;Mechanism of the dissolution of As-S chalcogenide glass in n-butylamine and its influence on the structure of spin coated layers

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Abstract

Chalcogenide glass thin layers are useful to many practical applications especially for the fabrication of infrared (IR) optical elements. In comparison to the conventional vacuum deposition methods of their preparation, recently chemical methods such as spin coating are gaining attention. They involve dissolution of the source bulk glass in appropriate solvent and then depositing its thin layer. Chemical processes occurring during the glass dissolution and thin layer deposition determine the physico-chemical properties of deposited thin layers. The structure of chalcogenide bulk glasses ($\text{As}_x\text{S}_{100-x}$, where $30 \leq x \leq 40$) and their solutions in n-butylamine has been studied in this work by Raman spectroscopy. From the composition and time dependence of Raman spectra of solutions the mechanism of arsenic-sulfur glass dissolution involving the reaction of aliphatic amine solvent with homopolar S-S bonds is proposed and the presence of alkyl ammonium arsenic sulfide salts in thin layers is established.

Keywords: Chalcogenide glasses, Glass solutions, Spin coating, Raman spectroscopy

Introduction

Chalcogenide glasses (ChG) are interesting materials for various applications especially in IR optics [1-4] due to their high refractive index, large transmission window in IR and common photosensitivity [5]. Many practical applications require the ChG in a thin layer form e.g. in diffraction gratings, microlens arrays, etc. The thin amorphous layers of ChG are usually prepared by physical deposition techniques such as vacuum thermal evaporation, pulsed laser deposition or sputtering. Thin layers deposited by these vacuum deposition methods have highly disordered structure with high concentration of “wrong” homopolar bonds which are considered as the origin of their photosensitivity. Besides vacuum techniques, an alternative, simpler and cheaper chemical method makes use of the solution of glass in appropriate solvent and then depositing thin layers by multiple methods ranging from spin coating [7-9] on laboratory scale to printing and coating techniques suitable for mass production [10]. The spin coating method is inexpensive and technologically simple as it needs no high vacuum and the structure of deposited thin layers is closer to that of the original bulk glasses. The resulting layers do not exhibit photo-induced structural changes that are commonly shown by vacuum deposited thin films [11]. Furthermore the refractive index of as-prepared layers, which increases with annealing temperature and time, can be adjusted by post-deposition annealing [12]. A common drawback of spin coated thin layers is the presence of residual organic solvent, which can be reduced in principle by post-deposition annealing [7, 8].

The dissolution process (as the first and necessary part of thin layer preparation) has high influence on the structure of deposited thin layers, depending on the solvent employed. Proposed Chern's and Lauks's dissolving mechanism [13] was based on their findings from deposited solid thin layers. T. Guiton and C. Pantano have studied the dissolution mechanism of As-S ChGs in ethylenediamine by Raman spectroscopy of prepared solutions. They proposed different dissolving mechanism involving formation of chelated solvent-glass molecules [14].

In this work, the process of As-S ChG dissolution in an aliphatic n-butylamine solvent has been investigated by Raman spectroscopy and a different mechanism of the dissolution process is proposed. Contrary to previously reported ethylenediamine studies [14] the n-butylamine cannot chelate dissolved glass material and thus we can expect different dissolution mechanism.

Experiment

The source bulk samples of ChG compositions As_xS_{100-x} , where $x = 30, 33, 35, 38$ and 40 , were prepared by standard melt-quenching method using high purity (5N) elemental powders [15]. Synthesized bulk glass samples were grinded using Testchem S mill in order to obtain fine powdered glass samples (with particle size smaller than $0,05$ mm) suitable for dissolution in aliphatic n-butylamine (BA). The suspension of glass powder in BA was agitated using Vortex Wizard (VELP Scientifica) at 3 rpm speed. Glass was considered fully dissolved when no solid ChG particles were visible in the solution. All glass solutions were clear and homogeneous without any precipitates or turbidity during subsequent experiments. Spin coating method (Best Tools SC110) was used for depositing thin layers from the solution. Prepared ChG solutions were pipetted onto rotating soda-lime glass substrates and deposited layers were stabilized by annealing at 60°C for 20 minutes. Samples of thin layers were stored in a dark dry environment.

