ENERGY-DEPENDENCE OF LIGHT-INDUCED CHANGES IN g-As$_{45}$S$_{55}$ DURING RECORDING THE MICRO-RAMAN SPECTRA

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Light-induced structural changes of g-As$_{45}$S$_{55}$ were probed both by macro FT-Raman and energy-dependent micro-Raman spectroscopy. We suppose that new observed features in the Raman spectra of As-rich As-S glass are related to transformations of As$_4$S$_4$ molecules. Being initially in the structure of g-As$_{45}$S$_{55}$ closed and connected with glassy network only by weak Van der Vaals forces α(β)-As$_4$S$_4$ molecules are transformed into pararealgar p-As$_4$S$_4$ form during laser illumination. The effectiveness of transformations depends mainly from photon energies used for irradiation but transformation tendency observed for all used photon energies ranged from 1.65 to 2.54 eV. Observed Raman features and their structural origin are discussed.

1. Introduction

Theoretical and experimental investigations in the last years shown that chalcogenide glassy semiconductors (ChGS) continuous media are formed in a wide variety of basic short range order structural units (s. u.) than their crystal analogs [1-3]. The majorities are combined into the middle-range ordering (MRO) grouping (clusters), depending on concentration of additives and producing technology [4-6]. The ordering groups' geometry in ChGS system's bulk glasses and films determines physical properties [6,7]. During the few years a great importance starts to be given to structural fluctuations and separated nano-scale phases with homopolar As-As bonds for interpreting photo-induced phenomena in binary As-S glasses [8,9]. The concentration of nano-phases, $C_{n.f.} \sim 1.0$-2.0 % in g-As$_2$S$_3$ is much larger than that of charged defects ($C_{def} \sim 1$ p.p.m.) which is foreseen by model [10,11]. The model of charged defects [10,11] in glass is known for a long time and has been the most widely spread one used to explain the photo-induced absorption in ChGS. This model is also used to explain the optical behavior in ChGS induced by the light with the energy of photons (E) lower than the Tauc band gap (E_0) in the Urbach edge region of optical absorption spectra. We have experimentally revealed that the introduction of HgS into g-As$_2$S$_3$ increases the absorption in the weak absorption region and is accompanied by the separation of β-As$_4$S$_4$ [12]. However, the introduction of 20-30 mol.% of GeS$_2$ into melt of As$_2$S$_3$ decreases absorption coefficient (α) with a very small phase-separation of As$_4$S$_4$ "molecules" having As-As bonds.

During the last few years we intensely studied both the macro- and micro-Raman scattering of ChGS binary and ternary systems in combination with first-principles quantum-mechanical calculations of As(Ge)$_n$S$_m$ clusters for understand both the compositional dependences of clustering and structural transformation in ChGS during laser irradiation. Here we report the analysis of the energy-dependent transformations of micro-Raman scattering spectra of arsenic-rich As$_{45}$S$_{55}$ glass. It is known that arsenic-excess glass compositions contain As-As bonds. Some authors [13] pointed

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that such bonds can be attributed to presence of As_4S_4 molecules embedded in glassy matrix. Also, in [14] was concluded that As-excess glasses contain two types of As-As bonds: (i) built in the glassy matrix and, (ii) structured in dissolved molecules of As_4S_4. Others [15] suppose that As-As bonds incorporated into the network rather than existing in discrete units such as As_4S_4 molecules. Enhancement of 231 cm^{-1} band in the spectra exited by 5145 Å was interpreted by [15,16] as results primarily a resonance As-As bonds.

2. Experimental and theoretical details

2. 1. Glass preparation and Raman spectroscopy

The As-rich glasses of As-S binary system were synthesized by melt quenching from 873 K and cooling rate of 1 K/s.

