

Comparison of solution processed As₃₃S₆₇ thin films deposited using primary amines of various aliphatic chain length

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Highlights

- Various amines used for deposition of As₃₃S₆₇ spin-coated films were studied
- Thin films in optical quality prepared from amines with 3-6 carbons in chain
- Carbon chain length in amine influences only conditions of film deposition process
- Structure and properties of deposited films depend only on annealing temperature

Abstract

Solution processed thin chalcogenide films gain attention due to their interesting optical properties and simplicity of the deposition. The influence of the aliphatic chain length in primary amines used for As₃₃S₆₇ thin films deposition by spin-coating and their subsequent characterization had been studied in this paper, particularly films prepared from solutions based on n-propylamine, n-butylamine, n-pentylamine and n-hexylamine were investigated. As-prepared thin films were annealed at temperatures below glass T_g, particularly 65 – 140 °C. Results gave evidence that variety in physical and chemical properties of studied amines influences required conditions of deposition process of the thin film only (such as source glass dissolution time, thin film thickness, thickness shrinkage). The structure, optical properties (n, E_g), surface roughness, organic residual content and chemical resistance of deposited thin films are not significantly influenced by used amine but mostly by the post-deposition annealing temperature. Thin films composition remains uninfluenced by neither used amine nor the annealing temperature within studied range.

Introduction

Chalcogenide glasses (ChG) are semiconducting optical materials which are in the focus of material science for many decades due to their interesting physical and chemical properties such as wide IR transparency region and high values of refractive index [1, 2]. ChG, mostly in a thin film form, are often photosensitive. Magnitude of photoinduced changes of material's structure and consequently its properties (e.g. chemical resistivity, optical properties, etc.) depends mainly on the composition, form and history of the sample as well as the conditions of the exposure. Change of chemical resistance often leads to selective etching in alkaline solutions [3].

Many applications demand ChG in a thin film form on the suitable substrate. Various coating methods can be used for deposition of thin films [4]. Generally, these deposition methods can be divided into two main groups. First group is based on formation of thin films from gaseous phase – physical vapor deposition methods e.g.: thermal evaporation [5], laser ablation [6] or sputtering [7]. Second group of methods is based on the solubility of ChG in volatile organic bases and formation of thin films from glass solution – e.g.: spin-coating [8], dip-coating [9], electrospray [10] or spiral-bar coating [11]. In comparison with physical vapor deposition methods, solution processed thin film deposition methods offer advantage in the possibility of source solution doping (e.g.: glass composition modification [12])

or formation of composite material by introducing extrinsic materials such as nanoparticles [13]) and potential for large scale deposition and structuring by frequently used printing techniques. On the other hand, solution processed chalcogenide thin films usually contain residual amount of organic solvents influencing the thin films properties. However, these organic residues can be significantly reduced by proper post-deposition thermal treatment [14].

Primary aliphatic amines proved to be suitable solvents for quantitative dissolution of source bulk ChG and subsequent deposition of thin films in good optical quality by spin-coating method [15, 16]. So far, n-propylamine and n-butylamine solvents are mainly used in solution processing techniques due to their high volatility [8]. Presented paper offers comparison of solution processed thin films of $As_{33}S_{67}$ composition prepared from primary amines with various length of the aliphatic chain ranging from n-propylamine to n-hexylamine. Thin films were deposited by spin-coating method targeting their high optical quality and similar thickness.

Experimental details

The source $As_{33}S_{67}$ bulk ChG was prepared by standard melt-quenching method using high purity elements (5N). The glass synthesis was performed in vacuum ($\sim 10^{-3}$ Pa) sealed quartz ampule in rocking tube furnace at 850°C for 32 hours following quenching of the ampule in cold water.

Prepared $As_{33}S_{67}$ bulk glass was powdered in agate bowl and weighted into glass vials according to planned concentrations. The four aliphatic primary monoamines were used as a solvents: n-propylamine (n-PrNH₂) containing three carbon atoms in aliphatic chain, n-butylamine (n-BuNH₂) containing four carbon atoms in aliphatic chain, n-pentylamine (n-PenNH₂) containing five carbon atoms in aliphatic chain and n-hexylamine (n-HexNH₂) containing six carbon atoms in aliphatic chain. The n-BuNH₂, n-PenNH₂ and n-HexNH₂ solution were prepared by weighting of 0.1 g of glass powder per 1 ml of amine solvent. The n-PrNH₂ solution was prepared by weighting of 0.05 g of glass powder per 1 ml of amine solvent in order to achieve similar thickness of as-deposited thin films as in case of higher amine solutions. Glass was considered fully dissolved when no solids particles were visible in the solution. All obtained solutions were clear without any precipitation or turbidity.

