

10<sup>th</sup> International Conference on Solid State Chemistry, Pardubice, Czech Republic

## Wavelength dependence of photostructural transformations in As<sub>2</sub>S<sub>3</sub> thin films

Andriy Kovalskiy<sup>a\*</sup>, Miroslav Vlcek<sup>b</sup>, Karel Palka<sup>b</sup>,  
Roman Golovchak<sup>c</sup>, Himanshu Jain<sup>c</sup>

<sup>a</sup>Department of Physics and Astronomy, Austin Peay State University, Clarksville, TN 37044, USA

<sup>b</sup>Faculty of Chemical Technology, University of Pardubice, Pardubice, 53210, Czech Republic

<sup>c</sup>Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

---

### Abstract

Spectral dependence of photostructural transformations on the surface and in the interior of thermally evaporated As<sub>2</sub>S<sub>3</sub> thin films is studied under the influence of bandgap, sub-bandgap and super-bandgap light. For the given light intensity ( $W \sim 15 \text{ mW/cm}^2$ ) the irradiation by bandgap and super-bandgap light leads to partial restoration of pyramidal structural units in the film, which is a characteristic of the bulk glasses of this stoichiometric composition. The mechanism of photostructural transformations on the surface of the film exhibits strong spectral dependence. S-rich layer is formed upon irradiation by super-bandgap UV light. The sub-bandgap light does not cause any noticeable photostructural transformations at this light intensity.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.

*Keywords:* chalcogenide glass; photoinduced effects; Raman spectroscopy, X-ray photoelectron spectroscopy

---

### 1. Introduction

Chalcogenide glass (ChG) thin films have been recognized as promising materials in various applications such as optical storage and memory devices [1], photo- and electron resists [2], sensing platforms [3], etc. Most applications are based on the well-known photoinduced phenomena in this type of materials. Light interaction with the thin layers can cause a variety of photostructural transformations on the surface and inside of the films. Origin of these changes strongly depends on parameters of light (mainly intensity, wavelength, time of irradiation and pulse characteristics, though beam shape, and polarization can play an important role too) as well as the characteristics of the thin films (chemical composition, prehistory, thickness and preparation method).

It is known that for the continuous mode of irradiation and moderate light intensities only the bandgap and super-bandgap radiations cause noticeable structural changes inside the ChG films [4], while sub-

bandgap light modifies the structure only at high intensities and/or for pulsed irradiation [5]. However, details of the spectral dependence of photostructural transformations in ChG thin films are unavailable. Much less is known about the structural changes on the surface of the films as irradiation conditions are varied.

In this study we use Raman spectroscopy and high-resolution X-ray photoelectron spectroscopy (XPS) methods to identify the mechanism of photostructural transformations in the volume and on the surface of the thermally evaporated stoichiometric  $\text{As}_2\text{S}_3$  thin films under the influence of light with different energy from super- to sub-bandgap regions.

## 2. Experimental

### 2.1 Bulk samples preparation

The high purity (5N) elemental powders were melted in evacuated quartz ampoules for 8 hrs at temperatures  $900^\circ\text{C}$  in rocking furnace, and then the melt was quenched in cold water. Standard synthesis procedure was used.

### 2.2 Thin layers preparation

Thin layers with thickness about 1000 nm were deposited onto microscopic slides by thermal evaporation (Tesla Corporation, model UP-858, starting pressure  $1 \times 10^{-3}$  Pa) using planetary rotating sample holders. The deposition rate of thin layers (measured by the dynamical weighing method using a SV-1843 A MIKI-FFV system) was about 1 nm/s. Only low-level red illumination was used in the laboratory during the preparation and measurements to minimize any photoinduced effects produced by the ambient lighting.