FT-Raman spectra were measured using the Bruker IFS 66 interferometer equipped with CCD detector and coupled to a Bruker FRA 106 Raman module. A macro-Raman set-up was used for FT-Raman part of measurement. The near-IR Nd:YAG laser with wavelength of 1064 nm (E_1=1.17 eV) was used as excitation source. For measurements of micro-Raman spectra the Dilor-Labram and Renishaw system 1000 Raman spectrometers (typical resolution of 1-2 cm^{-1}) equipped with CCD detectors were used. All measurements were performed at room temperature in back-scattering geometry. The micro-Raman systems consist of a microscope equipped with different objectives. The laser sources used for micro-Raman scattering excitation 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 recording micro-Raman spectra the laser beams where focused by means of the 50x objective. Optical filters, limiting the output power as low as 80 μW were used in order to avoid the visible photo-structural changes. The excitation time during micro-Raman spectra recording was limited to 60 sec. for excited photon energies ranged from E_2 to E_4. For excited photon energy of E_4 the excitation time of 600 sec. was used.

2.2. Calculational method

The computations consists of first-principles calculations on small atomic realgar-like (α, β) As_4S_4 and pararealgar-like (p) As_4S_4 molecules as depicted in Figure 2. These clusters represented the local structures of (α,β)-As_4S_4 and p–As_4S_4 crystals, respectively. All calculations were performed using the Gaussian-03 quantum-chemical program package [17].

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 triple-zeta (TZ) valence Pople 6-311G* [18] basis set was used for the Ge and S atoms. The corrected exchange functional proposed by Becke and the widely used gradient-corrected correlation functional of Lee, Yang, and Parr (LYP) (BLYP) lead to underestimate of calculated frequencies for closed As-S clusters according to our previous theoretical research. Therefore, the Becke's three-parameter hybrid functional (B3) that defines the exchange functional as a linear combination of Hartree-Fock, local and gradient-corrected exchange terms (B3LYP) [19] was used here. Subsequent second derivative calculations, using the same method and basis set, verified the obtained structures as true energy minimum geometries.

The calculated vibrational frequencies and Raman intensities of both realgar-like (α, β) and pararealgar (p) As_4S_4 molecules are listed in the Table 1.

3. Results and discussion

3.1. Edge absorption and influence of excited photon energies

Firstly, it should be noted here that exciting photon energies (E_1 and E_2) lies in low-energy range (week absorption, α<1 cm^{-1}) of the absorption edge spectra of As-S glasses, where α~exp (hν/E_ω) (E_ω~200÷300 meV) is adjacent to the Urbach edge. The exciting photon energy of E_3

correspond to the Urbach edge region, $\alpha > 10$ cm^{-1}. The light with photon energy of E_4 is closed to the Tauc band gap (E_0), $\alpha > 5*10^3$ cm^{-1}. Finally, the absorption coefficient α of As-S glasses is maximal when photon energy of $E_5 > E_0$ was used, $\alpha > 10^4$ cm^{-1}. Therefore, different exciting photon energies (E_1-E_5) are corresponds to the different ranges of absorption spectra of As-rich As-S glasses.

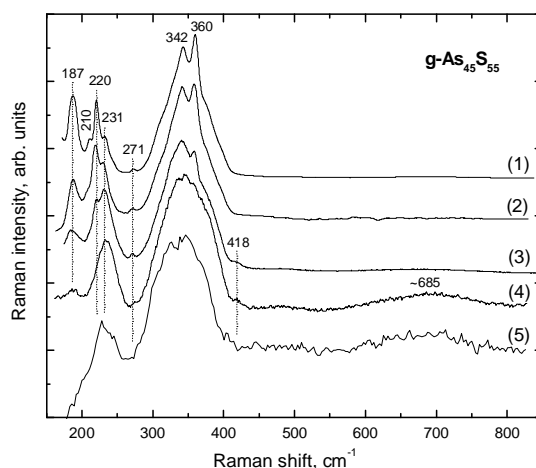The results of FT-Raman and energy-dependent micro-Raman spectra of g-As$_{45}$S$_{55}$ are shown in Fig. 1.