The thin films were deposited using spin-coating method (spin-coater Best Tools SC110) onto soda-lime glass substrates. The rotation speed for deposition of thin films from each solution was chosen with respect to the volatility of the individual amines targeting same thickness of prepared thin films (~ 270 nm); particularly 2800 rpm for n-PrNH₂ solution, 6000 rpm for n-BuNH₂ solution, 3000 rpm for n-PenNH₂ solution and 1700 rpm for n-HexNH₂ solution was used. Duration of the deposition was 120 s for all solutions. Immediately after deposition the thin films were soft baked on hot plate for 20 minutes at temperatures ~ 15 °C below the boiling point of each particular amine.

The soft baked thin films were annealed at temperatures 65, 90, 115 and 140°C (hard bake) for 60 minutes in argon filled chamber in order to avoid surface oxidation.

The transmission spectra of thin films were measured using UV-VIS-NIR spectrometer (Shimadzu UV3600) in spectral range 190 – 2000 nm. The measurements were performed on three separate samples for each individual treatment. For determination of thicknesses and refractive index the transmission spectra were fitted by procedure described in [17] based on Wemple-DiDomenico's equation [18] and Swanepoel's model of thin films on substrate [19]. Values of optical bandgap were determined using Tauc's method for semiconductors [20]. Presented error bars represent standard deviation of calculated values obtained from all samples of the same treatment.

Compositions of source bulk glass and thin films were investigated using energy dispersive X-ray analysis (EDS) by Aztec X-Max 20 detector (Oxford Instruments) installed in scanning electron microscope LYRA 3 (Tescan). The analysis were performed using accelerating voltage 20 kV for bulk glass and 5 kV for thin films. Samples were measured at five 400 x 400 μm areas. Error bars represent

standard deviation of measured values. AFM scans of the thin films were obtained using Solver Next (NT-MDT) microscope equipped with NSG10 tips (NT-MDT). Surface roughness of thin films was determined from the AFM scans as root mean square value (RMS) according to ISO 4287/1 norm. Samples were measured at four 5 x 5 μm areas. Error bars represent standard deviation of measured values.

The IR spectra of studied thin films were recorded in 6000 – 30 cm^{-1} region (resolution 4 cm^{-1} , 64 scans) using Vertex 70v FTIR spectrometer (Bruker) equipped with single-bounce diamond ATR crystal.

Structure of bulk glass and thin films was investigated by MultiRAM (Bruker) FT-Raman spectrometer. Measurements were performed using 1064 nm Nd:YAG laser excitation beam with 15 mW beam intensity for bulk glass and 55 mW for thin films (resolution 2 cm^{-1} , 64 scans). Presented Raman spectra were normalized by the intensity of the most intensive band in the spectrum.

Prepared thin films were etched in solution of 0.1 vol.% n-BuNH₂ in dimethylsulfoxide at 25°C. Etching rates were evaluated by procedure described in [21].

Results and discussion

Length of the aliphatic carbon chain in primary amines significantly influences their physical and chemical properties. From the point of view of solution processed thin film deposition methods, two main parameters are crucial for film deposition – boiling point and vapor pressure (Fig. 1).

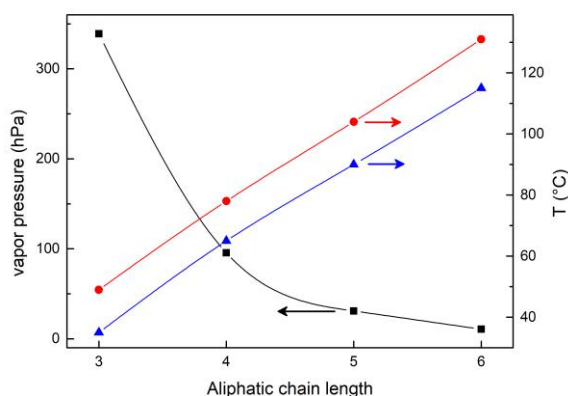


Fig. 1 Aliphatic chain length dependence of the vapor pressure (black squares), the boiling point temperature (red circles) and used soft bake temperatures (blue triangles) [22-25].

Boiling point of the source ChG solution is primarily dictated by the boiling point of used amine, which sets the soft bake temperature for as-deposited thin film stabilization. Soft baking induces major release of chemically non-bonded solvent, which significantly reduces reactivity of as-deposited thin film and thus preserves thin film from quick degradation in the ambient atmosphere. Used soft bake temperature is usually 10 – 15 °C below the boiling point of the used amine to avoid hasty release of amine molecules, which could roughen the thin films surface. Soft bake temperatures in presented experiments were set ~ 15 °C below the boiling point of each particular amine solution - 35 °C for n-PrNH₂ based solutions, 65 °C for n-BuNH₂ based solutions, 90 °C for n-PenNH₂ based solutions and 115 °C for n-HexNH₂ based solutions. Hard bake temperature was chosen with respect to temperature of the glass transition of bulk As₃₃S₆₇ ChG ($T_g = 145$ °C [26]) to 140 °C.

