Comparison of structural transformations in bulk and as-evaporated optical media under action of polychromatic or photon-energy dependent monochromatic illumination

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Light-induced structural changes of As-S glasses and films were probed both by macro FT-Raman and photon-energy dependent micro-Raman spectroscopy using different spectral composition of photoactive light: polychromatic or different wavelengths of laser radiation. The polychromatic illumination and thermal treatment leads to continuous decrease in intensity of characteristics vibrational modes of molecular or cage-like species like As_4S_4, As_4S_3, etc. Under laser illumination the picture is different, new observed features in the Raman spectra of As-rich As-S glass are related to transformations of As_4S_4 molecules: $\alpha(\beta)$-As_4S_4 transform into pararealgar p-As_4S_4 form during laser illumination. The effectiveness of transformations depends mainly on photon energies used for irradiation, but the tendency to transform is observed for all used photon energies ranging from 1.65 to 2.54 eV. Experimental photon-energy dependent Raman spectroscopy used together with *ab initio* DFT calculations indicate that the mechanism of photo-induced changes in As-S glasses and films is defined by spectral width of illumination source.
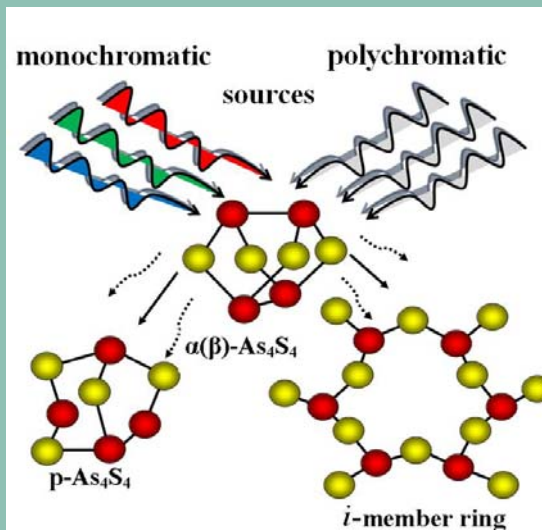
Photo-induced structural transformation in As-S chalcogenides under mono- and polychromatic illumination.

1 Introduction Amorphous chalcogenides (Chs) are a class of materials with a potential application possibility in nanotechnology mainly due to photo-induced changes in their structure and properties [1,2]. A deep understanding and control of these processes at the nanoscale would significantly increase the performance of modern optoelectronic devices made of these materials [2,3]. Recording media based on such glasses have shown good results in many applications: high density information storage, holography, diffractive optics, etc. Amorphous Chs have high values of nonlinear refractive index and have many of the properties necessary for the all-optical signal processing.

Therefore, the investigation of induced effects in Chs media have great practical importance.

In this study the influence of poly- and monochromatic illumination on the structure of glassy and amorphous arsenic chalcogenides is reported and discussed.

2 Materials and methods

2.1 Materials synthesis and experiment The glasses of As-S binary system were synthesized from constituent pure elements by melt quenching technique. As-S films were prepared using thermal vacuum evaporation on clean glass substrates kept at room temperature. Care was taken during sample preparation to minimize their exposure to light sources. Some samples were annealed at $T=T_g-20$ °C, where T_g stands for glass transition temperature.

Polychromatic exposure was carried out either by xenon (Xe) lamp (I=20 mW/cm^2, IR-cut-off filter) or by natural light.

Structural changes in differently treated samples were studied by using Raman spectroscopy. FT-Raman spectra were measured on a Bruker IFS 55 or IFS 66 interferometer coupled to a Bruker FRA 106 Raman module. Near-IR Nd:YAG laser with wavelength of 1064 nm ($E_1=1.17$ eV) was used as excitation source. A Renishaw system 1000 Raman spectrometer (typical resolution of 1-2 cm^{-1}) equipped with CCD detector was used for recording the micro-Raman spectra. All measurements were performed at room temperature in back-scattering geometry. The laser sources used for these measurements in As-S glasses were as follows: (i) a diode laser (785 nm, $E_2=1.58$ eV), (ii) a He-Ne laser (632.8 nm, $E_3=1.96$ eV), and (iii) an Ar-ion laser (514.5, $E_4=2.41$ eV and 488 nm, $E_5=2.54$ eV). During the experiments the laser beams where focused by means of the 50x objective. In micro-Raman experiments optical filters, limiting the output power were used in order to achieve nearly the same laser intensity on the sample (~10^3 W/cm^2). The excitation time during micro-Raman spectra recording was 60 sec. for E_2-E_4 excitation energies, and 600 sec for the E_5 excitation.

