in organic residuals content can be explained by combination of different electronegativity of sulfur and selenium atoms and lower solubility of some As-Se dissolution products. Results proved that the as-prepared As-S ChG thin films deposited from their aliphatic amine solutions are mainly composed from alkyl ammonium arsenic sulfide salts [15, 16, 18]. These salts consist of ChG clusters terminated at their surface by excess of negatively charged sulfur and charge compensating alkyl ammonium ion. The organic residuals can be also present in form of occluded molecules inside thin film matrix [45]. The thermal stabilization induces decomposition of alkyl ammonium salts and release of organic molecules. However, this process does not occur at the exact temperature but rather in wide temperature range with various stages of salts decomposition [15, 16, 26]. The solution processed as-prepared  $\text{As}_{30}\text{Se}_{70}$

thin films probably also contain similar alkyl ammonium arsenic selenide salts, but due to the lower selenium electronegativity (in comparison with sulfur) the ChG-amine bond is weaker and higher amount of organic residual molecules is released during the first stabilization annealing (soft baking) at 60 °C. The experiment with dissolution of  $\text{As}_{30}\text{Se}_{70}$  ChG in pure  $\text{PrNH}_2$  (Fig. 1 (A)) also confirmed, that not all of As-Se dissolution products are fully soluble in  $\text{PrNH}_2$ . However, similar substantial precipitation was not reported for dissolution of stoichiometric or sulfur rich As-S ChGs in aliphatic amines [15, 16, 17, 18, 21, 26]. The presence of insoluble compounds in  $\text{PrNH}_2/\text{As}_{30}\text{Se}_{70}$  solution indicates that some of the dissolution products are not bonded to  $\text{PrNH}_2$  molecules, which can be also subsequently reflected in lower content of organic residuals in deposited  $\text{As}_{30}\text{Se}_{70}$  thin films.

To study the oxygen content which can be also connected with content of organic residuals in form of MeOH, the set of samples was deposited on clear silicon substrates. It was found that the oxygen content has not exceeded 2 at. % for all studied samples. Moreover, the oxygen content has not significantly changed with annealing temperature and thus we assume that the oxygen presence can be attributed to the presence of native oxygen film on silicon substrate and/or arsenic oxides formed on the surface of  $\text{As}_{30}\text{Se}_{70}$  thin films during storing or their transportation.

The structure of source bulk glass and deposited  $\text{As}_{30}\text{Se}_{70}$  thin films was analyzed by Raman spectroscopy (Fig. 7). The most intensive Raman bands of various structural vibrations lie in narrow region between 200-300  $\text{cm}^{-1}$  due to the similar molecular weight of As and Se atoms. The main structural units of source  $\text{As}_{30}\text{Se}_{70}$  bulk glass are  $\text{AsSe}_{3/2}$  trigonal pyramids with band at 226  $\text{cm}^{-1}$  [41, 46, 47]. Two additional strong bands at 239 and 253  $\text{cm}^{-1}$  are present in measured spectrum of source bulk glass. They can be attributed to the vibrations of Se-Se chains [41, 46, 47] and  $\text{Se}_8$  rings [41, 46, 47] formed as a result of significant selenium overstoichiometry.

The Raman spectrum of as-prepared  $\text{As}_{30}\text{Se}_{70}$  thin film differs from the spectrum of source bulk glass. The most intensive band in the spectrum at 253  $\text{cm}^{-1}$  belongs to the vibrations of  $\text{Se}_8$  rings. The broad shoulder below 200  $\text{cm}^{-1}$  gives an evidence of additional structural units, which are not present in source bulk glass. According to [46, 47] they can be attributed to the vibrations of  $\text{As}_4\text{Se}_4$  arsenic rich cage-like structural units. These units were probably formed during dissolution of source bulk glass when selenium atoms were removed from the former  $\text{AsSe}_{3/2}$  trigonal pyramids enabling the formation of  $\text{As}_4\text{Se}_4$  arsenic rich fragments and formation of additional Se-Se chains  $\text{Se}_8$  rings. The similar dissolution mechanism which involved the formation of arsenic rich structural units was also reported for As-S chalcogenide glasses deposited from various amines solutions [15, 16, 26, 48]. The presence of very weak bands at 2800-3000  $\text{cm}^{-1}$  prove that deposited thin films also contain residual organic molecules.

The Raman spectra confirm that annealing of solution processed  $\text{As}_{30}\text{Se}_{70}$  thin films induces structural polymerization similar to the As-S or Ge-S spin-coated thin films [19, 20, 26]. The spectra show that the bands of  $\text{Se}_8$  rings and arsenic rich  $\text{As}_4\text{Se}_4$  units are proportionally decreasing while the intensity of  $\text{AsSe}_{3/2}$  trigonal pyramids band is increasing. The spectra indicate that observed thermo-induced structural changes occur in several steps in dependence on annealing temperature. The structure of thin films annealed at 80-100 °C and 110-130 °C are almost identical. Thus, from the structural point of view there is not big difference if the sample which was annealed at 110 °C (where specular optical quality has been maintained) or samples annealed at 120 or 130 °C (where samples undergo significant surface degradation). The main difference would be only in the content of organic residuals as it was proved by EDS analysis (see Fig. 6). However, the structure of  $\text{As}_{30}\text{Se}_{70}$  thin film annealed at 130°C is still partially different from the source bulk glass.