Volatility of the solvent, represented by the vapor pressure, significantly influences the thickness of deposited thin film (together with solution concentration and deposition speed). Vapor pressure steeply decreases with prolonging carbon chain length in the primary amines (Fig. 1). As a result, the

thickness of thin films prepared from the solutions of same concentrations significantly decreases with prolongation of the aliphatic chain in the amine (Fig. 2), other deposition conditions being fixed.

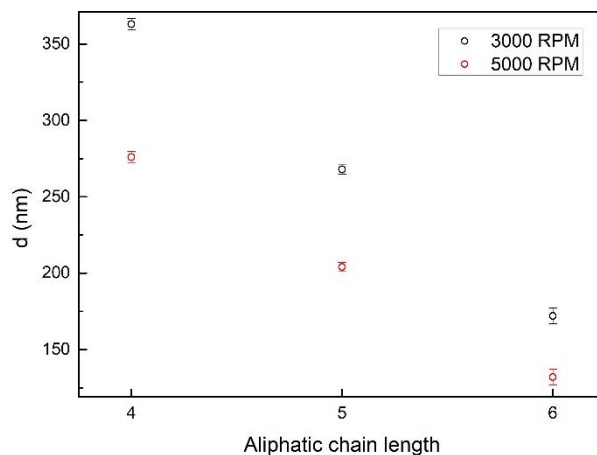


Fig. 2 Thickness of soft-baked $As_{33}S_{67}$ thin films prepared from n-butylamine (n-BuNH₂), n-pentylamine (n-PenNH₂) and n-hexylamine (n-HexNH₂) based solutions of same concentration (0.1 g of ChG per 1 ml of the solvent) spin-coated at 3000 and 5000 RPM. Results of n-PrNH₂ based solution are not presented because thin films cannot be prepared in good optical quality under given conditions.

The prolongation of aliphatic carbon chain in primary amines decreases their chemical reactivity with $As_{33}S_{67}$ ChG, which increases the time needed for complete dissolution of the bulk glass. Fig. 3 shows the dependence of the time needed for complete dissolution of the ChG (in concentration 0.1 g of ChG per 1 ml of the solvent) on the length of the carbon chain in the amine. After complete dissolution of $As_{33}S_{67}$ ChG clear solutions without any precipitates or turbidity were obtained. Acquired glass solutions were used for thin films deposition. Rotation speeds were adjusted for each particular amine solution so that thin films of same thickness ~ 270 nm were obtained after soft bake. In case of n-PrNH₂ solution the glass concentration had to be decreased to 0.05 g per 1 ml of n-PrNH₂ as well due to the high volatility of n-PrNH₂ in order to reach targeted thickness. The aim for the same thickness of soft baked thin films was chosen in order to be able properly compare properties of annealed thin films which are influenced by the thin film thickness such as organic residuals content, thickness shrinkage and others.

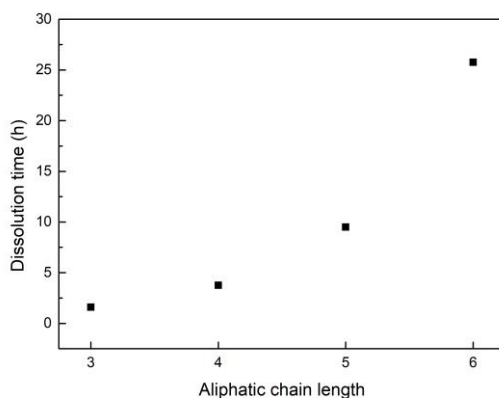


Fig. 3 Aliphatic chain length dependence of the time needed for complete dissolution of $As_{33}S_{67}$ bulk ChG in concentration 0.1 g of ChG per 1 ml of the amine.

The compositions of the thin films prepared from all studied amine solutions and annealed at all used temperatures were verified by EDS (table 1). Results showed minor arsenic depletion (~1.5 - 2 at. %) in all studied thin films (both soft and hard baked) in comparison with source bulk material $As_{33.6}S_{66.3}$, which is in good agreement with results published on solution processed thin films of similar compositions [27]. Aliphatic chain length or annealing temperature do not affect the glass composition of the thin film.

Table 1: Compositions of solution processed thin films prepared from $As_{33}S_{67}$ bulk glass dissolved in various amines and annealed at all studied temperatures.