### 2.3 Irradiation

As-prepared thin films were exposed to halogen lamp (intensity,  $W \sim 10 \text{ mW/cm}^2$ ) and to LEDs with peak wavelengths 375, 405, 450, 525, 570, 630, 690, 740 and 790 nm ( $W \sim 15 \text{ mW/cm}^2$ ) for 60 min. All exposures were carried out in air.

### 2.4 Raman spectroscopy

Raman spectra were obtained using BRUKER IFS 55 IR spectrometer with FRA 106 accessory, pumping laser Nd:YAG laser (1064 nm), and the following experimental conditions: 50 mW, 200 scans, resolution  $2 \text{ cm}^{-1}$ . The material for Raman measurements was taken by scratching the thin films into specially designed sample holders.

### 2.5 X-ray photoelectron spectroscopy

XPS is a analysis technique with about 65% of the signal originating from the outermost  $\sim 30 \text{ \AA}$  of the surface. The XPS spectra were recorded with a Scienta ESCA-300 spectrometer using monochromatic Al  $K_\alpha$  X-rays (1486.6 eV). The analysis area was a spot  $\sim 3\text{--}4 \text{ mm}$  long and  $\sim 250 \text{ \mu m}$  wide. Data acquisition was restricted electronically to a region smaller than the X-ray illuminated area. The XPS data consisted of survey scans over the entire binding energy (BE) range and selected scans over the core level

photoelectron peaks of interest. An energy increment of 0.05 eV was used for recording the core level spectra. The reproducibility of the measurements was checked on different regions of the film surface, as well as on different samples. The surface charging from photoelectron emission was neutralized using a low energy (<10 eV) electron flood gun [6]. The XPS data were calibrated according to impurity carbon 1s line (284.8 eV). Data analysis was conducted with standard Casa-XPS software package. For analyzing the core level spectra, Shirley background was subtracted and a Voigt line shape was assumed for the peaks. Concentrations of appropriate chemical elements were determined from the area of core level peaks taking into account the experimentally determined sensitivity coefficients. Each 2p core level spectrum of S and 3d core level spectrum of As included one or more spin orbit doublets consisting of  $2p_{3/2}$  and  $2p_{1/2}$  components for S,  $3d_{5/2}$  and  $3d_{3/2}$  components for As. The number of doublets within a given peak was determined by an iterative curve fitting process in which a doublet was added only if it significantly improved the goodness of fit of the experimental data to the envelope of the fitted curve. The parameters used to link the As  $3d_{5/2}$  and  $3d_{3/2}$  peaks were: a peak separation of 0.70 eV and an area ratio of 7/5. For S 2p core level the parameters were 1.6 eV and 2/1, respectively. These reference values were obtained experimentally for a number of chalcogenide glasses using the same Scienta ESCA-300 spectrometer. The FWHM was assumed to be the same for the peaks within one doublet. However, differences between FWHM values for different doublets of the same core level peak were allowed. The mix between the Gaussian and Lorentzian fractions in the Voigt function was chosen to be the same for all doublets of a given core level. With these constraints the uncertainty in the peak position (BE) and area (A) of each component was ~0.05 eV and ~2%, respectively.

### 3. Results and Discussion

#### 3.1. Raman spectroscopy

Raman spectroscopy is one of the most useful methods to study photostructural transformations in the volume of the amorphous thin film. In the case of ChG it is important to use the excitation laser of appropriate wavelength to avoid any photoinduced effects during the measurements. The energy of Nd-YAG laser light ( $\lambda=1064$  nm) used in our study is far below the bandgap level and “neutral” in respect to photostructural transformations. Significant photo-induced structural relaxation effect, which could complicate the present analysis of Raman data, is also not observed for stoichiometric  $As_2S_3$  under the photoexposure with this wavelength [7].