2.2 Theoretical modeling The computations consist of first-principles calculations on small atomic realgar-like $\alpha(\beta)$-As$_4$S$_4$ and pararealgar-like p-As$_4$S$_4$ molecules (Fig. 1). These clusters are present in the local structure of the respective As$_4$S$_4$ crystals [5-8].

All calculations were performed using the Gaussian-03 quantum-chemical program package [9]. The self-consistent field (SCF) and density functional theory (DFT) methods were applied for geometry optimizations of the clusters using the Berny optimization procedure. The optimizations of the structure of $\alpha(\beta)$-As$_4$S$_4$ and p-As$_4$S$_4$ were performed along D$_{2d}$ and C$_s$ symmetry, respectively. The LANL2DZdp ECP basis set of Hay and Wadt [10] with polarization function [11] was used for As and S atoms. The hybrid B98 Becke exchange-correlation functional was used [12] during the calculations.
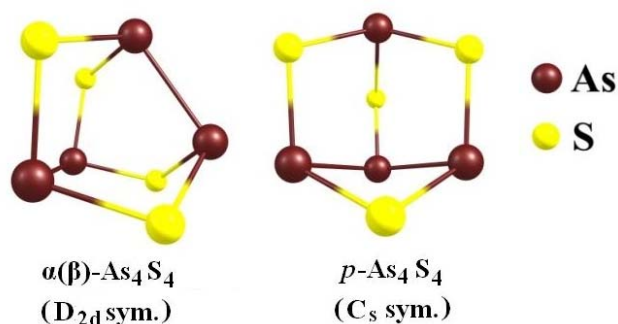

Figure 1 Geometrical structure of realgar- and pararealgar type As$_4$S$_4$ molecules.

Subsequent second derivative calculations, using the same method and basis set, verified the obtained structures as true energy minimum geometries. The vibrational frequencies and Raman intensities of both realgar-like and pararealgar As$_4$S$_4$ molecules were calculated (Tab. 1).

Table 1 Calculated vibrational mode frequencies, ω (cm^{-1}) and Raman intensities, I^R (>2Å^4/a.m.u.) of $\alpha(\beta)$-As$_4$S$_4$ and p-As$_4$S$_4$ molecules (B98/LANL2DZdp ECP).

ω (Sym.), cm^{-1}	I^R, (Å^4/a.m.u.)	ω (Sym.), cm^{-1}	I^R, (Å^4/a.m.u.)
$\alpha(\beta)$-As$_4$S$_4$		p-As$_4$S$_4$	
145.7 (B$_1$)	8.1	105.2	2.8 (A')
162.6 (E)	2.7	144.2	6.8 (A')
177.4 (B$_2$)	9.5	156.4	8.3 (A'')
182.6 (A$_1$)	15.9	171.4	8.5 (A')
217.6 (E)	2.9	183.5	4.6 (A'')
221.0 (A$_1$)	10.7	205.1	5.8 (A')
226.2 (B$_2$)	2.2	215.2	11.3 (A')
329.8 (E)	2.8	220.5	4.5 (A'')
341.5 (B$_2$)	12.8	238.4	9.2 (A')
359.6 (A$_1$)	46.5	310.5	3.9 (A')
		327.3	3.7 (A'')
		332.5	15.3 (A')
		340.6	37.3 (A')
		350.0	3.2 (A'')
		356.6	3.6 (A')
		378.1	2.5 (A')

3 Results Raman spectra of g-As$_{45}$S$_{55}$ recorded with different excitation wavelengths are presented in Fig. 2. The spectral transformations shown in Fig. 2 demonstrate continuous decreases in intensity of peaks which are characteristic for the vibrations of realgar type As$_4$S$_4$ molecules, at 188, 220 and 360 cm^{-1} with the increasing excitation energy. At the same time, the peak intensity at 231 cm^{-1} increases. Also, the 228/245 and 325/346 cm^{-1} doublets appear in the spectrum (Fig. 2, curve 5).
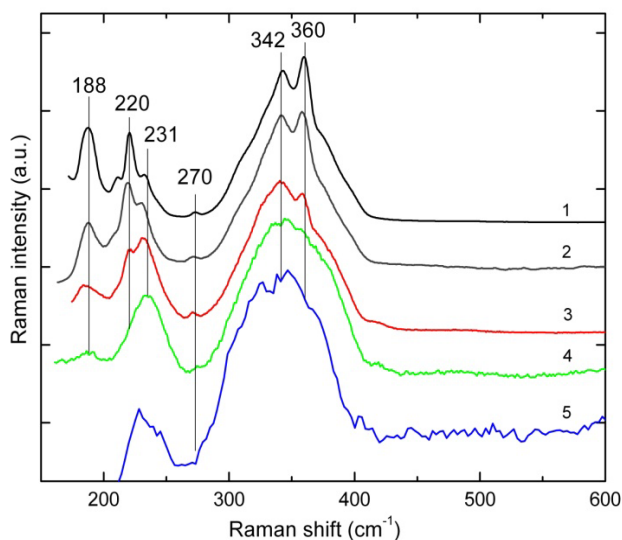
Figure 2 Raman spectra of g-$As_{45}S_{55}$ excited by lasers operating at 1064 (1), 785 (2), 632.8 (3), 514.5 (4) and 488 nm (5).