Temperature (°C)	n-propylamine		n-butylamine		n-pentylamine		n-hexylamine	
	As	S	As	S	As	S	As	S
35	31.6	68.4	-	-	-	-	-	-
65	31.5	68.5	31.7	68.3	-	-	-	-
90	31.4	68.6	31.6	68.4	31.6	68.4	-	-
115	31.6	68.4	31.5	68.5	31.7	68.3	31.6	68.4
140	32.1	67.9	32.2	67.8	31.9	68.1	32.0	68.0

All of prepared thin films (both soft and hard baked) were of specular optical quality, which is demonstrated by their transmission spectra together with the spectrum of the substrate (Fig. 4). Measured transmission spectra were evaluated by the procedure published in [17] providing the values of refractive index, optical bandgap and thickness of the thin films.

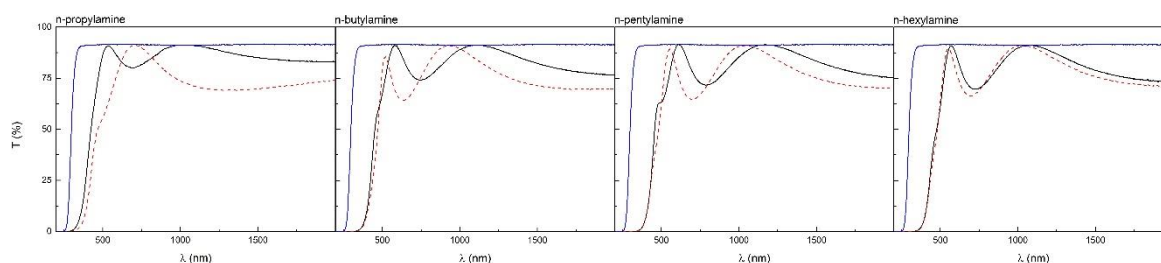


Fig. 4 Transmission spectra of soft (full black line) and hard (dashed red line) baked $As_{33}S_{67}$ thin films prepared from various amines together with the spectrum of the substrate (blue line).

Refractive index of as-deposited and annealed $As_{33}S_{67}$ thin films is not significantly dependent on the aliphatic chain length of the amine used for the source bulk glass dissolution - the annealing temperature dependence of refractive index values is almost identical for all studied amines (Fig. 5 left). Soft baked thin films exhibit slightly lower refractive index in comparison with their lighter (shorter carbon chain) counterparts but annealing of the thin film at temperatures above the boiling point of the amine unifies the refractive index values. The only exception are thin films prepared from n-HexNH₂, which show slightly lower refractive index than other thin films even after hard bake.

The difference between the refractive index of soft baked sample and the sample annealed just above the boiling point of the amine (first higher temperature) is decreasing with increasing aliphatic chain length of the amine. Possible explanation could be found in decreasing volatility of the amines with increasing carbon chain length and increasing degree of structural polymerization with increasing annealing temperature (structure of the thin films will be discussed later). Volatile n-PrNH₂ is released easily through only partially polymerized structure of the thin film resulting in large change in refractive

index. On the other hand low volatile n-HexNH₂ does not migrate easily through the highly polymerized structure and thus remains partially entrapped decreasing the overall value of the refractive index even of hard baked samples.

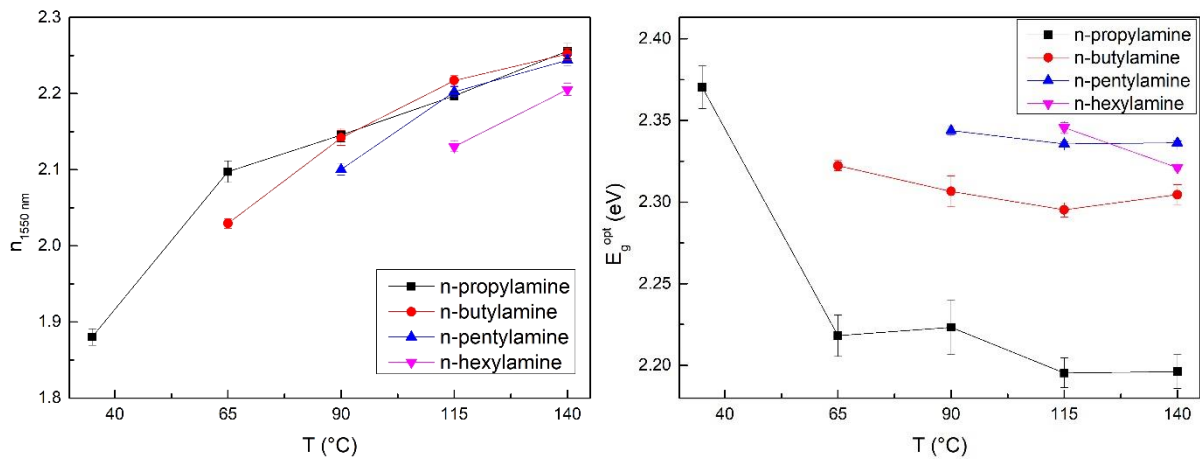


Fig. 5 Annealing temperature dependences of the refractive index at $\lambda = 1550$ nm (left) and optical bandgap (right) of As₃₃S₆₇ thin films prepared from various amines.