Fig. 1. FT-Raman spectrum of g-As$_{45}$S$_{55}$ excited with E_1=1.17 eV (1) and micro-Raman spectra of the same sample excited with E_2=1.58 eV (2), E_3=1.96 eV (3), E_4=2.41 eV (4), and E_5=2.54 eV (5).

The dominant sharp features in the FT-Raman spectrum of g-As$_{45}$S$_{55}$ excited using photon energy of E_1 (Fig. 1, curve 1) corresponds to the well-defined modes of β-As$_4$S$_4$ [20]. All spectral modes at 187, 210, 220, and 360 cm^{-1} indicate the presence of β-As$_4$S$_4$ content in As-rich glassy. But we observed spectral changes of the spectra depending on the wavelength of the exciting radiation. In [20] was revealed that realgar (α) and β-phase fast transform to pararealgar under radiation with wavelength below 600 nm. There are three molecular crystals of As$_4$S$_4$ with known crystal structures. First two, α- and β-As$_4$S$_4$, have identical molecules arranged in different packing [20]. The third form, pararealgar have different molecular structure of α- and β-As$_4$S$_4$ compound (Fig. 2). Raman spectra of pararealgar differs from those of α- and β-As$_4$S$_4$ and contain doublet at 231-236 cm^{-1}, that have no counterpart in the Raman spectra of α- and β-As$_4$S$_4$. Therefore, the intensive bands with two peaks at about 231, 237 cm^{-1} in the Raman spectra excited with energies of E_4 and E_5 (Fig. 1, curves 4,5) can be attributed to presence of pararealgar in glassy As$_{45}$S$_{55}$. This suggestion is also confirmed by shift of maxims at 342-360 cm^{-1} (Fig.1, curve 1) to 330-350 cm^{-1} (Fig.1, curves 4,5) like for pararealgar [20].

3.2. Polymorph transition or resonant Raman effect?

In earlier work [15] were reported the resonant character of 231 cm^{-1} mode in the Raman spectra of stoichiometric and As-rich As-S glasses. Also were defined that resonance of homopolar As-As bonds occur but no in As-As of As$_4$S$_4$ form (α- and β-like As$_4$S$_4$ molecules in our case). Using several excited photon energies our observations can not support this simplest model. It seems that more complicated processes occurred in the structure of g-As$_{45}$S$_{55}$ with increasing of excited photon energy. However, important to be noted here that these processes most likely can be related both to the polymorph transition and resonant effects of As-As bonds.

Now we must to explain tendency of decreasing mode intensity at 187 cm^{-1} with simultaneously increasing of peak at 231 cm^{-1} which we observed in the Raman spectra with increasing of exciting photon energy (Fig. 1, curves 2,3). Raman spectra excited using photon energies of 1.58 and 1.96 eV indicates the structural transformation of $\alpha(\beta)$-As$_4$S$_4$ molecules to pararealgar form. Moreover observed spectral features (Fig. 2, curves 2, 3) can elucidate both the mechanism of such transformation and intermediate phase structure. For definitely explanation changes occur in glass structure during Raman spectra measuring the first-principles calculations of vibration spectra and tentative mode assignment of As$_4$S$_4$ molecules (Fig. 2, Table 1) were performed. The methodology used for calculations (DFT, hybrid B3LYP functional, and 6-311 G* basis set) gives excellent agreement of vibrational frequencies with experimental data [20] especially for stretching vibrations of heteropolar As-S bonds. However, for homopolar As-As stretching vibrations our calculations gives underestimated vibrational frequencies by about 10 cm^{-1} in comparison with experimentally observed. It can be connected with interaction of As$_4$S$_4$ molecules in the crystal state. But pseudopotential-based DFT calculations [21] of vibration modes of As$_4$S$_4$ monomer and network models shows that even As-S vibrational frequencies are overestimated by about 10 cm^{-1}. Therefore, such deviations in frequencies occurred mainly by method and basis set used for calculations.
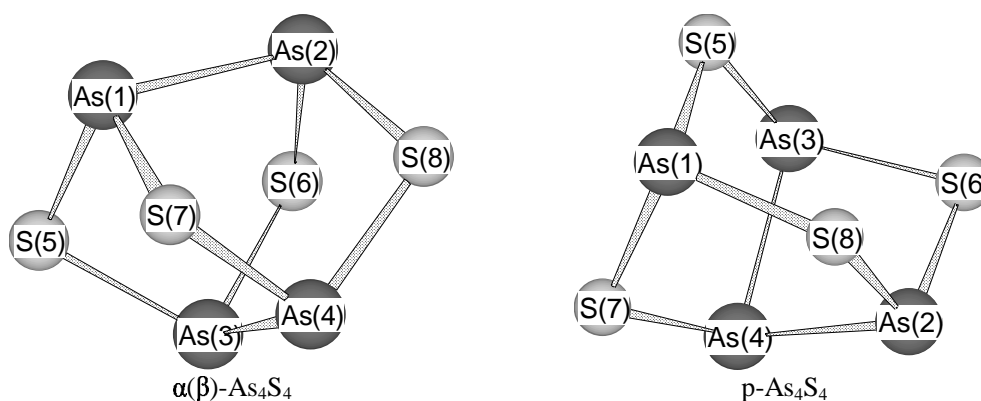