Photo-induced transformations can also be detected in the Raman spectra of amorphous As_2S_3 films illuminated by Xe-lamp (Fig. 3). However, the polychromatic illumination leads to continuous decreases in intensity of characteristics vibrational modes of molecular or cage-like species like As_4S_4, As_4S_3 etc. The thermal treatment of the sample shows the same effect in the Raman spectra (Fig. 3, curve 8). Similar behaviour is also characteristic for exposed $As_{42}S_{58}$ films.
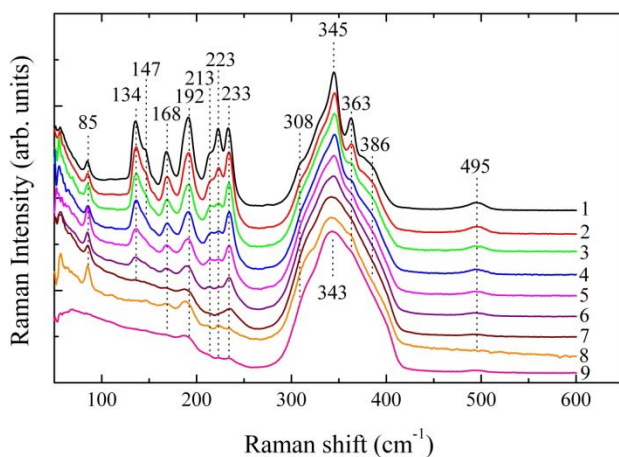

Figure 3 Raman spectra of as-deposited (1), illuminated by Xe-lamp during 5, 12, 20, 40, 80, 150 min. (2-7, respectively) and annealed (t=2 h, T=160 °C) (8) a-As_2S_3 films and vitreous As_2S_3 glass (9). All spectra were measured using laser operating at 1064 nm.

4 Discussion The evolution of the spectral features in Fig. 2 indicate the realgar-pararealgar transformation during illumination of the sample by laser, which was also supported by DFT calculations [4-7,13].
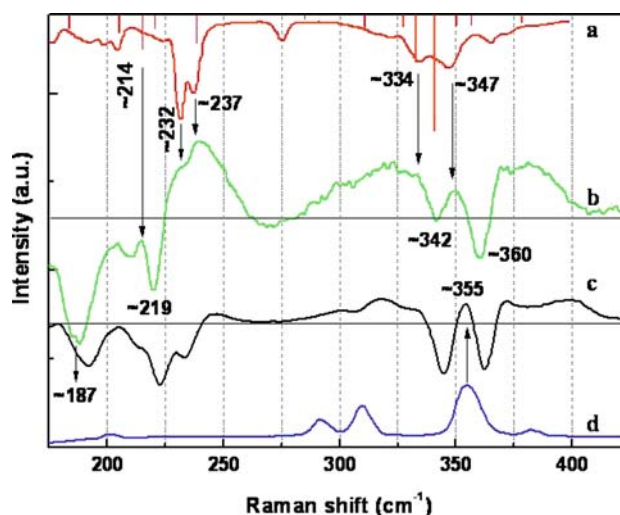

Figure 4 Differential Raman spectra of As-rich As-S samples: $As_{45}S_{55}$ glass ($I^R(E_4)$-$I^R(E_1)$) (b) and $As_{42}S_{58}$ film (I^R(ill.)-I^R(unill.) before and after 80 min. Xe-lamp illumination at P=14.5 mW) (c). The Raman spectra of pararealgar crystal [14] and calculated Raman spectra of p-As_4S_4 molecule (a) together with the Raman spectra of polycrystalline As_2S_3 (d) are shown for comparisons.