Optical bandgap values of soft baked thin films prepared from various amine solutions exhibit similar values ~ 2.34 eV. Annealing of thin films prepared from n-PrNH₂ solution shows significant drop of the optical bandgap to 2.2 eV. On the other hand the annealing temperature dependences of the films prepared from n-BuNH₂, n-PenNH₂ and n-HexNH₂ show no significant change of the bandgap with increasing temperature and the bandgap values after hard bake are of similar values 2.3 – 2.33 eV. We assume that significant drop of optical bandgap values in thin films prepared from n-PrNH₂ solution might be connected with expected higher porosity and presence of cavities as demonstrated by Waldman et al. in Ge-Sb-S thin films deposited from the same solvent [28].

The change of thin films thickness in dependence on the annealing temperature was studied as well (Fig. 6). Annealing of soft baked thin films at temperatures above boiling point of used amine causes significant release of amine molecules, which leads to significant decrease of the thin films thickness. Further increase of the annealing temperature induces additional decrease of the thickness up to the hard bake temperature. Most intensive thickness shrinkage (~ 45 %) of all studied thin film was observed in case of thin films prepared from n-PrNH₂ (Fig. 6 right). Prolongation of the carbon chain in the amine molecule significantly decreases the shrinkage of the thin films thickness after hard bake.

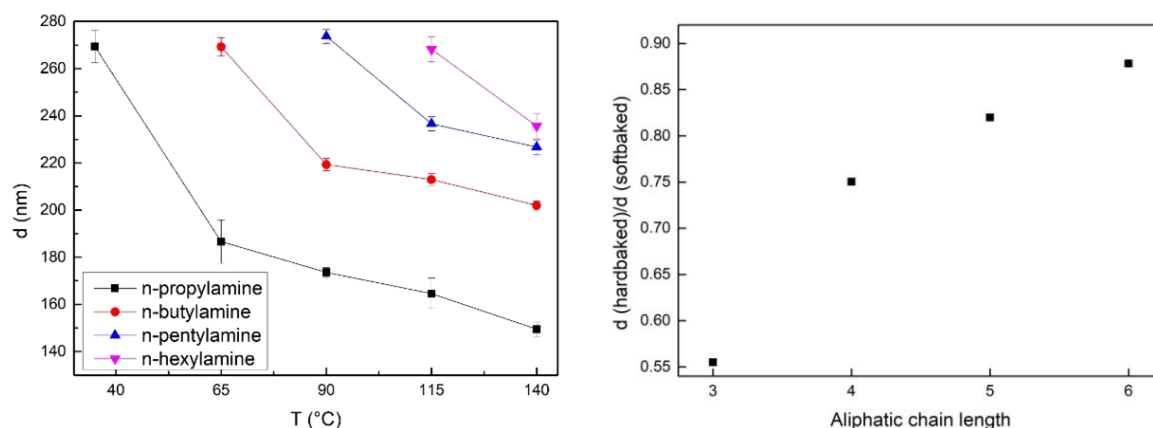


Fig. 6 Annealing temperature dependence of the $As_{33}S_{67}$ thin film thickness (left) and shrinkage of the thin films in dependence on the aliphatic chain length in used amine (right).

Unavoidable consequence of the thin films shrinkage induced by annealing is roughening of the thin films surface leading to the increase of the surface roughness. AFM scans of soft and hard baked thin film prepared from studied amines are given in the Fig. 7.

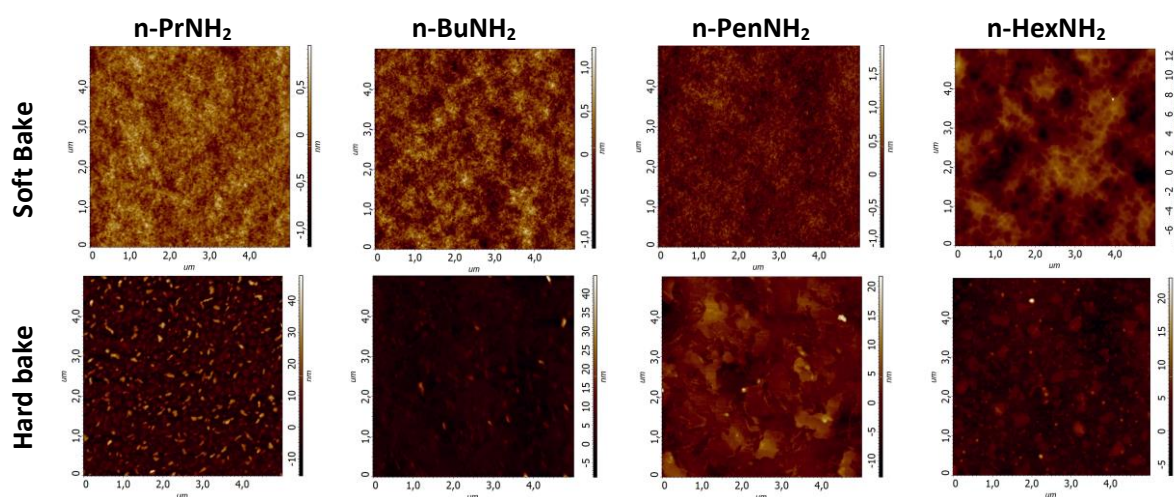


Fig. 7 AFM scans ($5 \times 5 \mu\text{m}$) of soft and hard baked thin films prepared from glass solutions based on various amines.