The structure of source bulk samples, their solutions in BA and spin coated thin films was determined using FT IR spectrometer IFS55 with Raman module FRA106 (Bruker) with excitation by Nd:YAG laser (1064 nm). Recording of a single Raman spectrum (2 cm^{-1} resolution, 200 scans) took 10 minutes. The time of spectra stated in this paper represents the beginning of a given measurement. To study the

presence of specific structural units during glass powder dissolution the suspensions of ChG dissolving in BA were analyzed spectroscopically at the level above the settled solid part i.e. only the structure of the solution (not the solid part) was investigated. The measured Raman spectra are normalized by the intensity of the most intense band in the spectrum, i.e. the solvent-related band at 2936 cm^{-1} for solutions of ChG in BA and arsenic sulfide band at 342 cm^{-1} for solid samples (bulks and deposited thin layers), respectively.

Results and discussion

The structure of bulk $\text{As}_x\text{S}_{100-x}$ ChG (where $30 \leq x \leq 40$), their solutions in BA and finally the spin coated thin layers prepared from these solutions was determined by Raman spectroscopy. The presence of strong bands at 310 and 342 cm^{-1} in the spectra of the source bulk samples in Fig. 1 confirms that the basic structural unit of all the studied glass compositions is $\text{AsS}_{3/2}$ trigonal pyramid [16-19]). In addition, the structure comprises of realgar-like structural units of As_4S_4 (minor shoulder at 364 cm^{-1} [17, 19]), S_8 rings (475 cm^{-1} [17, 21]) and S-S chain fragments (495 cm^{-1} [17, 21, 22]). The bands in the region at $100\text{-}230\text{ cm}^{-1}$ correspond to heavy As-As vibrations in the As rich structural units (such as As_4S_4) [17]. Figure 1 further indicates that the most significant differences between the structures of these bulk glasses are in the contents of S_8 rings, S-S chains fragments and As_4S_4 structural units. The intensities of S_8 (475 cm^{-1}) and S-S (495 cm^{-1}) bands increase and the intensity of As_4S_4 shoulder (364 cm^{-1}) decreases with increasing sulfur content in bulk glasses. The overstoichiometry of sulfur atoms allows further reaction with arsenic atoms during glass synthesis and thus decreasing the concentration of arsenic-rich As_4S_4 structural units (with As-As homopolar bonds) as observed in the measured Raman spectra [23]. In the spectra of $\text{As}_{30}\text{S}_{70}$ bulk glass the S_8 band even exceeds the band due to S-S chain fragments because of the high overstoichiometry of sulfur atoms [23]. As we will see later, the sulfur content has the main influence on the kinetics and the nature of the dissolving process of As-S bulk glasses.

Fig. 1. The Raman spectra of studied chalcogenide bulk glasses $\text{As}_x\text{S}_{100-x}$ where $30 \leq x \leq 40$.

Raman spectra of pure BA, sulfur and $\text{As}_{40}\text{S}_{60}$ ChG fully dissolved in BA were measured in order to identify the bands in Raman spectra of arsenic-sulfur ChGs dissolved in amine based solutions as shown in Fig. 2. The bands at 276, 350, 399, 438, 482 and 499 cm^{-1} represent the vibrational modes of BA molecules [24]. After dissolving sulfur in BA, new bands appear at 145, 190, 238 cm^{-1} and the intensities of bands at 438 and 499 cm^{-1} increase. According to the Daly et al. [22, 25] these bands correspond to the S_4^{2-} and S_3^- structural units. They suggest that during the dissolution of pure sulfur and sulfur-rich compounds, the opening/breaking and distortion of S_8 rings occur. There are also changes in the intensities of the bands in the region that represents amine vibrations, viz. 3250-3350 cm^{-1} [22, 25] (Fig. 2-B), presumably due to chemical interaction between BA and sulfur. A similar process can be expected in the dissolution of arsenic-sulfide ChGs. The presence of the same ionic sulfur and BA bands (145, 190, 238, 438 and 499 cm^{-1}) in the Raman spectra of $\text{As}_{40}\text{S}_{60}$ in BA confirms this assumption [22, 25]. Additional bands appear at 322, 378 and 415 cm^{-1} in the Raman spectra of $\text{As}_{40}\text{S}_{60}$ dissolved in BA, the intensity of the band at 350 cm^{-1} increase and there is also a trace of additional bands in the spectral region at 100-230 cm^{-1} . To our best knowledge the presence of these bands has not been reported yet. Their position does not correspond to any structural units in bulk $\text{As}_{40}\text{S}_{60}$ glass [16-21] but due to their absence in the spectrum of sulfur we conclude that they must belong to the dissolved structural units of arsenic sulfide glass.