The Raman spectrum of the freshly prepared  $As_2S_3$  thin film shows that there is a dominant band at  $345\text{ cm}^{-1}$ , which corresponds to the presence of  $AsS_{3/2}$  pyramids (Fig. 1). The shoulders at  $312$  and  $380\text{ cm}^{-1}$  are assigned to the interactions between these  $AsS_3$  pyramids. The very intense bands between  $135\text{ cm}^{-1}$  and  $234\text{ cm}^{-1}$  and also at  $363\text{ cm}^{-1}$  are related to the vibration of the units containing As-As such as  $As_4S_4$ , together with additional relatively strong double bands with maxima at  $495\text{ cm}^{-1}$  and  $474\text{ cm}^{-1}$ . These two bands are evidence of S-S containing structural units such as  $-S-S-$  chains ( $495\text{ cm}^{-1}$ ) and  $S_8$  rings ( $474\text{ cm}^{-1}$ ) that are present and connect individual  $AsS_{3/2}$  pyramids [8].

The irradiation of the  $1\text{ }\mu\text{m}$  thick  $As_2S_3$  film with monochromatic light of different wavelength leads to significant structural changes at the energies equal to or higher than the bandgap value ( $525\text{ nm}$  or  $2.36\text{ eV}$ , Fig. 1a). For bandgap light or polychromatic halogen lamp exposure the shapes of Raman spectra are very close to that of the spectra for bulk  $As_2S_3$  with significantly less expressed bands associated with homopolar bonds [2]. It can be seen that the bandgap light modifies the structure much more effectively than the higher energy UV radiation ( $375\text{ nm}$ ). The explanation is rather evident and relates to the energy dependence of light penetration depth, calculated according to the Beer-Lambert law (Fig. 2). We can

expect that if the penetration depth of light is sufficient to cover the entire thickness of the film, the structural transformations will be similar and independent of the wavelength. The significant change of the Raman spectra (Fig. 1a) after light illumination of the film occurs, mainly due to the photopolymerization process. One of the main polymerization schemes is: [2]



The sub-bandgap light with wavelengths from 570 to 790 nm does not cause any noticeable photostructural transformations (Fig. 1b) at the light intensity employed in the present experiment i.e. 15 mW/cm<sup>2</sup>.

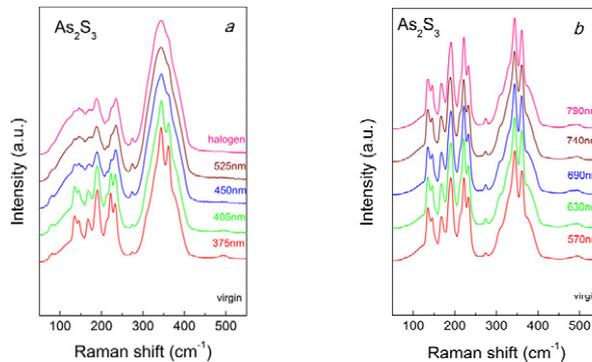


Fig. 1. Raman spectra of thermally deposited  $\text{As}_2\text{S}_3$  thin films irradiated with (a) bandgap, super-bandgap and polychromatic light and (b) sub-bandgap light ( $W=15 \text{ mW/cm}^2$ )

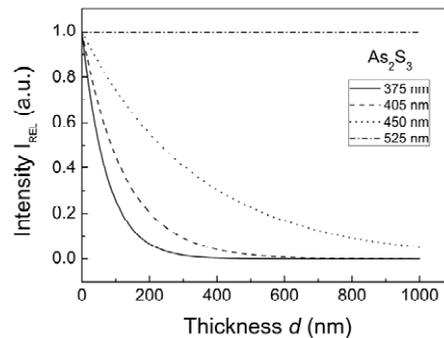


Fig. 2. Wavelength dependence of the penetration depth of light in  $\text{As}_2\text{S}_3$  thin films

To obtain the normalized Raman spectra for ChG films irradiated by light of different wavelength, it is necessary to minimize the influence of light penetration depth. With this aim the thinnest possible ChG layers should be irradiated (200 nm thickness seems to be optimal in this case). It will be the topic of our next study.