Similar transformation was also found in differential Raman spectra of stoichiometric $As_{40}S_{60}$ glass composition [4]. For detail analysis and comparisons of the processes of photo-induced structural changes in As-S glass and film we used differential Raman spectra of Ar-rich samples (Fig.4, curves b and c). As a result of laser or Xe-lamp illumination both spectra show the decreasing intensity of peaks characteristics for realgar-like As_4S_4 vibrations at ~360, ~342, ~219, and ~187 cm^{-1} (Tab. 1). However, the detailed analysis of the differential Raman spectra shows that the vibrational modes of paralealgar crystal can clearly be resolved at ~347, ~334, ~237 and ~232 cm^{-1} in the spectrum of $As_{45}S_{55}$ glass illuminated by Ar-ion laser with photon energy of 2.41 eV (E_4), together with the band of free p-As_4S_4 molecule at ~214 cm^{-1} (Fig. 4, curve a, Tab. 1). These peaks cannot clearly be seen in the spectrum of $As_{42}S_{58}$ film illuminated by Xe-lamp (Fig. 4, curve c). On the other hand, comparison of the differential Raman spectrum of $As_{42}S_{58}$ film (Fig. 4, curve c) with the Raman spectrum of orpiment-like polycrystalline As_2S_3 (Fig. 4, curve d) indicates the presence of vibrational band at ~355 cm^{-1} which is the main vibrational mode of polycrystalline As_2S_3. The main building block representing the local structure of orpiment is 12-member ring. According to our recent *ab initio* DFT calculations the amorphous As-S structures may contain other types of *i*-member ring structures with *i* ranging from 6 to 12 [15]. Therefore, it can be concluded that during polychromatic illumination the molecular-like structures may transform into rings of different types (*i*) and polymerize in the continuous random structural network. We found that for As-S rings the energetically most preferable value is *i*=10 [15]. Such processes

may be related to the broadening of the main band centred at ~343 cm^{-1} in the Raman spectrum of illuminated As_2S_3 film (Fig. 3, curve 7). It should also be noted here that such induced ring formation and transformations also take place during laser illumination of As-S glasses (Fig. 2, curves 4,5). According to our calculations the broad bands observed in the differential Raman spectra of illuminated As-S samples (Fig. 4, curves b and c) in the 290-330 and 370-400 cm^{-1} spectral regions could be related to ring transformations [15].

5 Conclusions

Experimental photon-energy dependent Raman spectroscopy used together with *ab initio* DFT calculations indicates that the mechanism of photo-induced changes in amorphous As-S Chs is defined by spectral width of illumination source. Intensive photo-induced realgar-pararealgar transformation of As_4S_4 molecules was observed in As-S glasses when using monochromatic laser illumination with a near bandgap photon energy. Alternatively, when using polychromatic Xe-lamp, the photo-induced transformation results mainly in polymerization and formation of orpiment-like (As_2S_3) structure containing rings of different size.

References

[1] I. Fekeshgazi, K. May, V. Mitsa, and A. Vakaruk, Physics and Applications of Non-Crystalline Semiconductors in Optoelectronics, edited by A. Andriesh and M. Bertolotti (Kluwer Academic Publishers, Dordrecht/Boston/London, 1997), Vol. 36, p. 243.

[2] E. F. Venger, A. V. Melnichuk, and A. V. Stronski, Photo-stimulated Processes in Chalcogenide Vitreous Semiconductors and their Practical Applications (Academperiodika, Kiev, 2007), Chap.2.

[3] A. Stronski, M. Vlček, and A. Sklenař, Quantum Electron. Optoelectron. **3**, 394 (2000).

[4] R. Holomb, N. Mateleshko, V. Mitsa et al., Non-Cryst. Solids **352**, 1607 (2006).

[5] D. L. Douglass, Chichang Shing, and Ge Wang, Am. Mineralogist **77**, 1266 (1992).

[6] P. Bonazzi, S. Menchetti, G. Pratesi, M. Muniz-Miranda, and G. Sbrana, Am. Mineralogist **81**, 874 (1996).

[7] R. Holomb, V. Mitsa, P. Johansson et al., Chalcogenide Lett. **2**, 63 (2005).

[8] P. Bonazzi, S. Menchetti, G. Pratesi, M. Muniz-Miranda, and G. Sbrana, Z. Kristallogr. **223**, 132 (2008).

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 03, Revision D.01 (Gaussian, Inc., Wallingford CT, 2004).

[10] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 284 (1985).

[11] C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert, and L. S. Sunderlin, J. Phys. Chem. A **105**, 8111 (2001).

[12] H. L. Schmider and A. D. Becke, J. Chem. Phys. **108**, 9624 (1998).

[13] R.M. Holomb and V.M. Mitsa, J. Optoelectron. Adv. Mater. **6**, 1177 (2004).

[14] M. Muniz-Miranda, G. Sbrana, P. Bonazzi, S. Menchetti, and G. Pratesi, Spectrochim. Acta **52**, 1391 (1996).

[15] R. Holomb, M. Veres, and V. Mitsa, J. Optoelectron. Adv. Mater. **11**, 917 (2009).