Fig. 2. Raman spectra of pure BA, sulfur and $\text{As}_{40}\text{S}_{60}$ dissolved in BA in the regions of strong scattering.

Chern and Lauks [13] proposed a dissolution mechanism of arsenic sulfide glass in aliphatic amines involving the formation of alkyl ammonium arsenic sulfide (AAAS) salts. The presence of these compounds was shown also in spin coated thin layers [13]. Based on these findings we could expect that during the dissolution of arsenic-sulfur ChGs the amine solvent disrupts the bonds between

sulfur atoms leaving behind small clusters of the original material. The atoms at the surface of these clusters are probably bounded by ionic sulfur, enabling their solubility in the amine solvent. The solution also contains dissolved sulfur fragments, which broke away from the bulk glass during the dissolution process.

The mechanism of dissolution suggested in [13] corresponds to the experimentally found compositional dependence of dissolving times (time needed for glass dissolution – i.e. no solid particles were visible in the solution) in BA both with and without agitating (Fig. 3). The liquid flow brings new fresh solvent to the glass surface and thus the agitating process distinctly decreases dissolving times [26]. The XPS measurements [27] of As-S bulk glasses gave evidence that the bulk $\text{As}_{40}\text{S}_{60}$ samples of stoichiometric composition contains no more than 4% of the sulfur bonded in the amine-reactive S-S structure. By contrast, the sulfur-rich samples with composition $\text{As}_{30}\text{S}_{70}$ contains 60% of sulfur atoms bonded in S-S structure [27]. Thus with increasing sulfur content in the bulk glass the amine solvent has increasing options of possible reaction sites (specifically, the S-S homopolar bonds), which would explain why the dissolution time decreases

Fig. 3. Compositional dependences of dissolving time of chalcogenide As-S glasses for dissolution processes both with and without agitating. Solid lines are given to guide the eye.

The reactivity of the S-S bonds in the glass to BA solvent is obvious from the Raman spectra of arsenic-sulfur ChG solutions in BA measured during the first 10 minutes of glass dissolving process (Fig. 4-A) (measurement was started immediately after pouring the BA onto the glass powder). Comparing with the Raman spectrum of pure BA (Fig. 4-B) two new bands appeared at 190 and 438 cm^{-1} . Based on data in Fig. 2 these new bands correspond to the structural units of ionic sulfur S_4^{2-} and S_3^- [22, 25]. The intensities of these bands are strongly dependent on glass composition; they increase with the increasing content of sulfur in the bulk glass. There is also evidence of a new previously not described band at 415 cm^{-1} , which is visible as a shoulder in Raman spectra of S rich glass solutions. The intensity of this band varies with the same dependence as the ionic sulfur structural units i.e. it increases with increasing content of the sulfur in the dissolved bulk glass. Based on these findings the presence of this new band must be connected with sulfur, but also with arsenic since it is completely missing in the spectrum of sulfur solution. We suggest that this band most probably represents one of the vibrations of AAAS salts.