### 3.2. XPS measurements

Spectral dependence of photostructural changes on the surface of ChG thin films is a new topic and high-resolution X-ray photoelectron spectroscopy is the most appropriate method for such studies. The atomic structure of the surface of freshly prepared (thermally deposited)  $\text{As}_2\text{S}_3$  thin film consists mostly of heteropolar As-S bonds and  $\sim 10\text{--}15\%$  (depending on the preparation conditions) of As and S atoms within homopolar As-As and S-S bonds [2]. The As 3d and S 2p core level spectra for non-irradiated, as-prepared films are presented in Fig. 3. Every chemical environment consists of two peaks (or one doublet) combined according to the rules of spin-orbit splitting (see Sec. 2.5). The chemical composition of the film determined from the areas of core level peaks corresponds to the stoichiometric  $\text{As}_{40}\text{S}_{60}$  (precision of these results is  $\pm 2.0\%$  at. %).

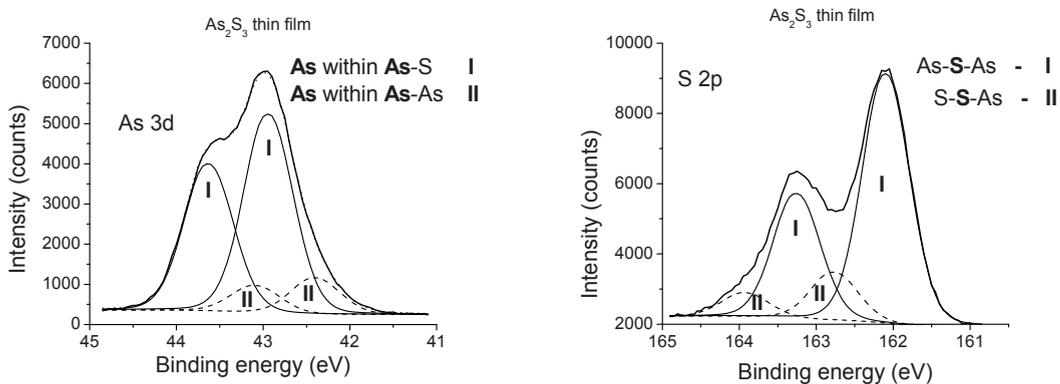


Fig. 3. Fitting of As 3d and S 2p core level spectra of as-evaporated  $\text{As}_2\text{S}_3$  thin film.

Irradiation of the as-evaporated  $\text{As}_2\text{S}_3$  thin film by bandgap light ( $\lambda=525\text{ nm}$ ,  $W=15\text{ mW/cm}^2$ ) leads to insignificant decrease of the concentration of heteropolar bonds on the surface of the film. The amount of homopolar bonds slightly increases. We do not observe any oxide components in the XPS spectra. This result is in good agreement with our previous data [9], where we exclude formation of  $\text{As}_2\text{O}_3$  or  $\text{As}_2\text{O}_5$  oxides on the surface of the  $\text{As}_2\text{S}_3$  films irradiated with bandgap light. Both S 2p and As 3d spectra (Fig. 4) contain a new third peak, which can be associated with surface defect states. Previously [9] we expected that the peak III on As 3d spectrum (fig. 4) could be associated with separate As-O bonds on the surface of the film but very low intensity of O 1s peak at current measurements does not support this prediction. The positions of the peaks is close to the predicted binding energies for the pair of defects ( $\text{As}_4^+$ ,  $\text{S}_1^-$ ), however further investigations are needed to confirm this conclusion. The irradiation with bandgap light did not change the chemical composition of the surface within the experimental error.