Fig. 2. Local molecular structure and bonding of crystalline $\alpha(\beta)$-As$_4$S$_4$ and p-As$_4$S$_4$ phases.

Tentative assignment of calculated Raman frequencies (Table 1) gives us following results: doublet peak with frequencies at 181 and 188 cm^{-1} is due to the stretching vibrations of homopolar As-As bonds; 219-220 and 228 cm^{-1} Raman modes attributed to deformational As-S-As and S-As-S vibrations of $\alpha(\beta)$-As$_4$S$_4$ molecules. Therefore, the intensity decreasing of band at 187 cm^{-1} with increasing photon energy is connected with destruction As-As bond(s) of such molecules. Breaking of these bonds doesn't much influence in intensity of deformation vibrations at 219-220 and 228 cm^{-1}. On the one hand, enhancement band intensity at 231 cm^{-1} in comparison with 220 cm^{-1} band in Raman spectra excited with near band gap radiation (Fig. 1, curve 3) may be assign to resonance of As-As bonds present in the network of glass, but not in $\alpha(\beta)$-As$_4$S$_4$ form. On the other hand, pre-resonance effect can be responsible for the breaking of homopolar As-As bond(s) in closed $\alpha(\beta)$-As$_4$S$_4$ molecules.

For elucidation of structural transformation of $\alpha(\beta)$-As$_4$S$_4$ to pararealgar molecule we calculated geometry and vibrational spectra of $\alpha(\beta)$-like As$_4$S$_4$ cluster with broken As-As bond. Detailed description of calculated results we will present sooner only one note we would like to mark here. The breaking of As-As bond lead to formation of two under-coordinated As atoms in the structure of As$_4$S$_4$ molecule. These centers produce the chemically unstable structure and which can be instantaneously transformed. We suppose that formation of over-coordinated (tri-coordinated) sulfur atom can interact with the As atoms and balance their chemical bond-saturation in metastable molecule. An interaction of such As and S atoms gives Raman frequency about 418 cm^{-1}. The bends at same frequency exist in experimental Raman spectra of g-As$_{45}$S$_{55}$ (Fig.1, curves 3-5). The microscopic nature of this peculiarity in the Raman spectra was not established at present.

Table 1. Vibrational frequencies (ω), Raman activities (I^{Ram}), force constants (f), and assignments of Raman-intense ($I^{Ram}>3$ Å^4/a.m.u.) deformational and stretching modes of $\alpha(\beta)$-As$_4$S$_4$ and p-As$_4$S$_4$ molecules calculated using DFT/B3LYP/6-311 G* level of theory.

