
Proceedings of the International Conference "Condensed Matter Physics", Jaszowiec 2000

RAMAN SPECTRA OF $\text{In}_{0.30}\text{Se}_{0.70}$ AMORPHOUS FILMS

J. WESZKA^{a,*}, PH. DANIEL^b AND A.M. BURIAN^a

^aCenter of Polymer Chemistry, Polish Academy of Sciences
M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland

^bLaboratoire de Physique de l'Etat Condensé, UPRES A RS n°6087
Université du Maine, Av. O. Messiaen 72085 Le Mans Cedex 9, France

Amorphous films of $\text{In}_{0.30}\text{Se}_{0.70}$ alloy thermally evaporated from one source onto borosilicate glass substrates were studied by Raman scattering at 300 K and 10 K. The Raman scattering spectra excited with 488 and 457.9 nm laser lines were recorded in a quasi-rectangular geometry with the use of a single channel spectrometer. All the Raman scattering spectra reveal a continuum spreading from the Rayleigh line up to about 250 cm^{-1} and rather featureless background due to second-order processes beyond it. The room temperature spectra show a strong feature at about 143 cm^{-1} that is lacking in the spectra taken at 10 K and, instead, a weak band at about 125 cm^{-1} is observed. The Raman scattering spectra recorded at both temperatures appear to be dependent on the excitation line within the $40\text{--}50\text{ cm}^{-1}$ range. The feature at about 143 cm^{-1} is attributed to Se chain modes while a weaker band at about 125 cm^{-1} observed at low temperature is due to Se_8 ring molecules. The dynamics of the $\text{In}_{0.30}\text{Se}_{0.70}$ films is treated in terms of a continuous random network composed of rather strongly interconnected InSe_4 tetrahedral clusters.

PACS numbers: 63.50.+x, 71.55.Jv

1. Introduction

Indium and selenium combine into several stable chemical compounds each available in various crystalline modifications [1–3]. Amorphous films of $\text{In}_{1-x}\text{Se}_x$ alloys within a broad x range are available by thermal vacuum evaporation [4, 5]. These materials are interesting for their potential applications in photovoltaics and microelectronics [6]. Our earlier studies completed on amorphous films of InSe_2 and In_2Se_3 compositions have shown their structure to be of a continuous random network type [7]. The aim of this paper is to present the Raman scattering (RS) spectra of amorphous films of the $\text{In}_{0.30}\text{Se}_{0.70}$ alloys with the 457.9 and 488 nm lines of an argon ion laser at room temperature and 10 K. An attempt is made to interpret recorded spectra in terms of the continuous random network.

*corresponding author; e-mail: polymer@uranos.cto.us.edu.pl

2. Experimental

Thin amorphous films of the In–Se alloys have been prepared by the thermal vacuum evaporation technique from one source. Bulk polycrystalline alloys of InSe_3 compositions synthesized directly from the high purity elemental indium and selenium were used as source materials. The as-prepared material was thermally evaporated onto borosilicate glass substrates kept at room temperature under the vacuum of 10^{-3} Pa. The thickness of the as-deposited films was evaluated with the use of an interference microscope to be about 2 nm. The composition of the films evaporated from the InSe_3 bulk material were determined by X-ray microanalysis to be $\text{In}_{0.30}\text{Se}_{0.70}$ (at% ± 1.5). The RS spectra have been recorded in a quasi-rectangular geometry with the use of a single channel DILOR Z24 Raman spectrometer with an oblique incidence of a laser beam on a film surface. While recording the RS spectra, specimens were kept in an evacuated cryostat to avoid any influence of the air scattering. Identical spectra were recorded from different spots on the surface of a given film and on different films of the same composition as well. The output power of both the 457.9 and 488 nm lines of an ion argon laser was equal to 100 mW, other conditions of spectra recording being the same. The spectra were recorded with the spectral resolution of about 10 cm^{-1} . Additionally, after each experiment the films were carefully examined against eventual damage brought to them by the laser beam used.

