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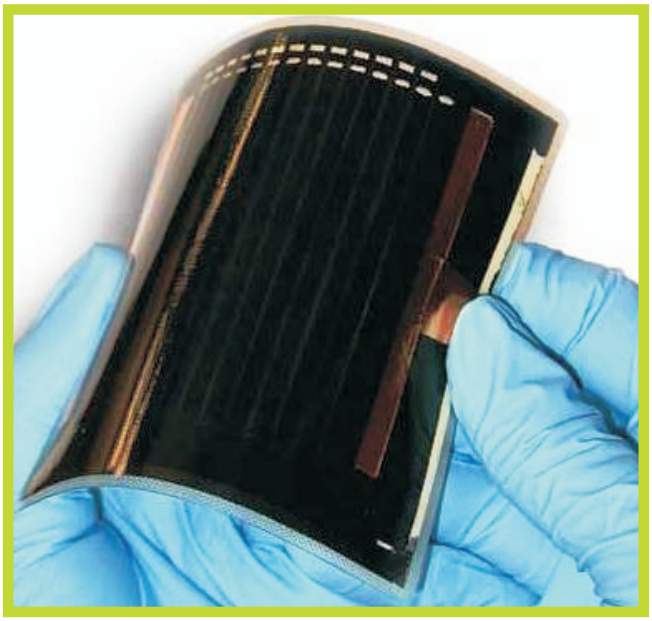
SYNTHESIS, STRUCTURAL AND OPTOELECTRICAL PROPERTIES OF INDIUM SELENIDE THIN FILM BY USING ELECTRO DEPOSITION TECHNIQUE



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Abstract :

In2Se3 thin films have been deposited onto stainless steel and fluorine doped tin oxide (FTO) coated glass substrates from an aqueous acidic medium by using electrodeposition techniques. Various preparative conditions of thin film deposition are outlined. The thin films were found to be uniform, well adherent and brown in color. The films were characterized using X-ray diffraction (XRD), scanning electron microscopy. The XRD analysis of the films shows the presence of polycrystalline nature with hexagonal crystal structure. SEM study reveals that the grains are homogenous, without cracks or pinholes and well covers the stainless still strips. The optical absorption and electrical conductivity was measured. The direct optical band gap value for the films was found to be 0.8 eV at room temperature and have specific electrical conductivity as 10-2 (Ohm) showing n-type conduction mechanism.

Key Words:- A. Electrochemical synthesis; B. Semiconductor, C. SEM and D. XRD

INTRODUCTION

The potential application of In^2Se^3 as absorber material in photovoltaic cells has resulted in a strong interest in the study of In2Se3 thin films of high crystalline quality and suitable optical and electrical properties [1–2]. It is well known that the structural, electrical and optical properties of the material, and thus the corresponding device performance, are highly dependent on growth conditions as well as on heat treatment. In2Se3 films have been successfully synthesized by numbers of physical and chemical vapour deposition processes for several years [3-5]. The study of layer compounds i.e., GaSe, GaTe, and InSe has experienced great developments in recent years. Their lamellar structure is the result of strong covalent bonding inside the successive four-fold atomic planes while the layers are bound together by much weaker forces, generally believed to be of van der Waals type [6-7]. Investigation of InSe thin films is attracting attention because of its practical application as a photovoltaic material [8-9].

The electrical, optical, and structural properties of InSe films show strong dependence on the film deposition technique, conditions, and the post-depositional annealing. The present study deals with an experimental investigation of the influences of substrate and annealing temperatures. On the structural and optical properties of InSe thin films grown by the thermal evaporation technique. The methods used were investigated by using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and transmission measurements InSe, is a semiconducting compound of the $A^{II}IB^{VI}$ family, the structures of which are defective[10]with respect to their metal atoms: only two thirds of the sites in the cation sub lattice are occupied. Semiconductors with such characteristics are suitable for sensor of small particles and they could be used in the manufacture of detectors of ionizing radiatior [11-16]. Moreover, InzSe3 has been shown to be a material with attractive properties for applications in electrochemical devices such as solid solution electrodes. The structure of In^2Se^3, thin films has been investigated by various authors [17] using different techniques and some discrepancies are obvious among the published results.