ω, cm^{-1}	I^{Ram}, Å^4/a.m.u.	f, mDyne/Å	Tentative assignment
$\alpha(\beta)$-As$_4$S$_4$			
171/181*	7.1	1.2	ν_{UP}(As-As)
178 /188*	15.7	1.2	ν_{P}(As-As)
219	3.2	1.7	δ(S-As-S)
220	10.5	2.0	δ(As-S-As)
228	4.1	1.1	δ(S-As-S)
347	13.7	2.8	ν_{E+A}(S-As-S)
362	43.9	2.8	ν_{A}(S-As-S)
p-As$_4$S$_4$			
174	10.5	0.8	δ(S-As-S; S$_{5,6,8}$, As$_{1,2,3}$)
186	5.5	0.8	δ(S$_5$-As$_1$-S$_7$; S$_7$-As$_1$-S$_8$)
207	6.4	1.5	δ(As$_1$-S$_7$-As$_4$)
218/228*	10.9	1.9	ν_{A}(As-As-As)
222/232*	3.4	2.0	ν_{E}(As-As-As)
240	6.9	2.1	δ(As-S-As; As$_{1,2,3}$, S$_{5,6,8}$)
315	3.6	2.2	ν(As$_1$-S$_7$); ν_{A}(S$_5$-As$_1$-S$_8$)
331	4.3	2.5	ν_{E}(S$_5$-As$_1$-S$_8$)
336	19.8	2.4	ν_{A}(As$_1$-S; S$_{5,7,8}$)
347	33.0	2.6	ν_{A}(As$_2$-S$_6$-As$_3$)

δ, ν – deformational and valence (stretching) vibrations, respectively.
A and E – symmetric and asymmetric vibrations; P and UP – phased and unphased vibrations.
 * - corrected frequencies of As-As stretches (see text for details).

So, the observed Raman features testify follows processes. The destruction of As-As bond(s) of realgar-like $\alpha(\beta)$-As$_4$S$_4$ molecule(s) (Figure 2) due to the laser illumination with energies E$_2$ and E$_3$ are observed. Re-arrangement of As-As bond most likely lead to formation of metastable molecule with over-coordinated sulfur. This metastable molecule especially with further increase of exciting photon energy (E$_4$ and E$_5$) transform to pararealgar form in glassy structure. Calculational results of p-As$_4$S$_4$ molecule predict high-frequency shift of As-As stretching vibrations (calc. 228 and 232 cm^{-1}) and low frequency shift of As-S stretching vibrations (calc. 336 and 347 cm^{-1}) in comparison with $\alpha(\beta)$-As$_4$S$_4$ form (181 and 188 cm^{-1} for As-As stretches; 347 and 362 cm^{-1} for As-S stretches). These results are in excellent accordance with experimental Raman spectra (Fig. 1).

Using exciting photon energy of E$_5$ the penetration depth is very small and during exposure time only surface of the sample has modified by laser beam. In consequence the well-defined broad band at ~685 cm^{-1} in the micro-Raman spectra excited with high photon energies (E$_4$ and E$_5$) is assigned to second-order Raman mode of As-S bonds stretches. The appearance of second-order scattering in molecules usually accompanies the resonant effects [22]. Therefore, the increases in intensity of second-order mode at ~685 cm^{-1} with increasing excited photon energy to E$_4$ and E$_5$ can

attribute to resonant Raman effects of As-S bonds because these energies are about the Tauc's band-gap of As-S glasses.

Sub-band-gap illumination can change the fluidity of As-S glasses. Intense He-Ne laser irradiation was found to even increases the thickness of film [23]. Among As_4S_4 polymorphs only pararelgar is more voluminous [24]. In the case of α-, β-As_4S_4 polymorphs there is direct evidence of transformation both into pararealgar with different rate during illumination in the visible light region. It means that formations of pararealgar-like structures can be useful to explanation of optico-mechanical phenomena in As-S glassy materials.

