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Optical and structural properties of amorphous and heat treated $In_{0.4}Se_{0.6}$ film of different thicknesses

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The optical gap (E_g^{opt}) of as-deposited $In_{0.4}Se_{0.6}$ film is found to increase with the thickness of the film. The optical gap attains a steady value after several heat treatments of the films at elevated temperatures. The values of optical gaps of $In_{0.4}Se_{0.6}$ films are found to depend on the temperature of the heat treatment. The effect of thickness and temperature of heat treatment on the optical gap of the film is interpreted in terms of creation or elimination of defects in the amorphous structure of $In_{0.4}Se_{0.6}$ film. X-ray diffraction spectra are taken for both as-deposited and heat treated $In_{0.4}Se_{0.6}$ films. From the results related to the radial distribution functions of the specimens it is noted that in the case of $In_{0.4}Se_{0.6}$ a transition from amorphous to crystalline states takes place at 523 K and above. The results also show that both the optical gap and the coordination number decrease with increasing temperature of heat treatment. Therefore it is evident that the heat treatment improves the long range order of $In_{0.4}Se_{0.6}$ but reduces the coordination in the short range.

1. Introduction

The optical and structural properties of indium selenide as one of the III–VI layered compounds are of great interest because of its unique structural characteristics and promising technical applications [1]. We have presented some results on the optical properties of indium selenide of several compositions in some recent papers [2, 3]. It has been observed that the variation of compositions of indium selenide has an influence on the optical properties of the films produced from this binary compound. The change in the composition of this layered compound is expected to change the short range order exhibiting interesting characteristics in its physical properties relating short range order and defects or disorder. The optical absorption and the optical gap depend on the short range order in the amorphous structure and defects associated with it. The variation of the optical gap and the structural properties of indium selenide film with thickness and composition of the films deserves a comprehensive investigation. The effects of heat treatment of the indium selenide films of different compositions may exhibit some important features in terms of amorphous to crystalline transition. However, reports are not available about the above mentioned observations for indium selenide films. To get a clear idea about the trend in the variations of optical and structural properties with composition experiments have been done on a composition of $In_{0.4}Se_{0.6}$. The experimental observations made on the structural change of $In_{0.4}Se_{0.6}$ films under heat treatment and thickness variation with the help of radial distribution function (RDF) studies by X-rays are presented in this paper. The change incorporated in the binary composition of the material is expected to affect the structural and optical properties of the film produced from $In_{0.4}Se_{0.6}$. Observations are also made on the affects of heat treatment and thickness variation of the optical gap of a-$In_{0.4}Se_{0.6}$ films. The heat treatment changes the number of disorder and defects present in the amorphous structure [2, 3]. As a result, the optical gap (E_g^{opt}) is expected to increase due to diminution of disorder and defect in the structural bonding. The relation between the optical gap, the optical absorption coefficient (α) and the energy ($\hbar\omega$) of the incident photon is given by [3, 4]

$$(\hbar\omega\alpha)^{1/2} \propto (\hbar\omega - E_g^{opt}) \quad (1)$$

Therefore the mechanism of disorder and defect interaction in amorphous chalcogenide is expected to be understood from the studies of the variation of the optical gap and the short range order as a function of thickness, heat treatment at different temperature for indium selenide film of different compositions.

The structure of an amorphous solid is specified by the short range order and the most important aspects of which are the nearest-neighbour distance and the coordination number. Fourier inversion of X-ray diffraction intensities yield a RDF from which nearest neighbour distance and coordination number are

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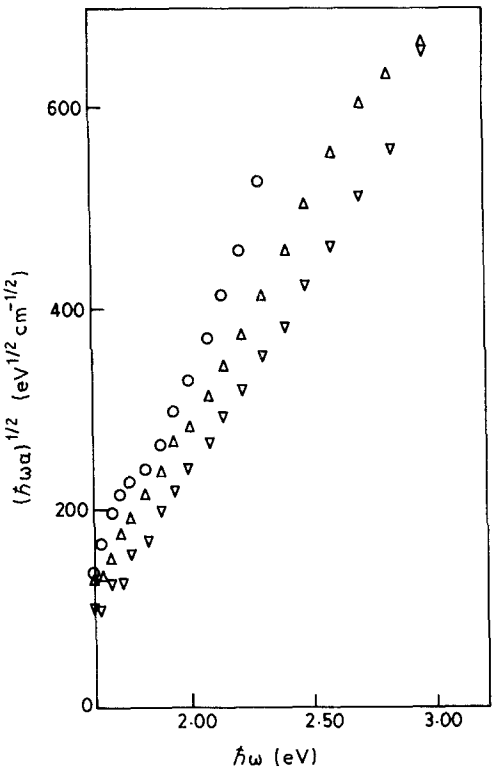