The Raman spectra of BA solutions with completely dissolved glass (A), and after subtracting solvent part of the spectrum (B) are presented in Fig. 5. Significant difference in Raman spectra is noticeable between both limiting compositions of the present series ($\text{As}_{40}\text{S}_{60}$ and $\text{As}_{30}\text{S}_{70}$). The Raman spectra of sulfur-rich solution of $\text{As}_{30}\text{S}_{70}$ glass shows significantly higher intensity of the band assigned to the structural units of ionic sulfur S_4^{2-} at 438 cm^{-1} in comparison with the Raman spectrum of $\text{As}_{40}\text{S}_{60}$ solution. The band corresponding to AAAS salts at 415 cm^{-1} is clearly visible in the spectrum of S-rich composition $\text{As}_{30}\text{S}_{70}$, while the spectrum of stoichiometric $\text{As}_{40}\text{S}_{60}$ shows this band at distinctively lower intensity. The spectrum of $\text{As}_{40}\text{S}_{60}$ solution further exhibits two additional bands at 322 and 378 cm^{-1} . These bands can be also assigned to the vibration of AAAS salts due to the lack of their presence in the Raman spectra of pure BA, and sulfur dissolved in BA (Fig. 2). Raman spectra for the $\text{As}_{30}\text{S}_{70}$ - $\text{As}_{40}\text{S}_{60}$ compositional range exhibit transition between the structures of these boundary compositions. Simultaneously with the sudden intensity decrease of the AAAS salt band at 415 cm^{-1} the intensities of the other bands 322 and 378 cm^{-1} increase with increasing As content.

Fig.4. Raman spectra of $\text{As}_x\text{S}_{100-x}$ chalcogenide glasses solutions in BA collected during first 10 minutes of dissolving process (A) and the same after BA spectrum subtraction (B)

Fig.5. Raman spectra of As_xS_{100-x} chalcogenide glasses solutions in BA collected after complete dissolution (A) and the same after BA spectrum subtraction (B)

Based on the above discussion of Raman spectra of As-S glass solutions in BA we can deduce that the chemistry of dissolution is sensitive to glass composition. Sulfur rich ChGs dissolve into different chemical products compared to the glasses with higher As content, close to the stoichiometric composition.

The kinetics of As-S glass dissolution in BA were investigated by recording Raman spectra at 0, 75, 150, 225, 300 and 375 minutes as measured from the time the ChG sample was introduced into the solvent (see Fig. 4). Measurements were performed at the solution level right above the settled solid ChG particles of the suspension i.e. undissolved ChG (solid part of the suspension) was not measured. The kinetics of the process is presented as dissolution time dependences of the relative intensities of bands undergoing changes during dissolution (Fig. 6).

The dissolution of samples of all compositions exhibits significant increase in the intensity of the Raman band at 438 cm⁻¹, which represents ionic sulfur S_4^{2-} . This fact indicates that ionization of the sulfur atoms forming ionic sulfur salts is the chemical mechanism of dissolution common to all compositions.

The bands at 322, 378 and 415 cm⁻¹ were all assigned to vibrations of AAAS salts of different structural units. Figure 6 shows that the ratio of their presence (bands relative intensity) varies with glass composition. Solutions of sulfur rich glass compositions ($As_{30}S_{70}$ and $As_{33}S_{67}$) exhibit a dominant band at 415 cm⁻¹ and the other salt related bands in significantly ($As_{30}S_{70}$) and slightly ($As_{33}S_{67}$) lower intensities. The salt band at 378 cm⁻¹ becomes dominant in solutions of the glass compositions close to the stoichiometric one ($As_{35}S_{65}$ – $As_{40}S_{60}$). The last of the salt related bands (322 cm⁻¹) remains the least intense in all studied glass solutions. Generally, with increasing As content of glass the band at 415 cm⁻¹ for respective solution decreases in its intensity, contrary to the increasing intensity of the bands at 322 and 378 cm⁻¹.

The ratio of the intensity of bands at 322 and 378 cm^{-1} also depends on glass composition. For $\text{As}_{30}\text{S}_{70}$ glass solution both bands exhibit the same intensity. With increasing As content their ratio increases as well in favor of the band at 378 cm^{-1} . These findings suggest that the chemistry of As-S ChG dissolution in BA depends significantly on the glass composition i.e. glasses of close compositions dissolve forming different chemical products. From the monotonic variation of measured kinetics we conclude that the dissolution processes lead directly to the final chemical products. Formation of no intermediate products was observed. In order to verify the stability of As-S solutions in BA the samples were repeatedly investigated by Raman spectroscopy during the next three weeks. The solutions were stable during this time indicating no changes in their spectra.