3. Results

The room temperature RS spectra recorded with both the 488 and 457.9 nm excitation lines of an ion argon laser are shown in Fig. 1a. They reveal a broad continuum spanning the frequency range from the Rayleigh line up to about 250 cm^{-1} . Peaks centered at about 40–50, 143, 205, and 240 cm^{-1} are observed at room temperature. The low frequency band peaking at about 40 cm^{-1} excited with the 488 nm line is shifted to about 50 cm^{-1} when the 457.9 nm line is used. The RS spectra recorded at 10 K with both excitation lines are illustrated in Fig. 1b. It is clearly seen that the overall intensity of the spectrum taken with the 488 nm line is distinctly higher than that when recorded with the 457.9 nm line. Changing from one excitation line to another was carried out by tuning the laser, the position of the sample being fixed. Similarly as at room temperature, a band peaking at about 40 cm^{-1} with the 488 nm radiation has a higher intensity and is blue shifted to about 50 cm^{-1} when the 457.9 nm line is used. The band observed at about 143 cm^{-1} in both spectra recorded at room temperature (Fig. 1a) disappears at 10 K (Fig. 1b). In all the spectra shown in Fig. 1 one can see rather featureless background beyond the continuum threshold up to 500 cm^{-1} . The spectra taken with both excitation lines at each temperature regimes are very similar, so only the spectra taken with the 457.9 nm line at both temperature regimes de-convoluted by means of Levensberg–Marquardt [8] least squares procedure are presented. These results are shown in Fig. 2 and in Tables I and II for room and 10 K temperatures, respectively.

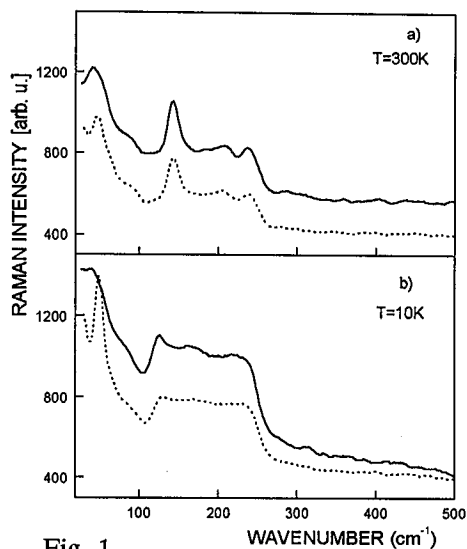


Fig. 1

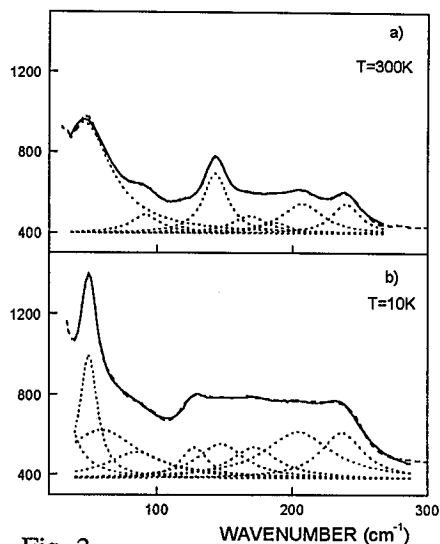


Fig. 2

Fig. 1. Raman spectra of the $\text{In}_{0.30}\text{Se}_{0.70}$ amorphous films recorded in two temperature regimes with $\lambda = 488$ nm (solid line) and 457.9 nm (dotted line) excitation lines. Temperature regimes: (a) 300 K, (b) 10 K.

Fig. 2. De-convoluted RS spectra of the $\text{In}_{0.30}\text{Se}_{0.70}$ amorphous film recorded at two temperature regimes with $\lambda = 457.9$ nm excitation line. Temperature regimes: (a) 300 K, (b) 10 K. The recorded spectra — dashed line; fitted curve — solid line; de-convoluted bands — dotted lines.

TABLE I

The estimated errors of the deconvolution of the spectrum presented in Fig. 2a.

No.	Peak position [cm^{-1}]	FWHM [cm^{-1}]	Peak area
1	45.59 ± 0.20	48.56 ± 1.21	41826.58 ± 1333.50
2	119.01 ± 1.85	19.29 ± 8.83	866.84 ± 498.96
3	143.13 ± 0.27	21.83 ± 1.47	10148.07 ± 1184.84
4	168.46 ± 4.60	33.20 ± 17.61	4382.56 ± 4570.59
5	186.91 ± 4.02	26.63 ± 28.36	2216.62 ± 5390.94
6	207.31 ± 2.77	37.76 ± 8.74	8613.97 ± 3895.00
7	239.57 ± 0.53	26.00 ± 2.85	5964.87 ± 1086.93
8	91.12 ± 0.71	26.88 ± 3.55	3755.56 ± 660.95

TABLE II

The estimated errors of the deconvolution of the spectrum presented in Fig. 2b.