Figure 1 $(\hbar\omega\alpha)^{1/2}$ as a function of photon energy $\hbar\omega$ for a-$In_{0.4}Se_{0.6}$ films at different thicknesses. (○ 465.8 nm, △ 292.4 nm, ▽ 244.3 nm)

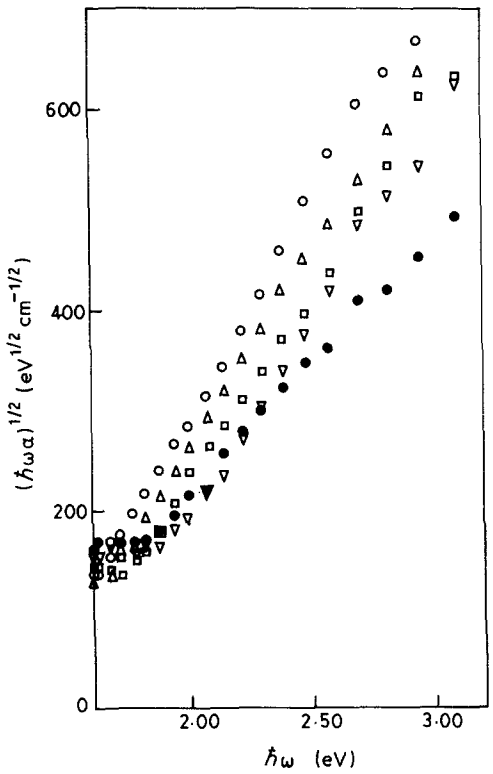

Figure 3 As Fig. 2 for 292.4 nm thick film.

obtained. The optical properties are connected with the short range features of amorphous solids.

2. Experiment and results

2.1. Film preparation and characterization

The bulk samples of $In_{0.4}Se_{0.6}$ were prepared by heating the mixture of indium and selenium in the required proportions in an evaluated ($\sim 5 \times 10^{-6}$ torr) glass capsule. The temperature of the system was raised stepwise to minimize the risk of explosion and ensure complete reaction of the elements to form a binary compound. In the first stage the capsule was heated at 513 K for 2 h and then at 653 K for a further 4 h, and finally at 823 K for 14 h. During heating the capsule was gently rocked. The capsule was quenched to room temperature. A lump of bulk amorphous $In_{0.4}Se_{0.6}$ was thus produced. From the bulk sample of $In_{0.4}Se_{0.6}$, amorphous indium selenide films of different thicknesses were obtained on clean thin glass substrates under a pressure of 10^{-6} torr (Edwards Speedivac). During deposition the substrates were kept at 300 K. The thickness of the film was determined by weighing. Diffuse halos characterizing the amorphous nature of the film materials were observed by X-ray diffraction pattern. The In : Se ratio of the film was determined by atomic absorption spectrometry and was found to be 39.9 : 59.9. This indicates that the stoichiometry of the deposited films remains almost the same as that of the starting material.

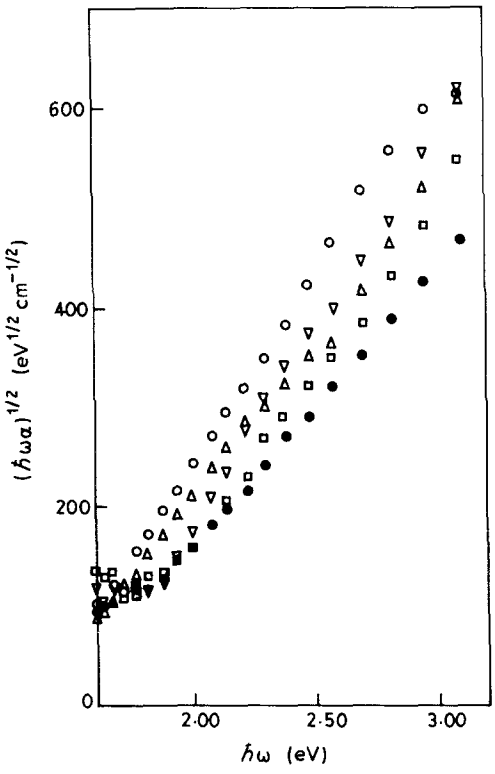

Figure 2 $(\hbar\omega\alpha)^{1/2}$ as a function of photon energy $\hbar\omega$ for $In_{0.4}Se_{0.6}$ film of thickness 244.3 nm heat treated at different temperatures (○ 300 K, △ 373 K, ▽ 423 K, □ 523 K, ● 623 K)

