Investigation of nanophase separation in IR optical glasses $As_{40}Se_{60}$ using resonant Raman scattering

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Abstract. Resonant Raman spectra of stoichiometric glass (g) g-$As_{40}Se_{60}$ have been investigated. It was observed that the increasing of excitation radiation energy $h\nu > E_0$ (E_0 is pseudogap width) changes a shape, intensity, and position of Raman peaks of g-$As_{40}Se_{60}$. The structure and vibration spectra of some As-Se clusters were calculated applying the *ab initio* method. In order to elucidate structural features of g-$As_{40}Se_{60}$, we combined the experimental Raman data and theoretical calculations.

1. Introduction

Photo-induced effects in amorphous chalcogenide semiconductors are widely investigated as both fundamental processes of structural transformations in amorphous solids and promising applications in optoelectronics due to the related changes of optical parameters [1]. Among chalcogenide glasses, As-S and As-Se systems are models for studying the structure and photoinduced phenomena in non-crystalline semiconductors. Much efforts have been devoted to study these materials by various techniques, for instance, Raman spectroscopy. A usage of excitation radiation of different energies causes some changes in the Raman peak position and their shape. Phenomena of resonant behavior of Raman bands at energies less than pseudogap width in As-S system glasses can be explained by creation of As-As and S-S bonds in the matrix structure [2].

Theoretical calculations [3] and X-ray photoelectron spectroscopy (XPS) experiments [4] suggest that even in stoichiometric $As_{40}Se_{60}$ glasses, there are wrong As-As and Se-Se bonds.

So, it is interesting to investigate resonant Raman spectra of g-$As_{40}Se_{60}$ at excitation energies $h\nu < E_0$ and $h\nu > E_0$.

2. Experimental technique

The technique of glass synthesis is described in [5].

Raman spectra of $As_{40}Se_{60}$ glasses were measured by RENISHAW SYSTEM 1000 Raman spectrometer with CCD (Charge Coupling Device) detecting cell. Raman scattering was excited by a diode laser with the wavelength 785 nm and output power 25 mW and a Spectra Physics Model 168 (Ar) laser with the wavelength 488 nm and output power 1W. The spectra were measured in a back scattering geometry. An output power was restricted by filters to avoid a photoinduced structural changes.

Raman spectrum excited by 1060 nm wavelength were taken by Fourier Transformation (FT) BRUKER IFS55 IR spectrophotometer with FRA-106 accessory, output power 90 mW [6].

For previous calculations of geometry and Raman spectrum, a linear As_2Se_3 cluster was chosen. Calculations were carried out by the ab initio Hartree-Fock method with 6–31 basis set, GAMESS (US) software [7]. Hydrogen atoms saturated the end atoms.

Geometrical parameters and vibrational spectra of As_2Se_5, As_4Se_6, and As_6Se_9 clusters were calculated by the *ab initio* Hartree-Fock method with LANL2DZ, GAUSSIAN-94 program packages [8].

3. Results and discussions

Recent investigations have shown that shape and position of Raman peaks in g-As_2S_3 depends on excitation wavelength. The energy of excitation radiation can be greater or lesser than the pseudogap width that causes a shift of maxima positions [9] by electronic processes influence.

Fig. 1 shows Raman spectra inherent to As_2Se_3 glass excited with light of different energies. The wavelengths are 1060, 785, and 488 nm with energies 1.17, 1.58, and 2.54, respectively. The latter energy value exceeds the pseudo bandgap energy of g-As_2Se_3 ($E_0 = 1.9$ eV [10]).

Raman spectra obtained using lasers with wavelengths 1060 and 785 nm, $hv < E_0$, comprise one broad band peaking at 227 cm^{-1}. Raman spectra of crystalline (c) c-Se (Fig. 2) and amorphous (a) a-As (Fig. 2) have intensive bands at 235, 250 and 227, 252 cm^{-1}, respectively. So, it is impossible to give an exact identification of structural units (s.u.) of g-$As_{40}Se_{60}$ by comparing the Raman spectra of g-As_2Se_3, c-Se and a-As. Some authors [11] suppose that it is enough to coincide the calculated vibration frequency of $AsSe_3$ "molecule" with experimental position of the Raman spectra band for assignment of maxima at 230 cm^{-1} to $AsSe_{3/2}$ s.u. vibration. But Raman scattering by bulk As_xS_{1-x} glasses shows that the vibrational modes of As_4S_4 monomers appear first near $x = 0.38$, and their concentration sharply increases with increasing x, suggesting that the stoichiometric glass ($x = 0.40$) is intrinsically phase separated into small As-rich (As_4S_4) and large S-rich clusters [12]. Since synthesis procedures of g-As_2S_3 and g-As_2Se_3 are similar, it is possible that the latter may contain not only $AsSe_{3/2}$ s.u. but $AsSe_{4/2}$ and Se-Se inclusions. Really, for a laser with $hv < E_0$ sensitive to the structural fragments of small sizes, Raman
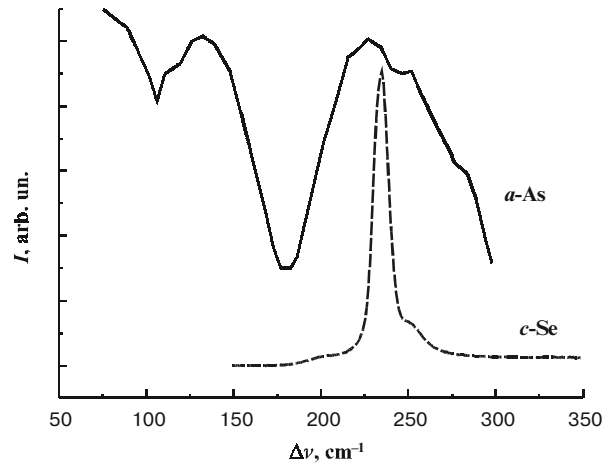