In this paper, we present a study of structural, optical and electrical properties of In2Se3, thin films prepared by electro deposition technique.

2. Experimental

2.1 Substrate cleaning:

The substrates were cleaned by boiling them in chromic acid for 1 hr which was followed by washing successively with detergent and alcohol. They were finally stored in double distilled water before use.

2.2 Preparation of the Solutions:

All the chemicals used for the deposition were of AR grade. All the solutions were prepared in double distilled water. The chemicals used were

1) Indium (III) Nitrate hydrate
2) Selenium powder, S. D. fine chem. Ltd. Boisar, Mumbai
3) Oxalic Acid
4) Anhydrous Sodium sulphite

The moderately stable source of selenium ion, sodium selenosulphate was prepared by following the method reported earlier. It was prepared by refluxing 5g grey selenium powder with 12g anhydrous sodium sulphite in 200 mL distilled water for 9 hours at 363 K. The resulting solution was filtered through Whatman filter paper No. 1 and stored in air tight container. The concentration of resulting solution was 0.25 M.

2.3 Deposition of the In2Se3 Thin Film:

To deposit, the In2Se3 thin film,the ingredients were used Indium nitrate, Oxalic acid, and sodium selenosulphate. In actual experimentation, 10 mL Indium nitrate (0.01M) solution was taken in 100 mL beaker. Maintain pH up to 2.2 by adding Oxalic acid (1M) and 10 mL sodium selenosulphate (0.25M) was added in the reaction bath at room temperature. The conducting material like stainless steel strips were mounted vertically on a specially designed substrate holder and supply the fixed Voltage is 0.8 eV (const.) for 40 min. After 50 min, the slides were removed, washed several times with double distilled water, dried naturally, preserved in a dark dessicator over anhydrous $CaCl^2$.

3. Characterization of In2Se3 thin films

The X-ray diffraction (XRD) study of In^2Se^3 film was carried out in the range of the diffraction angle 10º–80º with Cu Ka1 radiation using Philips PW-1710 diffractometer (λ=1.54056A˚). The layer thickness of the film was

estimated by the weight difference method. The electrical conductivity of In2Se3 thin film was measured using a 'dc' two-probe method. A quick drying silver paste was applied at the ends of the film for good ohmic contacts. For the measurements of conductivity, a constant voltage of 30V was applied across the sample. The current was noted at different temperatures. Maintaining a temperature gradient along the length of a film performed thermoelectric power measurements was made. The potential difference between the two points of contact separated by 1 cm was recorded with a digital microvoltmeter. A calibrated thermocouple (chromel–alumel, 24 gauge) with a digital indicator was used to sense the working temperature. The optical absorption measurements were made in the wavelength range 400–1000 nm by using a Shimadzu UV-3600 (Japan) UV–VIS–NIR double beam spectrophotometer at room temperature. An identical, uncoated glass substrate in the reference beam made a substrate absorption correction. The analysis of the spectrum was carried out by computing the values of absorption at every step of 2 nm. A JEOL-JSM 6360 scanning electron microscope (SEM) was used for the microscopic observations. Compositional analysis was done with EDAX.

4. Results and discussions

Fig.1 shows the voltammogram of In2Se3 taken at scan rate of 40 mV/s from 0 to −0.65 V cathodes with reversal to 0 V followed by the anodic sweep up to +0.65 V and then back to zero. During the cathodic scan, a sudden decrease in current occurred in the potential range of −0.30 to −0.45 V and a peak was observed at a potential of about −0.4 V. On decreasing potential further a plateau region is observed between potential ranges of − 0.4 to 0.6, during which a decrease in potential does not alter current appreciably. A sharp decrease in current on further reduction in potential to about −0.52 V (SCE) corresponds to deposition of In^2Se^3. The anodic back sweep resulted in Indium stripping and initiation of a reaction opposite to Se reduction.

