Temperature Induced Phase Change In Indium Selenide Thin Films Prepared By Thermal Evaporation Technique

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Abstract: ***In_2Se_3 thin films have been deposited by thermal evaporation method on glass substrates with a thickness of 300 nm. The films were annealed at different temperatures between 150°C and 350°C. X - ray diffraction revealed that as deposited films exhibits amorphous nature while annealing led to evaluation of crystalline phase. Which effects phase changes of amorphous to β - In_3Se_2 and on furtherannealing makes β - In_3Se_2 to γ - In_3Se_2. The direct band gap of as deposited and annealed films were found between 2.66 eV and 2.89 eV. PL emission occurs in the near ultraviolet (UV) and UV visible region.***

Keywords: Phase change, Indium Selenide, thin films, amorphous, thermal evaporation.

1. Introduction

In the last few years, much attraction has been focused on the III-VI group chalcogenide materials due to their enormous potential applications in solid state devices. Indium Selenide is a one of the most important semiconductors in III – VI group chalcogenides. In_2Se_3 thin films are widely used in Diode [1], photo electrochemical [2], Solar cells application [3] and particularly growing need for non – volatile memory devices like a Phase change random access memory (PRAM) [4]. It could play vital role in reversible phase change to store information. The materials changeits phase between amorphous and crystalline nature by applying temperature. This paper reports phase change properties of indium selenide thin films as a function of temperature.

2. Experimental Details

Thermally evaporated In_2Se_3 thin films were prepared on ultrasonically cleaned soda lime glass substrates at room temperature. In_3Se_2 (sigma Aldrich – 99.99% metal basis) compound were used as a source material. In_3Se_2 compounds were evaporated from Molybdenum boat (200A) under the vacuum pressure between 10^{-5} - 10^{-6}torr. The thicknesses of the films were fixed as 300 nm and controlled using *in-suit* quartz crystal thickness monitor. A constant evaporation rate ranging 1-3 A°/sec was maintained throughout the experiment. Films were annealed under open air atmosphere with the temperatures between 150°C - 350°C for about 30 minutes. X-ray diffraction studies of both as deposited and annealed films were carried out using Shimadzu XRD-6000 X-ray Diffractometer. Here the films were exposed to Cu Kα source and the scattering angles were varied from 0-90◦. The optical studies of the films were analyzed using UV-VIS-NIR spectrophotometer (Jasco-570 UV/VIS/ NIR Spectrophotometer) in the range of 200 to 2500 nm. Photoluminescence (PL) emission were studied by using Spectroflurometer (JASCO FP – 8200) recorded rangesfrom 200 to 900 nm with the excitation wavelength of 350 nm.

3. Structural Studies

The X-ray diffraction (XRD) studies were carried, to find the effect of annealing on the crystalline phase evaluation of In_2Se_3 thin films.

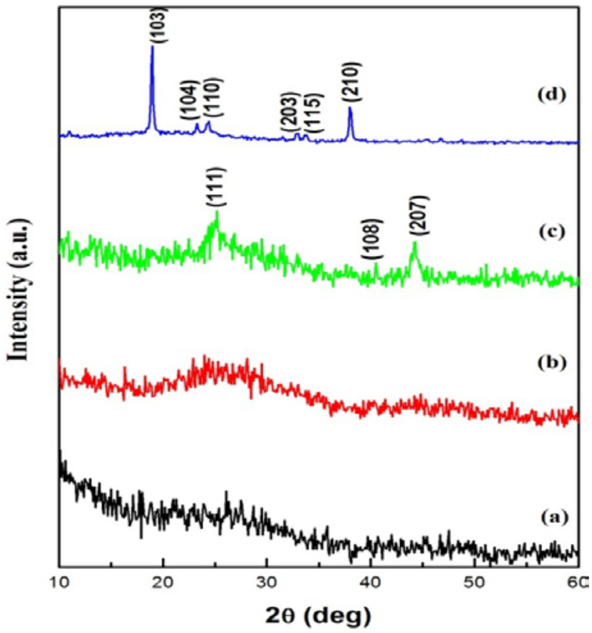

Figure 1: XRD pattern of In_3Se_2 films (a) as deposited, (b) 150˚C, (c) 250˚C and (d) 350˚C.

Fig.1a shows that as deposited In_3Se_2 film exhibits amorphous crystalline nature. There is no significant change upon annealing at 150˚ C. Annealing at same condition led to γ-In_2Se_3 and In_6Se_7 reported by chemical bath deposition method [5]. Different preparation condition and possible to

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re-orientation of grains, retain the amorphous crystalline nature at 150°C. Annealing at 250° improves crystallinity of film and planes were grown along (110), (206) and (207). The recorded peak were compared with JCPDS (Card No: 65-6915) which confirm evaluation of β - In_3Se_2 with hexagonal crystal structure. Further annealing at 350° C leads to well resolved crystalline peaks with (110), (201), (202) and(300) planes. These peaks are associated with γ - In_3Se_2 with hexagonal structure confirm from standard JCPDS (Card No: 89-0658) High temperature enhances crystalline quality and phase change occurs. The film was transformed from amorphous to β - In_3Se_2 for 250^0 C and β - In_3Se_2 to γ - In_3Se_2 for 350^o C. Similar phase changes were reported by Chemical bath deposition method [5] .The grain size of crystalline size of the films was calculated from Debye's equation (1).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

A. The calculated average grain size is 53 and 25 nm for annealed at 250°C, 350°C respectively.

B. Optical Studies

The values of the estimated energy gap for amorphous films are greater than that of obtained crystalline films, because in the polycrystalline material the electron transition is from band to band. But in amorphous materials the electron transitions occurs from extended states in the valance band to the localized states at the conduction band edge. The energy band gap values were found to be decrease with increase in annealing temperature. The decrease in optical energy band gap may be due to the formation of β - In_2Se_3 phase. It is observed that further annealing led to increase the band gap 2.66 eV to 2.84eV. This is due to smaller grain size and phase formation of γ- In_2Se_3. This phase transformation clearly confirmed from XRD results and the band gap value of β - In_2Se_3 andγ- In_2Se_3 relatively wider than reported results [6].