2.2. Optical absorption and optical gap

The optical absorption coefficient (α) of as-deposited amorphous 244.3, 292.4 and 465.8 nm thick $In_{0.4}Se_{0.6}$ films were measured using an SPM2, Carl Zeiss spectro-photometer in the spectral range of 1.2 to 3.6 eV photon energy. Samples of $In_{0.4}Se_{0.6}$ films were heat treated in air at 373, 423, 523 and 623 K. The heat treatment was carried out for 15 min in each case and the samples were quenched to room temperature. The intensity of the transmitted light through the heat treated films was measured. The heat treatment of $In_{0.4}Se_{0.6}$ films was repeated several times until the intensity of the transmitted light through the specimen became steady thus indicating the stability of the

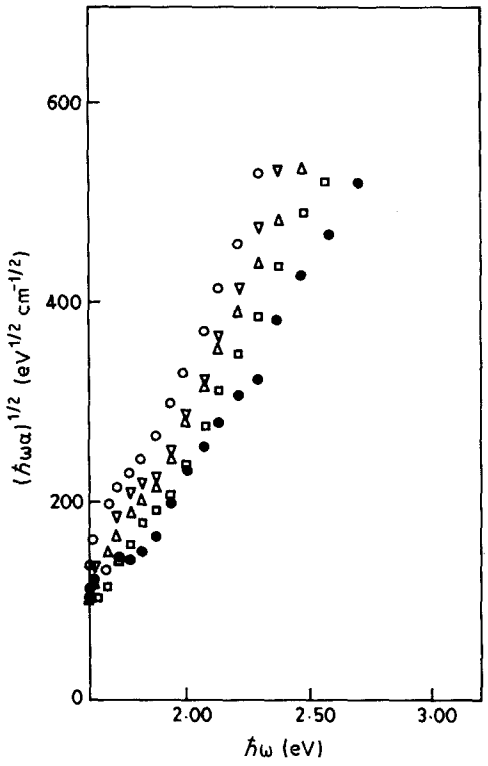

Figure 4 As Fig. 2 for 465.8 nm thick film.

structure of the film. Heat treatment below 373 K did not show any change in the absorption of light through the specimen. The optical absorption coefficient ($\alpha = t^{-1} \log_e(I_0/I)$) of as-deposited $In_{0.4}Se_{0.6}$ films of different thicknesses were measured. The quantity $(\hbar\omega\alpha)^{1/2}$ as a function of energy of the incident photon was calculated for as-deposited $In_{0.4}Se_{0.6}$ films and is shown in Fig. 1. Measurements of the absorption coefficient were made as a function of heat treatment at different temperatures for 244.3, 292.4 and 465.8 nm thick $In_{0.4}Se_{0.6}$ films. The quantity $(\hbar\omega\alpha)^{1/2}$ is plotted for 244.3, 292.4 and 465.8 nm thick $In_{0.4}Se_{0.6}$ films heat treated at different temperature in Figs 2, 3 and 4 respectively. The nature of the curves in Figs 1 to 4 are found to be identical with those of elemental amorphous semiconductors. From the linear parts of the absorption curves the values of E_g^{opt}

TABLE I The values of the optical gap as a function of temperature of heat treatment and thickness of a-$In_{0.4}Se_{0.6}$ films

Thickness (t) of a-$In_{0.4}Se_{0.6}$ films (nm)	Value of E_g^{opt} in eV heat treated at				
	300 K	373 K	423 K	523 K	623 K
244.3	1.35	1.31	1.51	1.48	1.40
292.4	1.38	1.33	1.47	1.32	1.19
465.8	1.44	1.37	1.42	1.44	1.44

are determined by using the least square method and are presented in Table I. The observed values of E_g^{opt} for $In_{0.4}Se_{0.6}$ films are in agreement with the order of the results obtained for InSe samples by others [3, 5, 6]. From Figs 2–4 it can be seen that the absorption of light by the specimen depends on the temperature of heat treatment.