4. Conclusions

We have used macro RT-Raman spectroscopy and energy-dependent micro-Raman spectroscopy together with first-principles calculations for investigation of light-induced structural transformations of As-rich $As_{45}S_{55}$ glass. The main results observed are as follows.

(i)   The transformations occur mainly from alterations of As_4S_4 molecules "implanted" in glass network. The real mechanism of this alteration is complicated and hardly can be established only by experimental Raman spectroscopy.

(ii)   Our calculations shown that $\alpha(\beta)$-As_4S_4 molecules transform to p-As_4S_4 by breaking of As-As bond(s) and further re-configuration of this bond(s) into pararealgar-like structures. This transformation lead to high-frequency shift of double peaks of As-As stretches from 181-188 to 228-232 cm^{-1} and low-frequency shift of As-S stretches from 347-362 to 336-337 cm^{-1} for $\alpha(\beta)$-As_4S_4 and p-As_4S_4, respectively.

(iii) The effectiveness of alterations depends from excited photon energies and according to our limited laser wavelengths has maxima at photon energy of E_4=2.41 eV. Further increases of exciting photon energy (E_5) lead to modifications of sample surface and intensely breaking not only As-As but also As-S bonds.

Acknowledgements

References

[1] R. M. Holomb, V. M. Mitsa, J. Optoelectron. Adv. Mater. **6**, 1177 (2004).
[2] R. Holomb, P. Johansson, V. Mitsa, I. Rosola, Phil. Mag. B, in press (2005).
[3] M. Popescu, F. Sava, A. Lorinczi, Chalogenide Letters **1**, 111 (2004).
[4] G. Lucovscky, C. K. Wong, W. B. Pollard, J. Non–Cryst. Sol. **59–60**, 839 (1983).
[5] R. Holomb, P. Johansson, V. Mitsa, Submitted to Physical Review B (2005).
[6] S. I. Simdyankin and S. R. Elliott, Phys. Rev. B. **69**, 144202 (2004).
[7] V. Mitsa, Doctoral Thesis, Institute of Semiconductors Physics, NAS of Ukraine, Kyiv (2003).
[8] Ke. Tanaka, J. Optoelectron. Adv. Mater. **3**, 189 (2001).
[9] K. Petkov, J. Optoelectron. Adv. Mater. **4** 611 (2002).
[10] Photo-Induced Metastability in Amorphous Semiconductors, edited by A. V. Kolobov (Wiley-VCH, Weinheim, 2003).
[11] M. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).
[12] N. I. Mataleshko, V. M. Mitsa, O. O. Kikineshi, Fizika A **8**, 17 (1999).
[13] S. N. Yannopoulos, Phys. Rev. B **68**, 064206 (2003).
[14] M. Frumar, Z. Polak, Z. Cernosek, J. Non–Cryst. Sol. **256–257**, 105 (1999).

[15] P. J. S. Ewen, A. E. Owen, J. Non–Cryst. Sol. **35–36**, 1191 (1980).

[16] C. Razzetti, M. P. Fontana, Phys. Stat. Sol. (B) **70**, 173 (1975).

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb et al., Gaussian, Inc., Pittsburgh PA (2003).

[18] V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, J. Chem. Phys., **109**, 1223 (1998).

[19] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[20] M. Muniz-Miranda, G. Sbrana, P. Bonazzi, S. Menchetti, and G. Pratesi, *Spectrochimica Acta Part A*, **52**, 1391 (1996).

[21] D. G. Georgiev, P. Boolchand, *Phil. Mag.* **83**, 2941 (2003).

[22] *Raman Spectroscopy of Gases and Liquids*, edited by A. Weber (Springer-Verlag, Berlin, Heidelberg, New York, 1979).

[23] Ke. Tanaka, *C. R. Chimie* **5** 805 (2002).

[24] D.L. Douglass, C. Shing, and G. Wang, *American Mineralogist*, **77**, 1266 (1992).