Fig. 2. Raman spectra of crystalline Se and amorphous As taken at $\lambda = 785$ nm.

spectra of g-As_2Se_3, if using $\lambda = 488$ nm, differ from the spectra taken at $\lambda = 1060$, 785 nm (Fig. 1).

Raman spectra of g-$As_{40}Se_{60}$ taken at $\lambda = 488$ nm contains the broader band with maxima at 230 cm^{-1}. On broad maxim it is clearly seen peaks at 220 and 228 cm^{-1} that can be assigned as assymetric and symmetric vibrations of $AsSe_3$ pyramid. From high-frequency side there is a shoulder at 276 cm^{-1} that can be a mode of As-Se bond vibrations in As_4Se_4 molecules (Table 1). The band broadened from low-frequency side (up to 200 cm^{-1}) at $\lambda = 488$ nm can be ascribed to the presence of As-As bonds in $As_{3/3}$ s.u. Similar situation was observed in the resonant Raman spectrum of g-$As_{40}S_{60}$ [13].

As can see from Fig. 1 broaden low frequency side of Raman line of g-$As_{40}Se_{60}$ excited with $\lambda = 488$ nm has shoulders at 190 and 208 cm^{-1} that are most intensive bands at Raman spectra of crystalline As_4Se_4 (Table 1) and may be assigned to vibrations of As-As bonds [15]. A frequency
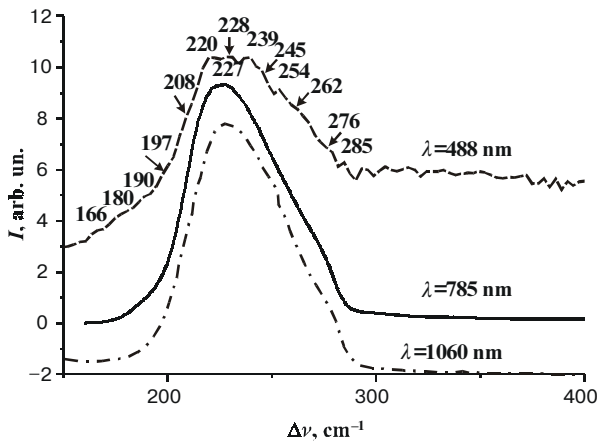

Fig. 1. Raman spectra for g-$As_{40}Se_{60}$ excited with light of different wavelengths indicated.

Table 1. Band positions and their assignment in Raman spectra of crystalline As_4Se_3 [14] and As_4Se_4 [15].

	c-As_4Se_3 [12]		c-As_4Se_4 [13]	
A1	280 (m.)	νAs-As	275 (w.)	νAs-Se
	266 (m.)	As-Se	248 (very s.)	νAs-Se
	256 (s.)	As-Se	235 (m. w.)	νAs-Se
	242 (s.)	νAs-Se	216 (m. w.)	νAs-Se
	236 (w.)	νAs-Se	207 (s.)	νAs-As
	188 (w.)	Se-As-Se, As-Se-As	190 (s.)	νAs-As
	196 (s.)	As-As	152 (w.)	δAs-Se-As
	166 (w.)			
	140 (w.)		144 (m.)	δAs-Se-As

s – strong, m – medium, w – weak, sh – shoulder
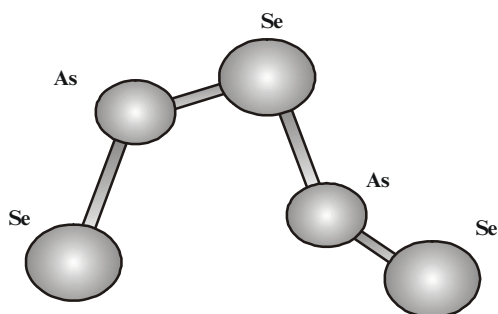
Fig. 3. The optimized geometry of As_2Se_3 cluster (hydrogen atoms are not shown).