2.3. Radial distribution function by X-rays

The X-ray diffraction intensities (I_s) for the as-deposited and heat treated $In_{0.4}Se_{0.6}$ films of different thicknesses were recorded in the region from 5 to 60° ($= 2\theta$) until the intensity became small and uniform. The experiment was done with the help of a Philips X-ray diffractometer (PW 1730/PW 1710) using nickel filtered CuK_α radiation operated at 40 KV and 20 mA. In order to obtain the actual intensities scattered by the material of the film a recording was also taken of the intensities (I_o) diffracted from a similar glass substrate. Figs 5–7 show XRD curves of as-deposited and heat treated $In_{0.4}Se_{0.6}$ films of different thickness. Some sharp peaks are observed in the XRD curves for $In_{0.4}Se_{0.6}$ film of thickness 244.3 nm heat treated at 523 K (curve b in Fig. 5) and 623 K (curve c in Fig. 5). The heat treatment below 523 K did not show any sharp peaks in the XRD spectrum. The observed peaks are superimposed on a very broad maximum showing the existence of two sets of diffraction patterns. Similar peaks are also observed in the XRD curves for 292.4 nm thick $In_{0.4}Se_{0.6}$ film 292.4 nm heat treated at 623 K (curve c in Fig. 6) and for $In_{0.4}Se_{0.6}$ film of thickness 465.8 nm heat treated at 523 K (curve b in Fig. 7). The diffraction of X-rays from amorphous $In_{0.4}Se_{0.6}$ causes the broad maximum in these curves and the sharp peaks are due to diffraction from

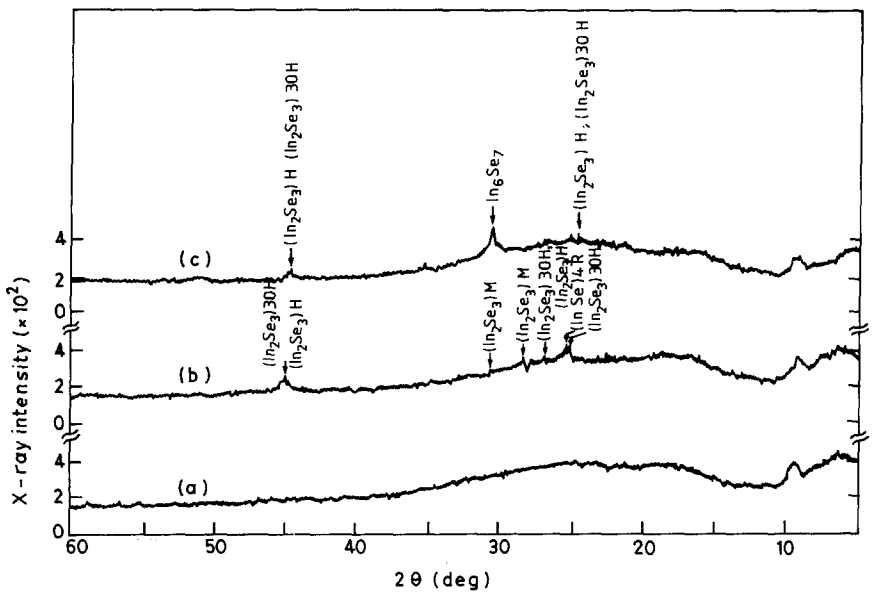

Figure 5 X-ray diffraction (XRD) spectra of $In_{0.4}Se_{0.6}$ films of thickness 244.3 nm 'a' is for as-deposited and 'b', 'c' are for heat treated samples at 523 and 623 K respectively.