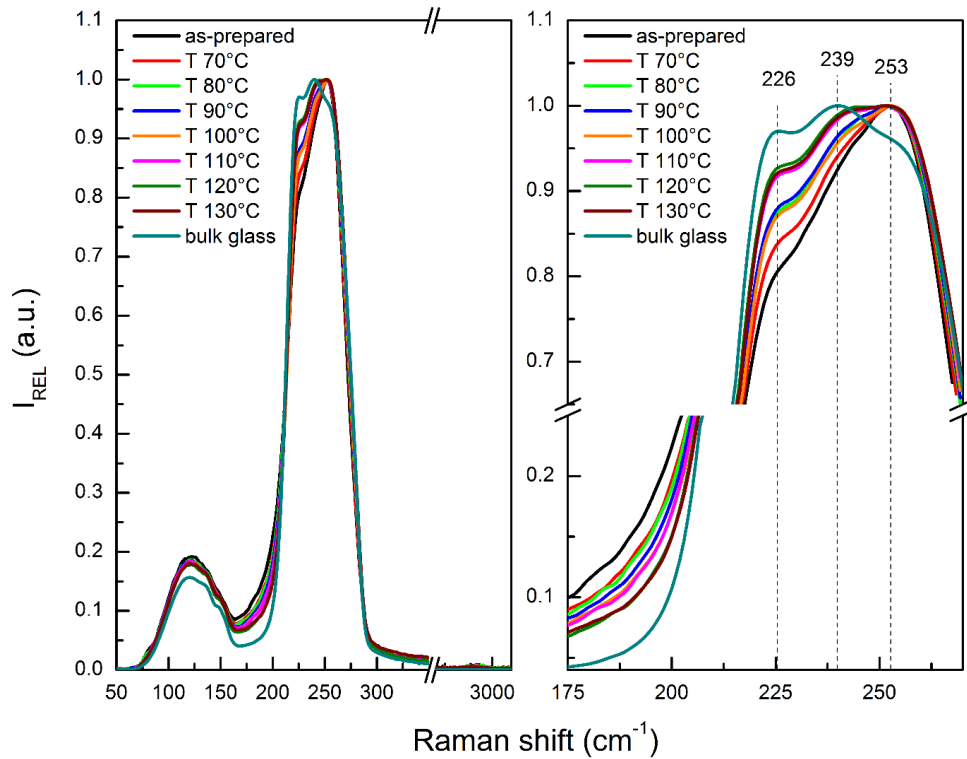


Fig. 7. Raman spectra of source bulk glass and deposited  $\text{As}_{30}\text{Se}_{70}$  thin films annealed at various temperatures.

#### 4. Conclusion

The pure n-propylamine ( $\text{PrNH}_2$ ) and 10 vol. % solutions of 1-propanethiol ( $\text{PrSH}$ ) or methanol ( $\text{MeOH}$ ) in  $\text{PrNH}_2$  were chosen to dissolve selenium-rich  $\text{As}_{30}\text{Se}_{70}$  chalcogenide glass. The bulk glass was quantitatively dissolved without any precipitation only in  $\text{PrNH}_2$ - $\text{PrSH}$  and  $\text{PrNH}_2$ - $\text{MeOH}$  binary solvents. Prepared  $\text{As}_{30}\text{Se}_{70}$  chalcogenide glass solutions were used for thin film deposition by spin-coating technique. The thin films prepared from  $\text{PrNH}_2$ - $\text{PrSH}$  solution were opaque and this multi-component solvent proved to be unsuitable for deposition of thin films in specular optical quality. Contrary, the thin films prepared from solution in  $\text{PrNH}_2$ - $\text{MeOH}$  binary solvent had a specular optical quality and they were further analyzed.

Optical properties of deposited  $\text{As}_{30}\text{Se}_{70}$  thin films have been studied by spectroscopic ellipsometry (SE). With increasing annealing temperature, thickness of studied samples is decreasing resulting in densification of their structure which was also reflected in gradual increase of refractive index. The optical parameters of  $\text{As}_{30}\text{Se}_{70}$  thin film thermally stabilized at 110 °C were very similar to the optical parameters of  $\text{As}_{30}\text{Se}_{70}$  thin films deposited by more conventional thermal evaporation. However, the annealing of deposited thin films at or above the  $T_g$  (120 and 130 °C) induced significant surface degradation. Both SE and AFM techniques proved that the deposited thin films had a very low surface roughness and the annealing temperature changed it only negligibly. The composition of deposited thin films was studied by EDS which confirmed that the studied  $\text{As}_{30}\text{Se}_{70}$  thin films are of the same composition as the source bulk glass and the content of organic residuals in thin films was significantly reduced by thermal treatment. The thermal treatment also induced structural polymerization. Thus, the  $\text{PrNH}_2$ - $\text{MeOH}$  solvent mixture proved to be appropriate for deposition of selenium rich  $\text{As}_{30}\text{Se}_{70}$  thin films in specular optical quality.

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