Fig. 5. The optimized geometry of As_2Se_5, As_4Se_6, As_6Se_9 clusters.

position of shoulder at 197 cm^{-1} in Raman spectra of g-$As_{40}Se_{60}$ coincides with one of more intensive Raman band of crystalline As_4Se_3 (Table 1). The shoulders that appear on the lowfrequensy side of main band of g-$As_{40}Se_{60}$ at irradiation with wave energy 2,54 eV may be due to the exciting of homopolar As-As bonds. Indeed it is impossible to give an exact assignment of these bonds to molecules As4Se4(3) on Raman data.

Such indefinition exists at interpretation of high frequency side of main Raman band of g-$As_{40}Se_{60}$. Existence of shoulder at 254 cm^{-1} may be related to the presence both of Se-Se bonds in free Se (Fig. 2) and As-Se bond vibrations of As_4Se_3 molecule. The bend at 245 cm^{-1} may exist due to As-Se bonds of As_4Se_4 molecule.

For g-As_2S_3 Kawazoe et al. [16] have reported resonance enhancement of Raman peaks sterming from As-As and S-S homopolar bonds, which are assumed to provide band tail states of the valence band.

So, we can made a conclusion that structural study needs methods which may give exact information about
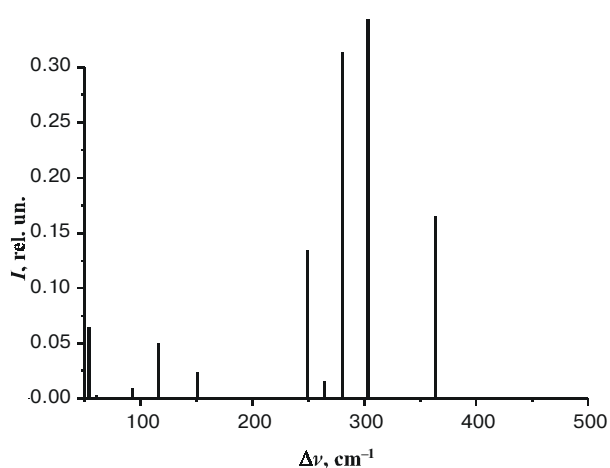
bond types. For example we used [17] x-ray photoelectron spectroscopy for As-GeS_2 system.

Using short wavelength laser radiation to excite the Raman signal gives a series of low intensity bands in the range above 300 cm^{-1} (Fig. 1). An assignment of these bands can be made using quantum-chemical calculations.

First of all, we choose a simple chain cluster As_2Se_3. Geometry of this cluster is shown in Fig. 3. To keep the atom valency, hydrogen atoms were used.

Schematic geometry of the following clusters are shown in Fig. 5

An important feature of As_2Se_5 cluster is Se-Se bonds at the ends of clusters. The ends of As_4Se_6, As_6Se_9 clusters were closed by the double Se bond.

A calculated freguencies at 300 cm^{-1} may be assigned to vibrations of Se-Se bonds at the cluster ends (Fig. 6). The vibrations of Se atoms at the ends of As_2Se_3, As_4Se_6 and As_6Se_9 clusters have frequency at 360 cm^{-1} (Fig. 6). So, the low intensive bands at 300 and 350 cm^{-1} in the Raman spectra of g-$As_{40}Se_{60}$ may be related to the vibra-
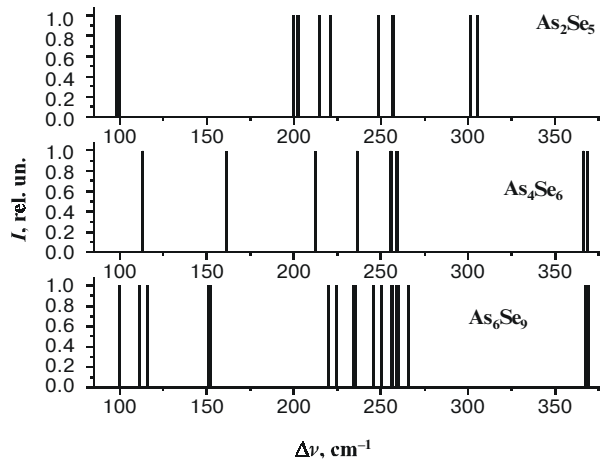

Fig. 4. Raman spectra of As_2Se_3 cluster.

Fig. 6. Vibration spectra of clusters.

tions of Se-Se and As-Se ends, respectively. The same situation was observed for another cluster types Ge-S and As-S [18, 19].

So, excitation of the Raman signal by energy $hv > E_0$ makes spectra more informative, which allows to reveal s.u. $As_{3/3}$, $As_2Se_{4/2}$, $Se_{2/2}$ in g-$As_{40}Se_{60}$ structure.

Acknowledgements

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