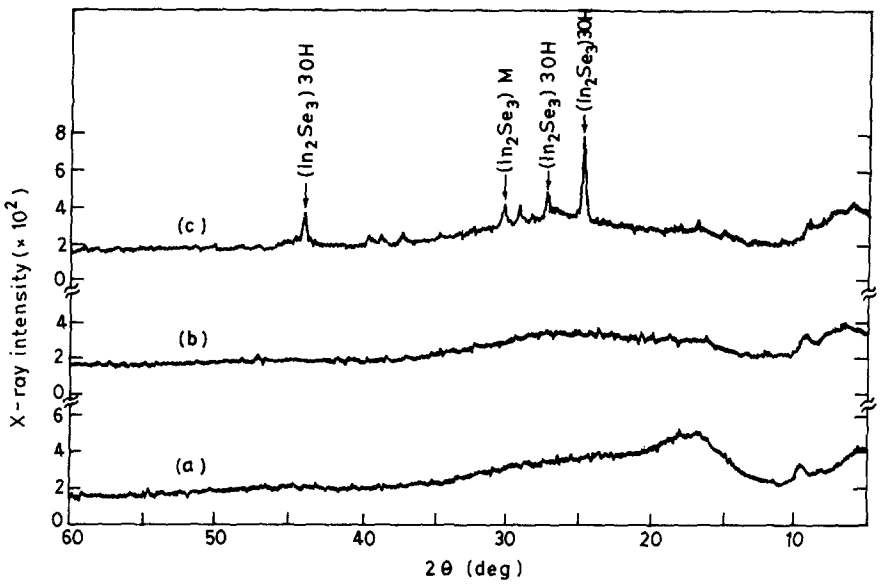

Figure 6 As Fig. 5 per 292.4 nm thick film.

crystals produced by annealing. The important peaks in each curve have been identified by the usual technique [7, 8].

The radial distribution (RDF) is computed from X-ray diffraction spectra (Figs 5–7). The detail of the procedure has been described by several authors [9, 10]. The X-ray intensities I_s (Figs 5–7) were corrected [11] for glass substrate scattering (I_o) and for absorption in the films using the relation

$$I_f = I_s - I_o \exp(-2\mu t/\sin\theta)$$

where t is the thickness and μ is the linear absorption coefficient of the material of the film. This expression was further corrected for polarization (p) and absorption (A_f) for X-ray in the film as

$$I_{fc} = I_f p^{-1} A_f^{-1}$$

where

$$p = \frac{1 + \cos^2 2\theta}{2}$$

and

$$A_f = \frac{1}{2\mu}[1 - \exp(-2\mu t/\sin\theta]$$

The independent scattering (Σf^2) curves of $In_{0.4}Se_{0.6}$ were obtained by using the tabulated values of atomic scattering factors of indium and selenium [12]. The corrected intensities I_{fc} in an arbitrary unit were then brought to the absolute scale (e.u.) I_{obs} by matching Σf^2 following the high angle method [13]. The RDF has been calculated from the corrected intensities (e.u.) according to the equation

$$4\pi r^2 \varrho(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi}\int_0^\infty ki(k)\sin kr dk$$

where $i(k) = (I_{obs} - \Sigma f^2)/\Sigma f^2$, ϱ_0 = average atomic density, (atom/nm³) and $k = (4\pi \sin\theta)/\lambda$. RDF $4\pi r^2\varrho(r)$ is the most probable number of atoms within the volume of the sphere lying between r and $r + dr$ from the centre of the atom. In computing the RDF $4\pi r^2\varrho(r)$, a suitable damping factor 0.01 is used to weight down the inaccurate part of the $ki(k)$ curve [9]. The obtained RDF curves are shown in Figs 8–10. The RDFs of as-deposited $In_{0.4}Se_{0.6}$ films of the different thicknesses (244.3, 292.4 and 465.8 nm) under investigation are found to be nearly identical in nature indicating no long range order in the amorphous films.

A small peak at $r = 0.07$ nm observed in RDF (Figs 8–10) is considered to be spurious as no legitimate peak can occur from r smaller than the sum of the smallest pair of atomic radii involved. The area under the first proper peak representing the number of nearest neighbours has been calculated by considering the right-hand side of the first peak to be symmetrical to the left-hand side. This method minimizes the contribution from atoms in other coordination shells [14].

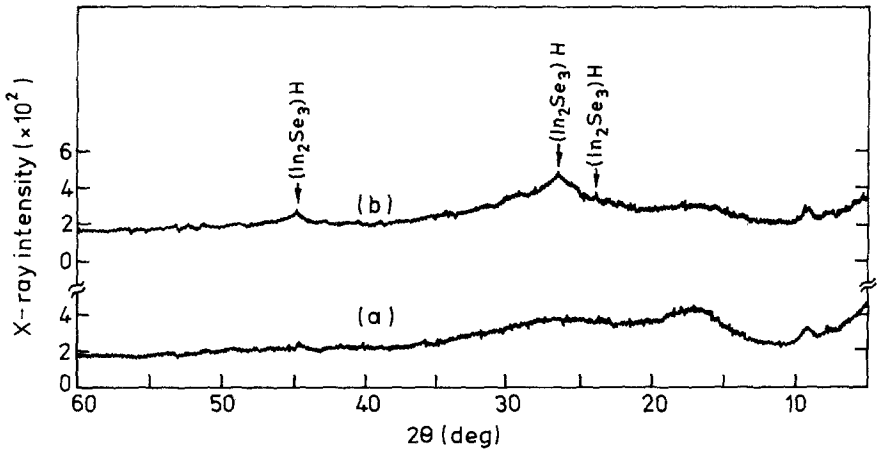

Figure 7 As Fig. 5 for 465.8 nm thick film.