Although the dissolution mechanism of As-S ChGs is a relatively complicated issue we propose one possible interpretation of the presented data. As discussed above, three different products of As-S glass dissolution in BA are identified by the bands in Raman spectra at 322, 378 and 415 cm^{-1} . Their ratio is significantly dependent on glass composition (Fig. 5 and 6). As suggested by Chern and Lauks [13] and confirmed by our experimental results, the primary reaction of the As-S ChG occurs between BA and S-S bonds. The fraction of these homopolar bonds in glass is crucial for determining its rate of dissolution [27]. We can assume that the sulfur rich ChGs will contain higher concentration of S-S homopolar bonds and lower concentration of As-As homopolar bonds, thereby forming small clusters of the AAAS salts upon dissolving in BA. With increasing arsenic in dissolving glass the concentration of the homopolar S-S bonds (the major reaction sites for BA solvent) decreases and so we can expect the formation of larger clusters due to the increasing concentration of the relatively “unbreakable” As-As homopolar bonds. The smaller clusters’ vibrations would occur at higher frequencies of Raman spectra, in contrast to the vibrations of the larger clusters at lower frequencies. This proposed mechanism is in a good agreement with the measured Raman spectra (Fig. 4 and 5).

Fig. 6. Relative intensities (relatively to the most intensive band in the spectra i.e. solvent-related band at 2936 cm^{-1}) of the AAAS salts bands at 322 , 378 , 415 cm^{-1} and ionic sulfur band at 438 cm^{-1} as a function of dissolution time. Solid lines are given merely to guide the eye.

The Raman spectra of prepared thin layers were measured as shown in Fig. 7. These spectra show that the structure of the spin coated layers is very similar to the structure of original bulk glasses (Fig. 1). There are, however, significant differences in the relative intensities of the bands which correspond to As_4S_4 structural units (369 cm^{-1}), S_8 sulfur rings (151 , 218 and 475 cm^{-1}) and S-S chains (495 cm^{-1}). The intensities of bands for sulfur rings increase with increasing sulfur content in the glass. The bands at $2800\text{--}3000\text{ cm}^{-1}$ in Fig. 7 prove the presence of BA solvent residue in deposited thin layers [14, 30, 31]. There is a new band at 415 cm^{-1} which is not present in the Raman spectra of source bulk glasses [15-21]. The intensity of this band also increases with slightly the increasing

content of sulfur in the original glass. Following Chern and Lauks [13], who showed the presence of AAAS salts in spin coated layers, and due to the corresponding band in the Raman spectra of glass solutions, we assign this band to these salts in thin layers as well.

Previously, Chern and Lauks observed the release of amine solvents during annealing of prepared layers at 100°C [13, 28, 29]. Following their observations and in order to verify the assignment of 415 cm^{-1} band to the presence of AAAS salts, the thin layer with the highest content of this compound ($\text{As}_{30}\text{S}_{70}$ thin layer) was annealed at 100°C in inert Ar atmosphere for 60 minutes. The Raman spectrum of annealed thin layer in Fig. 8 does show a decrease in the intensity of the band at 415 cm^{-1} , hence in the content of AAAS salts in thin layer. Thus, the Raman spectrum of annealed thin layer further gives an evidence of the glass structure polymerization as the concentration of As_4S_4 clusters and S_8 rings decreases while the concentration of $\text{AsS}_{3/2}$ increases.

Fig. 7. The Raman spectra of spin coated As-S thin amorphous layers prepared from the studied solutions.

Fig. 8. The Raman spectra of as-prepared and annealed thin chalcogenide layer of $As_{30}S_{70}$ composition.

Conclusion

The Raman spectra of the solution of As_xS_{100-x} ($30 \leq x \leq 40$) glasses in n-butylamine (BA) during dissolution have established the presence of ionic sulfur and three different alkyl ammonium arsenic sulfide (AAAS) salts. The formation of AAAS salts and the ratio of their content in solutions depends significantly on the composition of glass. We assume that the primary reaction between As-S ChG and BA solvent occurs at S-S homopolar bonds, and therefore their concentration has a major impact on the nature and the rate of dissolution process. The sulfur rich ChGs containing higher concentration of S-S homopolar bonds form smaller clusters of AAAS salts. With decreasing content of sulfur in ChGs the concentration of S-S homopolar bonds also decreases resulting in the formation of larger AAAS salts' clusters.