No.	Peak position [cm ⁻¹]	FWHM [cm ⁻¹]	Peak area
1	49.29±0.64	15.68±3.25	15324.30±11111.44
2	59.10±39.48	67.65±445.38	25567.21±395010.39
3	25.20±476.50	21.53±106.09	20163.06±1005397.91
4	85.02±39.38	53.81±183.61	11109.41±175236.90
5	127.86±2.02	24.24±11.46	6002.57±7829.19
6	147.38±3.96	43.54±38.60	11830.72±22563.10
7	172.21±4.96	43.25±31.73	10614.83±21525.09
8	204.32±3.86	61.69±28.97	22579.39±21362.90
9	236.78±1.22	39.30±5.54	14298.35±5683.19

4. Discussion

The recorded RS spectra reveal predominantly vibrational density-of-states (VDOS) character with some admixture of a molecular-like one. The fitted curves shown in Figs. 2a and b appear to nearly coincide with the recorded spectra. The de-convoluted bands at about 168 and 186 cm⁻¹ (Fig. 2a) and at 172 cm⁻¹ (Fig. 2b) are attributed to the A_1 bond stretching mode of a tetrahedral InSe₄ cluster in accordance with the reported 175 cm⁻¹ value [9]. The band at about 240 cm⁻¹ is due to a triple degenerate F_2 bond stretching mode of a tetrahedral InSe₄ cluster within the valence force field model [10]. The broad band at about 210 cm⁻¹ is attributed to vibrations of "water-like" In-Se-In units bridging InSe₄ clusters. These are probably the most flexible elements of the network [10]. The low frequency features at about 50, 70, and 90 cm⁻¹ are expected to be due to the bond bending modes of tetrahedral clusters [11]. The shape of the presented spectra is thought to be consistent with the above interpretation and supports an idea of the In_{0.30}Se_{0.70} amorphous film being composed of rather strongly interconnected tetrahedral InSe₄ clusters bridged with fragments of Se polymer chains or Se₈ ring molecules locally distributed or by the shared Se atoms. This is consistent with the presence of the 143 cm⁻¹ mode related to the Se chain vibrations and the 125 cm⁻¹ band related to the Se₈ ring [12]. Difficulties brought while recording the RS spectra of the In_{0.30}Se_{0.70} films with an ion argon laser suggest that the conditions are far away from any resonance. Nevertheless, the observed intensity redistribution in the spectra taken with various laser lines point out that some resonance enhancement occur. The disappearance of the 143 cm⁻¹ band in the low temperature spectra is attributed to temperature induced bond contractions. In fact, as the bonds shorten, the distances between atomic species are shortened too, so interactions become stronger and local fragments of the Se_n chains are expected to break down and form Se₈ ring molecules. This is consistent with the 143 cm⁻¹ band disappearance and the 125 cm⁻¹ mode related to Se₈ ring vibrations appearing.

5. Conclusions

The RS spectra of the $\text{In}_{0.30}\text{Se}_{0.70}$ amorphous films reveal mixed vibrational density of states and molecular-like character. The bands observed in the spectra at 143 and 125 cm^{-1} are attributed to Se_n polymer and Se_8 ring molecules, respectively. The structure of the $\text{In}_{0.30}\text{Se}_{2.0.70}$ film is composed of InSe_4 tetrahedral clusters interconnected by shared Se atoms or local Se_n polymer chains or Se_8 ring molecules. The disappearance of the 143 cm^{-1} band is attributed to the contraction of interatomic bonds and breaking of the Se chains and formation of Se_8 ring molecules. The background spreading beyond the threshold at about 250 cm^{-1} is attributed to the two-phonon RS.

References

- [1] J.H.C. Hogg, H.H. Sutherland, D.J. Williams, *Acta Crystallogr. B* **29**, 1590 (1973).
- [2] A. Likforman, D. Carré, J. Etienne, B. Bachet, *Acta Crystallogr. B* **31**, 1252 (1975).
- [3] A. Likforman, D. Caré, R. Hillet, *Acta Crystallogr. B* **34**, 1 (1978).
- [4] J.C. Bernède, A. Conan, A. Godoy, *J. Phys., Condens. Matter* **8**, 3439 (1996).
- [5] S. Marsillac, J.C. Bernède, A. Conan, *J. Mater. Sci.* **31**, 581 (1996).
- [6] M. Yudasaka, K. Nakanishi, *Thin Solid Films* **156**, 145 (1988).
- [7] J. Weszka, Ph. Daniel, A. Burian, A.M. Burian, A.T. Nguyen, *J. Non-Cryst. Solids* **265**, 98 (2000).
- [8] D. Marquardt, *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
- [9] C. Julien, A. Khelifa, N. Benramdane, J.P. Guesdon, *Mater. Sci. Eng. B* **27**, 53 (1994).
- [10] M.F. Thorpe, F.L. Galeneer, *Phys. Rev. B* **22**, 3078 (1980).
- [11] F.L. Galeneer, *Phys. Rev. B* **19**, 4292 (1979).
- [12] G. Lucovsky, in: *The Physics of Selenium and Tellurium*, Ed. W.C. Cooper, Pergamon, Oxford 1969, p. 269.