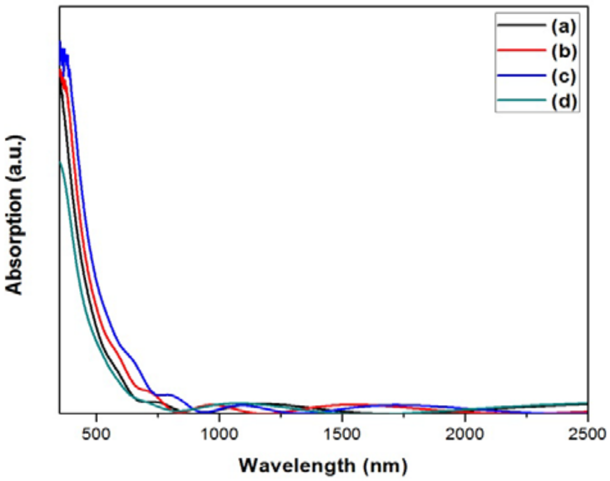

Figure 2: Optical absorption spectra of In3Se2 films (a) as deposited, (b) 150°C, (c) 250°C and (d) 350°C

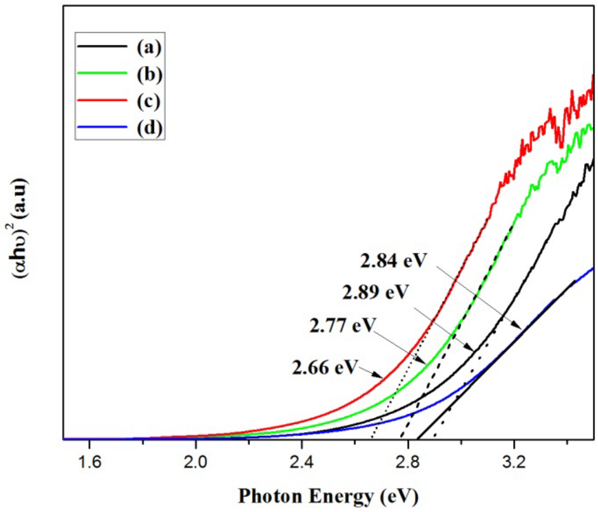

Figure 3: optical band gapof In_3Se_2 films (a) as deposited, (b) 150°C, (c) 250°C and (d) 350°C.

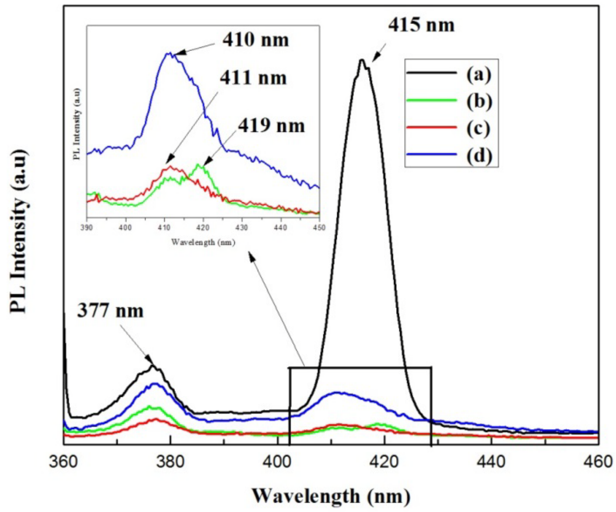

Figure 4: PL emission spectra of In_3Se_2 films (a) as deposited, (b) 150°C, (c) 250°C and (d) 350°C.

Fig. 4 shows room temperature PL spectra of as deposited and annealed Indium Selenide thin films. The films were excited at 350 nm and PL emission occurs in the near ultraviolet (UV) and UV visible region. Well defined two emission peaks were observed from the PL spectra, one emission was ultra violet (377 nm) for all the films which centered at 377 nm and another one is violet emission centered at 415, 419, 411 and 410 nm respectively for as deposited and annealed samples. It was observed that the PL intensity decreases for the annealed films. For 150°C annealed films slightly red shifted (inset graph) compared to amorphous film, which may be due to re – orientation of grain. Change in intensity is associated with phase change in Indium Selenide thin films as observed in XRD pattern.

4. Conclusion

Indium Selenide thin films were prepared by thermal evaporation techniques on the glass substrate and annealed at various temperatures between 150°c and 350°C. The XRD pattern revealed that as deposited film has amorphous nature.

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Thermal annealing enhanced the crystallinity and it exhibits β - In_3Se_2 and γ - In_3Se_2 with hexgonal crystal structure for 250˚C, 350˚C, respectively. The calculated direct band gap of as deposited and annealed films were found between 2.66 eV and 2.89 eV. The change in optical band gap values of the films could be associated with change in crystallographic phase formation of β - In_2Se_3 (decrease in band gap) γ- In_2Se_3 (increase in band gap). It was observed that the PL intensity decreases for the annealed films. For 150˚C annealed films slightly red shifted compared to amorphous film, which is due to re - orientation of grain. Impact of annealing on the phase change also reflected in PL intensity of the films.

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