Thin films prepared from n-PrNH₂, n-BuNH₂ and n-PenNH₂ exhibit surface roughness < 1 nm after soft bake. Roughness increases with increasing annealing temperature up to 7.5 nm (for thin films prepared from n-PrNH₂) or 2-4 nm (for thin films prepared from n-BuNH₂, n-PenNH₂ and n-HexNH₂). Higher surface roughness of thin films deposited from n-PrNH₂ solution can be explained by significantly higher thermally induced shrinkage during hard baking.

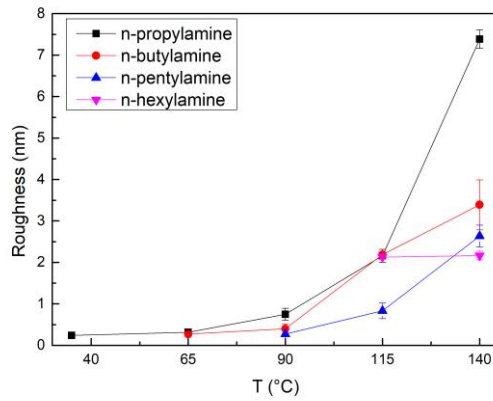


Fig. 8 Annealing temperature dependence of the $As_{33}S_{67}$ thin film surface roughness of thin films deposited from solutions based on various amines.

The content of organic residuals inside thin films matrix was determined by EDS analysis using relative content of nitrogen atoms. Thin films were deposited from aliphatic mono-amines and thus the content of nitrogen is proportional to the content of organic amine-based residuals. The trends in thermally induced release of organic residuals can be observed from Fig 9. The annealing temperature dependences of relative nitrogen content in studied thin films prepared from various amines is very similar. It indicates that chemically bonded solvent molecules are released by the same mechanism at same temperatures and extending length of aliphatic chain doesn't significantly hinder their thermally induced removal from thin film matrix (with 270 nm thickness). The data also proved that soft-baked thin films deposited from n-PrNH₂ have notably higher content of organic residuals than other studied samples and thermally induced release of organic residuals is more pronounced which is subsequently reflected in the higher thermally induced shrinkage and notable increase of thin films surface roughness (Figs. 6 and 8).

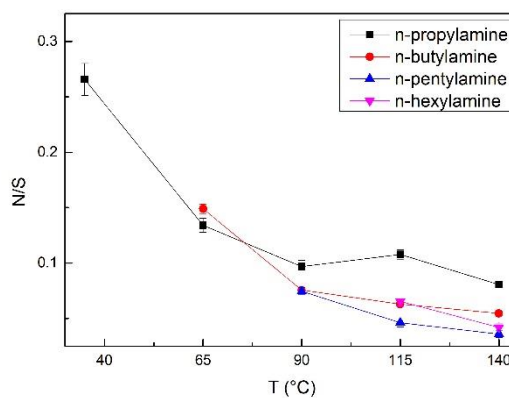


Fig. 9 The dependence of the nitrogen/sulfur ratio on the annealing temperature in spin-coated $As_{33}S_{67}$ thin films prepared from n-propylamine (n-PrNH₂), n-butylamine (n-BuNH₂), n-pentylamine (n-PenNH₂) and n-hexylamine (n-HexNH₂) solutions.

The content of organic residuals was also studied by FT-IR spectroscopy. ATR spectra of studied thin films are presented in Fig. 10. The spectra were normalized to the absorbance band corresponding to

the vibrations of glass substrate and presented in regions with characteristic vibrations of organic species. The most intensive bands in spectra are situated at 2870, 2930 and 2960 cm^{-1} which corresponds to the symmetric and asymmetric vibrations of CH_2 and CH_3 groups [29-31]. The wide shoulder around 3250 cm^{-1} confirms the presence of amino groups (symmetric and asymmetric N-H stretching vibrations) [31, 32]. The maximum of amine group related bands slightly shifts towards higher wavenumber with increasing length of aliphatic chain. The weak bands at 1465 and 1576 cm^{-1} can be attributed to the CH_2 bending vibrations and N-H bending vibrations, respectively [30-32]. As the temperature of annealing rises, the intensities of the bands are steadily decreasing. The most significant drop in bands intensities is always between soft baked first higher temperature annealed for all studied amines, which is in good agreement with results obtained by EDS analysis.