A comparison of Raman spectra of deposited thin layers vs. original bulk glasses shows an extra band at 415 cm^{-1} for the former and significant differences in the concentrations of As_4S_4 and sulfur structural units between them. The new band at 415 cm^{-1} is assigned to the presence of AAAS salts in prepared solid thin layers. Annealing the layers at $100\text{ }^\circ\text{C}$ mostly eliminates these salts by their thermal decomposition (connected with the release of organic residuals followed by gradual structural polymerization).

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References

- [1] A. Stronski, M. Vlcek, *Quantum Electron. Optoelectron.* 3 (2000) 394.
- [2] S. Wong, M. Deubel, *Adv. Mater.* 18 (2006) 265.
- [3] A. Zoubir, M. Richardson, *Opt. Lett.* 29 (2004) 748.
- [4] S. Song, S.S. Howard, *Appl. Phys. Lett.* 89 (2006) 041115.
- [5] T. Kanamori, Y. Terunuma, *J. Lightwave Technol.* 2 (1984) 607.
- [6] I. Ivan, M. Veres, *Phys. Stat. Sol.* 201 (2004) 3193.
- [7] G.C. Chern, I. Lauks, *J. Appl. Phys.* 55 (1984) 3795.
- [8] S. Shtutina, M. Klebanov, *Thin Solid Films* 261 (1995) 263.
- [9] E. Hajto, P.J.S. Ewen, *Thin Solid Films* 200 (1991) 229.
- [10] K. Palka, T. Syrový, *Opt. Mater. Express* 4 (2014) 384.
- [11] G.C. Chern, I. Lauks, *Thin Solid Films* 123 (1985) 289.
- [12] S. Song et al., *Opt. Express* 18 (2010) 5172.
- [13] G. C. Chern and I. Lauks, *J. Appl. Phys.* 54 (1983) 4596.
- [14] T. A. Guiton, C. Pantano, *Chem. Mater.* 1 (1989) 558.
- [15] T. Kohoutek, T. Wagner, *Journal of Non-Cryst. Solids* 354 (2008) 529.
- [16] R. Ston, Mir. Vlcek, H. Jain, *Journal of Non-Cryst. Solids* 236 (2003) 220.
- [17] M. Pisarcik, L. Koudelka, *Mater. Chem.* 7 (1982) 499.
- [18] R. Holomb, V. Mitsa, M. Vlcek, *Phys. Status Solidi* 8 (2011) 2705.
- [19] I. Ivan, M. Veres, *Phys. Status Solidi* 201 (2004) 3193.
- [20] D. Arsova, E. Skordeva, *Glass Phys. Chem.* 26 (2000) 247.
- [21] Z. Cernosek, J. Holubova, *Journal of Non-oxide Glasses* 1 (2009) 38.
- [22] F. Daly, C. Brown, *J. Phys. Chem.* 77 (1973) 15.
- [23] M. Frumar, Z. Polak, *Journal of Non-Cryst. Solids* 256 (1999) 105.
- [24] J. Teixeira-Dias, L. Batista de Carvalho, *Spectrochim. Acta* 42A (1986) 589.
- [25] F. Daly, C. Brown, *J. Phys. Chem.* 79 (1975) 4.
- [26] Y. Zha, M. Waldmann, *Opt. Mater. Express* 3 (2013) 1259.
- [27] R. Golovchak, O. Shpotyuk, *Phil. Mag.* 90 (2010) 4489.
- [28] G. C. Chern, I. Lauks, *J. Appl. Phys.* 54 (1983) 2701.
- [29] G. C. Chern and I. Lauks, *Bull. Am. Phys. Soc.* 27 (1982) 868.
- [30] S. A. Zenkin, S. B. Mamedov, *Glass Phys. Chem.* 23 (1997) 393.
- [31] Y. Zha, S. Fingerman, *Journal of Non-Cryst. Solids* 369 (2013) 11.