Much greater structural changes happen on the surface of the film, as determined by XPS, after irradiation by higher energy UV light of  $\lambda=375\text{ nm}$ . First of all, chemical composition of the top layer significantly changes to  $\text{As}_{32}\text{S}_{68}$ . Formation of the S-rich surface can be possible through the evaporation of relatively unstable, non-stable volatile fragments, or photoinduced diffusion. We support the former mechanism with evaporation of As-rich  $\text{As}_4\text{S}_4$  or/and  $\text{As}_4\text{S}_3$  units. We still need additional experimental data to confirm this mechanism, however the latest (and still unpublished) Raman studies in argon atmosphere made less possible volatilization of arsenic oxides, as it was generally expected.

The deficiency of As on the surface of the irradiated film results in predominantly pyramidal units for the As atoms, as established from the analysis of As 3d core level spectrum (Fig. 5). The noticeable excess of S on the surface leads to the formation of 3 different chemical environments (As-S-As; S-S-As and S-S-S) while preserving the usual twofold coordination of the S atoms (see S 2p spectrum in Fig. 5).

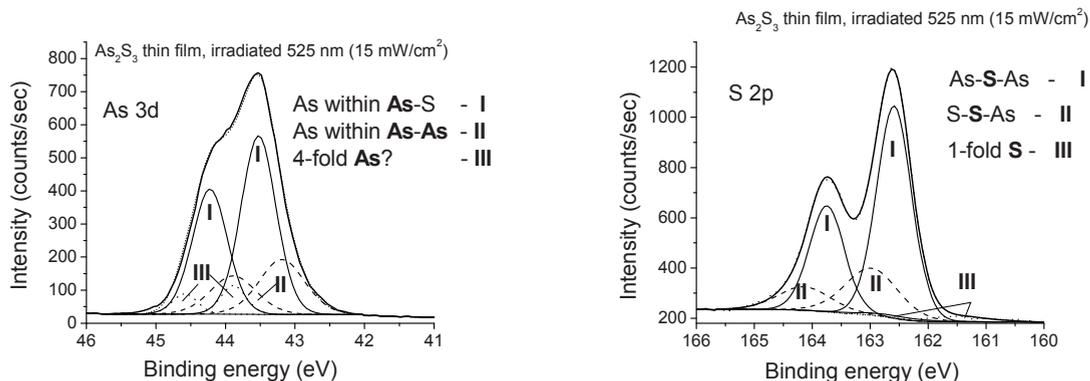


Fig. 4. Fitting of As 3d and S 2p core level spectra of As<sub>2</sub>S<sub>3</sub> thin film irradiated with bandgap light ( $\lambda=525$  nm,  $W=15$  mW/cm<sup>2</sup>).

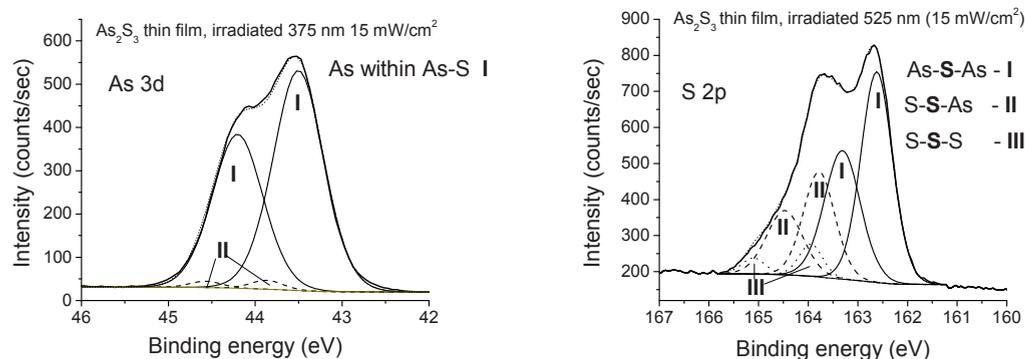


Fig. 5. Fitting of As 3d and S 2p core level spectra of As<sub>2</sub>S<sub>3</sub> thin film irradiated with super-bandgap light ( $\lambda=375$  nm,  $W=15$  mW/cm<sup>2</sup>).