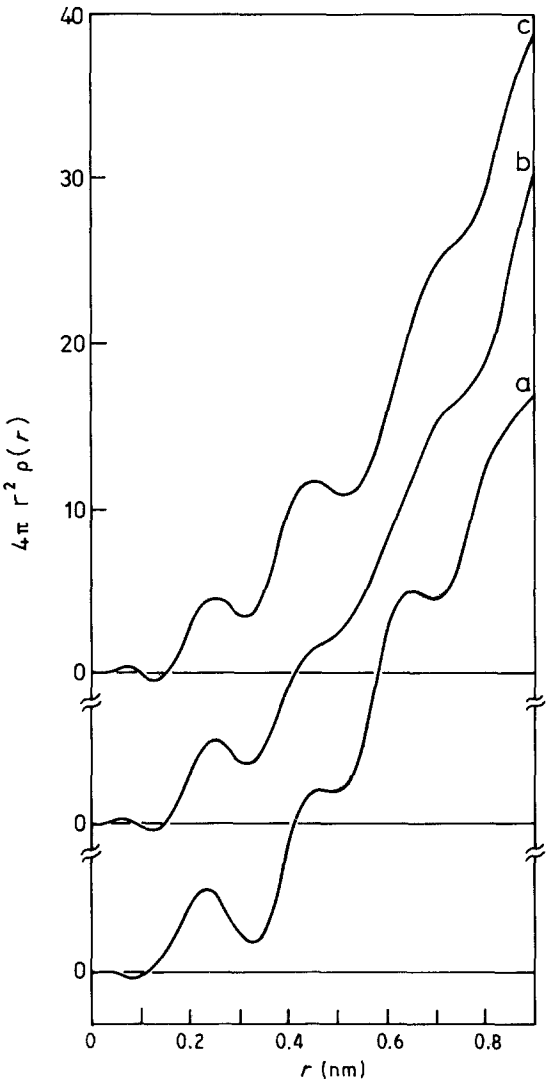

Figure 8 The radial distribution function, $4\pi r^2 \varrho(r)$ of $In_{0.4}Se_{0.6}$ films of thickness 292.4 nm. 'a' is for as-deposited, 'b', 'c' are for heat treated samples at 523 and 623 K respectively.

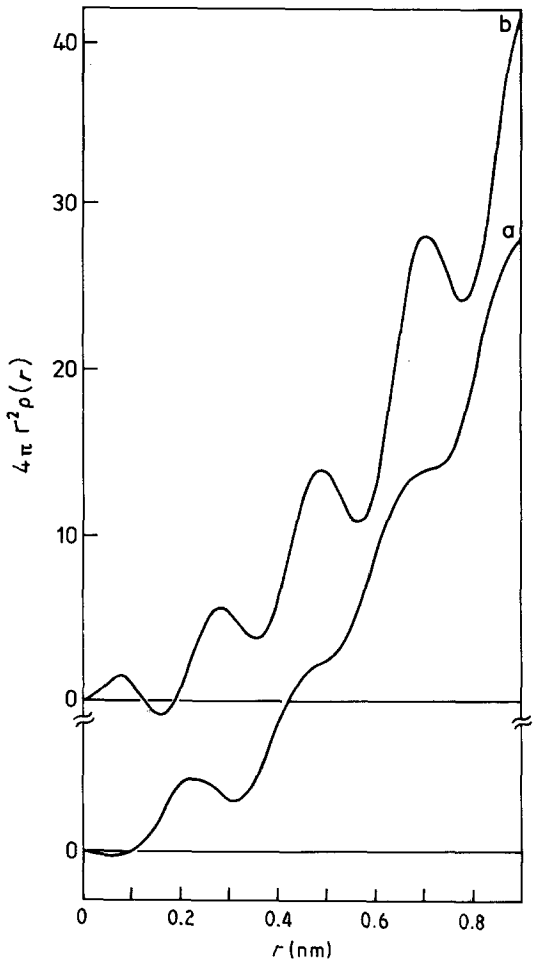

Figure 9 As Fig. 8 for 244.3 nm thick film.