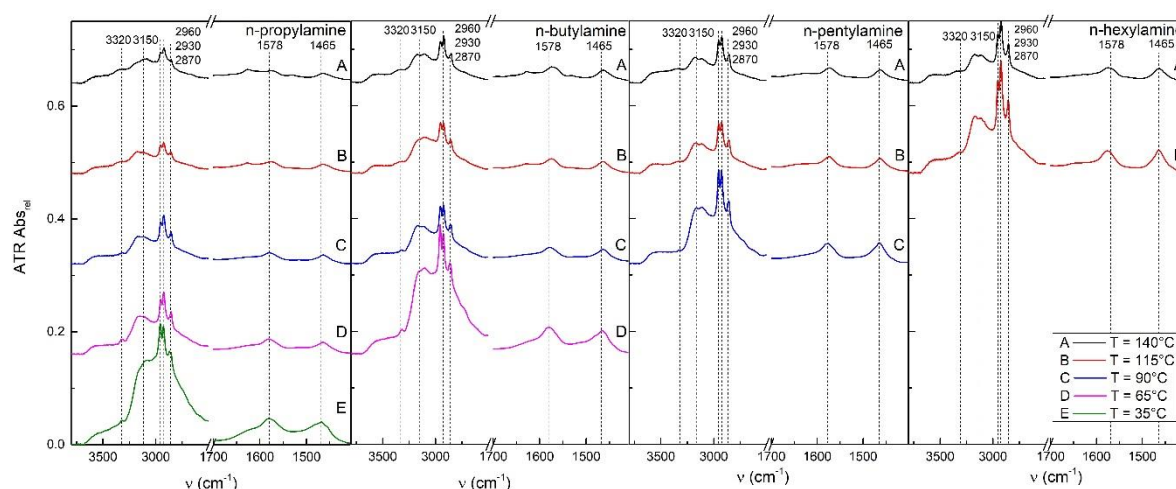


Fig. 10 IR spectra of spin-coated $\text{As}_{33}\text{S}_{67}$ thin films prepared from n-propylamine (n-PrNH₂), n-butylamine (n-BuNH₂), n-pentylamine (n-PenNH₂) and n-hexylamine (n-HexNH₂) solutions.

The structure of source $\text{As}_{33}\text{S}_{67}$ bulk glass and thin films was studied by Raman spectroscopy (Fig. 11). The Raman spectra of samples annealed at 140°C cannot be presented due to the very strong luminescence masking their Raman signal. The most dominant band with maximum at 340 cm^{-1} corresponds to the vibrations of $\text{AsS}_{3/2}$ trigonal pyramid units [33-35]. The intensive band with maximum at 375 cm^{-1} can be attributed to the vibration of arsenic-rich As_4S_4 realgar-like clusters [33, 35, 36]. The overstoichiometry of sulfur is manifested by presence of sulfur rings S_8 and sulfur chains S_n with bands at 150, 218 and 475 cm^{-1} (S_8 [37, 38]) and at 490 cm^{-1} (S_n [35, 36, 38]). In the spectra of spin-coated thin films there is also additional band at 418 cm^{-1} which is connected with the presence of alkyl ammonium arsenic sulfide (AAAS) salts originated from ChG dissolution [39, 40].

The dissolution of $\text{As}_{33}\text{S}_{67}$ CHG with subsequent thin film deposition followed by soft bake causes fragmentation of the glass structure [39]. Original polymer $\text{AsS}_{3/2}$ network, dominant in source bulk glass, is partially shattered producing arsenic-rich As_4S_4 clusters accompanied by S_8 rings and S_n chains. Annealing of $\text{As}_{33}\text{S}_{67}$ spin-coated thin films induces structural polymerization which is reflected in decrease of S_8 , S_n and As_4S_4 cluster bands intensities. Structural polymerization is also accompanied by thermal decomposition of AAAS salts resulting in a decrease in band intensity at 418 cm^{-1} . Generally, the structure of deposited thin films shifts with increasing annealing temperature closer to the structure of source bulk glass. Used aliphatic amine solvent does not significantly affect the structure of the $\text{As}_{33}\text{S}_{67}$ thin film, i.e. the structure of annealed films with corresponding stabilization temperatures are almost identical.