Irradiation by light with wavelengths 405 and 450 nm confirms the above trends with gradual change of chemical composition of the surface and formation of the S-rich layer.

It is interesting to note that the mechanism of photostructural transformations for the low intensity (0.5 mW/cm<sup>2</sup>) irradiation from 488 nm Ar-ion laser is completely different (data not shown here). The light causes decrease in concentration of homopolar irregular bonds and restoration of heteropolar As-S environment. This fact once more demonstrates the strong dependence of the observed photoinduced changes on the parameters of light.

#### 4. Conclusions

It is shown that the irradiation of thermally deposited  $\text{As}_2\text{S}_3$  thin films by bandgap and super-bandgap light with  $15 \text{ mW/cm}^2$  intensity significantly changes the structure of both internal and surface layers. The photostructural transformations inside the film are directed to the restoration of bulk-like structure characterized by small concentration of “wrong” homopolar bonds and dominance of  $\text{AsS}_3$  pyramidal units. The photoinduced structural changes on the surface of the film strongly depend on the energy of incident light. Bandgap irradiation does not change the chemical composition of the surface but the concentration of the defect states (“wrong” homopolar bonds and, possibly, coordination defects) increases. Super-bandgap light forms S-rich layer on the surface of the  $\text{As}_2\text{S}_3$  film. Sub-bandgap light does not cause any noticeable photostructural transformations either in the volume of the film or on the surface.

#### Acknowledgements

This work was supported by the grant P204/11/0832 from the Czech Science Foundation and NSF’s International Materials Institute on New Functionality in Glass (NSF Grant No. DMR 0844014). AK acknowledges also the financial support of the Summer Research Fellows Program (Austin Peay State University, Clarksville, TN, USA).

#### References

- [1] Wuttig M, Yamada N. Phase-change materials for rewriteable data storage. *Nat. Mater.* 2007; **6**: 824-832.
- [2] Kovalskiy A, Vlcek M, Cech J, Heffner WR, Waits CM, Dubey M, Jain H. Chalcogenide glass e-beam and photo resists for ultrathin grayscale patterning. *J. Micro/Nanolithogr. MEMS MOEMS.* 2009; **8**: 043012-1-11.
- [3] Hu J, Tarasov V, Agarwal A, Kimerling L, Carlie N, Petit L, Richardson K. Fabrication and testing of planar chalcogenide waveguide integrated microfluidic sensor. *Optics Express* 2007; **15**: 2307-2314.
- [4] Tanaka K, Shimakawa K. *Amorphous Chalcogenide Semiconductors and Related Materials*. New York, Dordrecht, Heidelberg, London: Springer; 2011.
- [5] Tanaka K, Hisakuni H. Photoinduced phenomena in  $\text{As}_2\text{S}_3$  glass under sub-bandgap excitation. *J. Non-Cryst. Solids* 1996; **198-200**: 714-718.
- [6] Golovchak R, Shpotyuk O, Kovalskiy A, Miller AC, Cech J, Jain H. Coordination defects in bismuth-modified arsenic selenide glasses: High-resolution x-ray photoelectron spectroscopy measurements. *Phys. Rev. B* 2008; **77**: 172201-1-4.
- [7] Kozdras A, Golovchak R, Shpotyuk O, Szymura S, Saiter A, Saiter JM. Light-assisted physical ageing in chalcogenide glasses: dependence on the wavelength of incident photons. *J. Materials Res.* 2011; **26**: 2420-2427.
- [8] Mori T, Matsuishi K, Arai T. Vibrational properties and network topology of amorphous As-S system. *J. Non-Cryst. Solids* 1984; **65**: 269-283.
- [9] Kovalskiy A., Jain H., Mitkova M. Evolution of chemical structure during silver photodiffusion into chalcogenide glass thin films. *J. Non-Cryst. Solids* 2009; **355**: 1924-1929.