The positions of peaks in RDF and the area under the first peak of as-deposited and heat treated 292.4 nm thick $In_{0.4}Se_{0.6}$ film are presented in Table II. The positions of peaks in RDF and the area under the first peak of heat treated 244.3 and 245.8 nm $In_{0.4}Se_{0.6}$ films are presented in Table III.

3. Discussion

It is seen from Table I that the optical gap increases with the increasing thickness of a-$In_{0.4}Se_{0.6}$ films. It has already been explained that unsaturated bonds are produced as a result of an insufficient number of atoms deposited in the amorphous films [15]. These bonds are responsible for the formation of some defects in the film which produce localized states in the band gap of amorphous solids. In the case of thicker films greater deposition builds up a more homogeneous network minimizing the number of defects and the localized states thereby increasing the optical gap. It may further be noted that the absorption curves in the case of thicker film have greater steepness indicating a reduction in the number of disorders.

In Table I, it may also be observed that there is a small decrease in the value of the optical gap of $In_{0.4}Se_{0.6}$ films of different thicknesses heat treated at 373 K. This decrease in the optical gap may be due to creation of defects [16] in the amorphous structure of $In_{0.4}Se_{0.6}$ films as a result of heat treatment at 373 K. Further heat treatment at higher temperature (423 K) eliminates these defects [16] thereby increasing the optical gap of $In_{0.4}Se_{0.6}$ films (Table I). However, the heat treatment of $In_{0.4}Se_{0.6}$ films at still higher temperatures (523 and 623 K) again reduces the optical gap of the films of thickness 244.3 and 292.4 nm whereas the optical gap of comparatively thicker film (465.8 nm) remains more or less unchanged.

X-ray diffraction studies were carried out in order to get an idea about the structural changes produced in $In_{0.4}Se_{0.6}$ film due to heat treatment at different elevated temperatures. A broad maximum is observed in the XRD spectra ('a' in Figs 5–7) of as-deposited $In_{0.4}Se_{0.6}$ films of different thicknesses. The grain sizes of the as-deposited films of different thicknesses are small [17] and the disorder within those grains being so high that no specific diffraction peak could be produced. Hence it is evident that the structure of the as-deposited $In_{0.4}Se_{0.6}$ films are non-crystalline irrespective of thickness of the films.

In the XRD spectra ('b' in Fig. 5 and in Fig. 7), sharp peaks are observed superimposed on a broad maximum for $In_{0.4}Se_{0.6}$ films annealed at 523 K, signifying the existence of two sets of diffraction patterns. The sharp peaks superimposed on a broad maximum are also observed in the XRD spectrum denoted by 'c' in Fig. 5 and Fig. 6 for the $In_{0.4}Se_{0.6}$ samples.

TABLE II Positions of peaks in RDF and area under the first peak of as-deposited and heat treated $In_{0.4}Se_{0.6}$ films of thickness 292.4 nm

Temperature of heat treatment (K)	Interatomic distances (nm) from a central atom			Area under the first peak
	First	Second	Third	
as-deposited	0.240	0.450	6.50	6.60
523	0.250	0.440	7.00	5.85
623	0.250	0.450	6.90	4.89

The broad maximum is caused by diffraction from amorphous $In_{0.4}Se_{0.6}$, and the sharp peaks are due to crystalline indium selenides produced as a result of heat treatment. As seen earlier $In_{0.4}Se_{0.6}$ films undergo amorphous to crystalline transition as a result of heat treatment made at and above 523 K. It may be noted that as a result of transition of a–$In_{0.4}Se_{0.6}$ films due to heat treatment at 523 and 623 K, In_2Se_3 along with some InSe and In_6Se_7 crystallites are produced. The In_2Se_3 crystallites are found to have monoclinic and hexagonal structures.