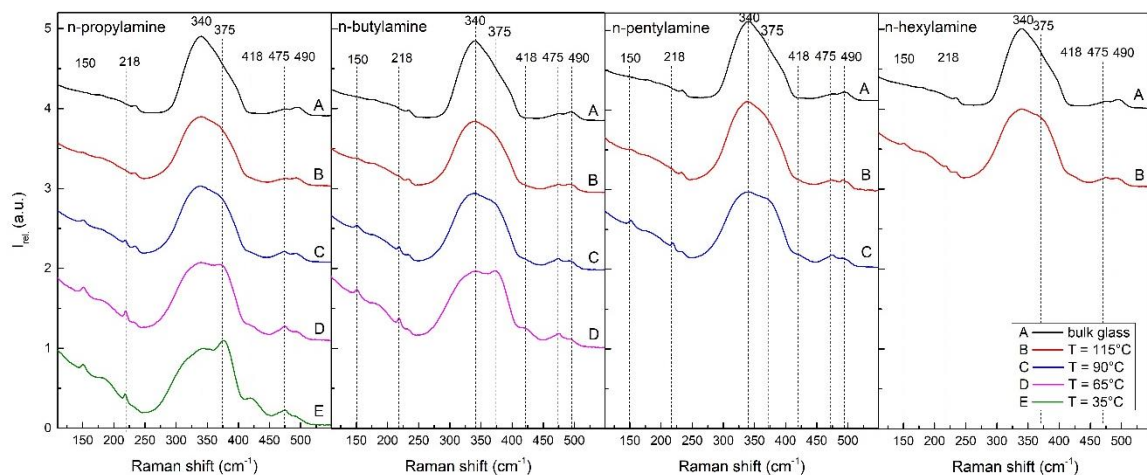


Fig. 11 Raman spectra of source bulk glass and spin-coated $As_{33}S_{67}$ thin films prepared from n-propylamine (n-PrNH₂), n-butylamine (n-BuNH₂), n-pentylamine (n-PenNH₂) and n-hexylamine (n-HexNH₂) solutions.

The chemical resistance of studied $As_{33}S_{67}$ thin films was tested by wet-etching in 0.1 vol.% n-BuNH₂ in dimethylsulfoxide etching solution at 25°C. The etching rates were calculated from obtained etching times and corresponding thicknesses of etched thin films. The thermal dependence of etching rates of studied thin films is presented in Fig. 12. Thin films annealed at 140 °C could not be completely etched due to their exfoliation. The thermally induced structural polymerization connected with increase of thin films compactness results in significant increase of chemical resistance. Although, the soft baked thin films are etched significantly faster, thin films annealed at same temperatures exhibit very similar etching rates independently on the length of aliphatic amine used during thin film preparation.

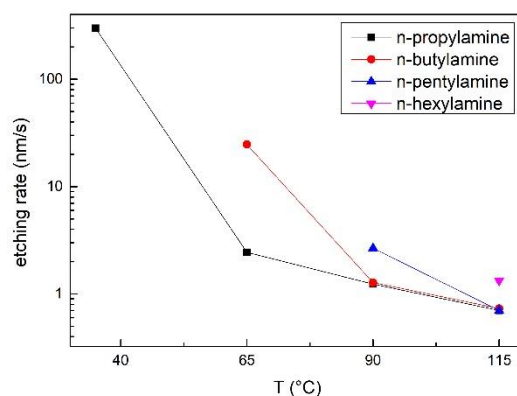


Fig. 12 Thermal dependence of etching rates of spin-coated $As_{33}S_{67}$ thin films prepared from n-propylamine (n-PrNH₂), n-butylamine (n-BuNH₂), n-pentylamine (n-PenNH₂) and n-hexylamine (n-HexNH₂) solutions.

Based on obtained findings, the length of aliphatic chain in amine solvent doesn't significantly influence physical and chemical properties of deposited $As_{33}S_{67}$ thin films. However, from practical point of view the n-BuNH₂ and n-PenNH₂ solvents offer slightly better conditions for preparation of As-S thin films in good optical quality. The n-PrNH₂ solvent is highly hygroscopic (which hardens its manipulation in ambient atmosphere) and thermally stabilized $As_{33}S_{67}$ thin films undergo significant

thickness contraction, which results in their higher surface roughness. On the other hand, the n-HexNH₂ solvent has high boiling point, which demands immediate thermal stabilization of freshly deposited thin films to avoid their degradation. Thus, the n-BuNH₂ and n-PenNH₂ solvents seems to be most suitable for deposition of As-S thin films.

Conclusions

The length of the aliphatic chain in primary amines influences the preparation process of spin-coated As₃₃S₆₇ thin films. The chemical reactivity of the amine with source bulk glass decreases with prolonging aliphatic chain length resulting in increasing glass dissolution time. Due to the lower volatility of higher amines the thin films prepared at same conditions are thinner. Structure, nitrogen content, optical properties and chemical resistance of deposited thin films are independent on the aliphatic chain length in amine used for the glass dissolution but depend only on the annealing temperature. All studied thin films exhibit slightly lower content of arsenic in comparison with source bulk glass. Composition of the thin films is not influenced by used amine neither by the annealing temperature.

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