The RDF of as-deposited $In_{0.4}Se_{0.6}$ film of different thicknesses exhibit a prominant peak and a few small peaks indicating the existence of only the short range order in the specimen [18, 19]. The RDF of as-deposited $In_{0.4}Se_{0.6}$ film of thickness 292.4 nm is shown in Fig. 8 (curve 'a'). The RDFs of as-deposited film of other thicknesses are not shown. In the RDF of $In_{0.4}Se_{0.6}$ film of thickness 292.4 nm heat treated at 523 K (curve 'b' in Fig. 8), the sharpness of the peaks is found to be reduced but the sharpness of the peaks is enhanced when heat treated at 623 K (curve 'c' in Fig. 8). The behaviour of the peaks in the RDF of $In_{0.4}Se_{0.6}$ film of thickness 244.3 nm heat treated at 623 K (curve 'b' in Fig. 9) and 465.8 nm heat treated at 523 K (curve in Fig. 10) may also be noted. Therefore it may be assumed that there is no long range order in $In_{0.4}Se_{0.6}$ films heat treated at 523 K. However, due to heat treatment of $In_{0.4}Se_{0.6}$ film at 623 K an improvement in the long range periodic rearrangement of atoms is reached. This is because of the increase in the sharpness of the peaks in RDF may be attributed [20, 21] to the better long range periodic order of arrangement of atoms in solids, which is supported by the XRD spectra of as-deposited and heat treated $In_{0.4}Se_{0.6}$ films. Therefore it indicates that an amorphous $In_{0.4}Se_{0.6}$ has partly undergone a transition to crystalline states as a result of heat treatment at 523 K and above.

The position (r_i) of the maxima of the peaks in RDF are given in Tables II and III. The positions of the first proper peaks of RDF for the as-deposited samples of

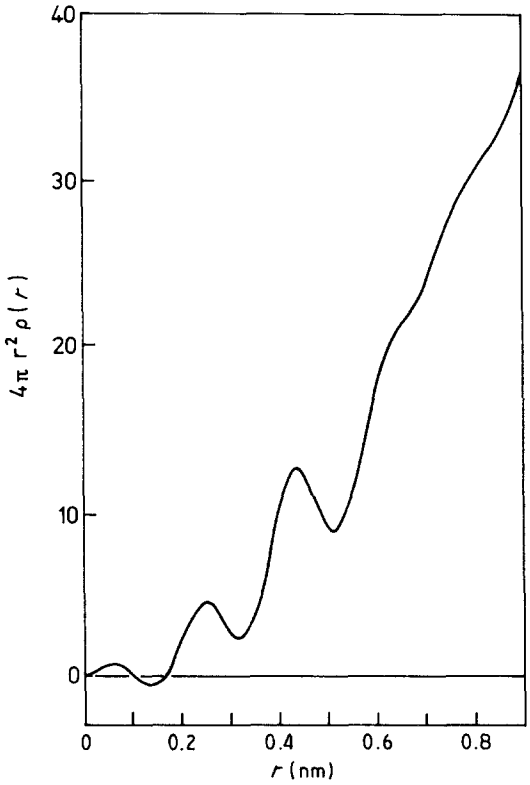

Figure 10 The radial distribution function, $4\pi r^2 \varrho(r)$ of $In_{0.4}Se_{0.6}$ film of thickness 465.8 nm heat treated at 523 K.

$In_{0.4}Se_{0.6}$ give the In–Se nearer neighbour separation. The slightly lower value of separation between the nearest neighbours [22, 23] may be due to presence of double bonded selenium atoms of radius 0.107 nm in amorphous $In_{0.4}Se_{0.6}$ films [24].

The RDF of the films of different thicknesses became different when the films are heat treated at 523 and 623 K as may be observed in Figs 8–10 and Tables II and III. Hence, the long range order achieved by heat treatment varies with the thickness of $In_{0.4}Se_{0.6}$ films. It can be observed from Tables I, II and III that both the optical gap and the coordination number of a $In_{0.4}Se_{0.6}$ film of thicknesses 244.3 and 292.4 nm decrease with increasing temperature of heat treatment from 523 to 623 K. Therefore it is evident that the heat treatment improves the long range order of a-$In_{0.4}Se_{0.6}$ but reduces the coordination in the short range order.

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TABLE III Positions of peaks in RDF and the area under the first peak of heat treated $In_{0.4}Se_{0.6}$ films of thickness 244.3 and 465.8 nm

Thickness of $In_{0.4}Se_{0.6}$ films (nm)	Temperature of heat treatment (K)	Interatomic distance (nm) from a central atom			Area under the first peak
		First	Second	Third	
244.3	523	0.240	0.450	0.650	5.88
	623	0.280	0.490	0.710	5.73
465.8	523	0.250	0.440	0.640	4.50

Jadavpur University for the use of the X-ray diffractometer and Dr R. N. Joardar for helps regarding computer calculations.

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