Optimization of preparative parameters for deposition of good quality stoichiometric In^2Se^3 thin films is most essential. The Fig.2 shows the variation of Isc and Voc with deposition time. From the graph it is observed that Isc and Voc increases with increase in deposition time, attains maximum values for film deposited at 50 minutes and further increase in deposition time both Isc and Voc decrease this indicates that the formation of good quality and almost stoichiometric compound at 50 minutes. The lower values of Isc and Voc may be originated due to increase in resistivity of In^2Se^3 thin films deviated from stoichiometry. The PEC cell with configuration In^2Se^3 / 0.1 M polysuphide / graphite is used to check the type of conductivity exhibited by In^2Se^3thin films. The polarity of dark voltage is negative towards In^2Se^3 photoelectrode and positive towards the graphite electrode for all samples showing n–type semiconducting behavior. The Fig.3 shows the variation of Isc and Voc with bath temperature. From the graph it is observed that both Isc and Voc increase with increase in bath temperature and attain maximum values for the film deposited at 70°C, indicating probably a better formation of stoichiometric semiconducting compound. Further increase in bath temperature results in decreased values of Isc and Voc. The lower values of Isc and Voc may be attributed to non-stoichiometric growth of In^2Se^3 thin films due to insufficient thermal energy provided during the deposition. Fig.4 shows the variation of Isc and Voc with pH of bath, which shows that Isc and Voc are maximum at pH = 3. This indicates that the formation of good quality photovoltaic material is possible from acidic aqueous bath. Electrodeposition of In2Se3 films was carried out at a potentiostatic mode at −520 mV / SCE. 1-2 □m thick layer was obtained within 50 min. of deposition time.

To study the crystal structure of In^2Se^3 film, X-ray diffractogram of the film was examined. The XRD pattern of In^2Se^3 deposited on stainless still substrate is shown in Fig. 5. The films are polycrystalline in nature. The crystallographic data for In^2Se^3 is shown in Table 1. The XRD analysis reveals that the obtained films were mono phased and crystallized in the hexagonal phase (ASTM Diff. File No. 71-0250). In2Se3 thin film shows prominent (111) (113) (124) (305) (139) (236) peaks. The lattice parameter and hkl planes are in fairly good agreement with standard values. The average grain size of the material was determined by using the Scherer formula:

$$D = K\lambda / \beta \cos\theta, \quad \text{----------} \quad (1.5)$$

where D is crystallite size, λ is the X-ray wavelength used in A °, β is the angular line width at half the maximum intensity, θ is Bragg's diffraction angle and K is constant. The average grain size was calculated by resolving the highest intensity peak. The average crystallite size of the as deposited In2Se3 thin film was found to be 210A °.

The surface morphology of indium selenide thin films was analyzed by using SEM. SEM images of indium selenide films are shown in Fig. 6. It is observed that the indium selenide thin film is homogenous, without cracks or pinholes and it well covers the glass substrate. It also suggests that the film is composed of minute grains, was uniformly distributed over a smooth homogenous background that may correspond to some amorphous phase of indium selenide thin film. The presence of fine background is an indication of one step growth by multiple nucleations.

The optical absorption spectra of indium selenide film deposited onto stainless still substrate were taken at in the wavelength range of 400–1000 nm. Fig. 7 shows variation of optical absorption with wavelength. The optical study

shows that the films are highly absorptive (α x10^4 cm-1). Indium selenide is a direct band gap semiconductor [18]. For an allowed direct band gap transition the absorption coefficient α can be related to the photon energy hν by

$$(\alpha h\nu)^2 = A (h\nu - Eg), \quad (1.6)$$

where A is a constant and Eg is the energy band gap. For a direct band gap semiconductor the $(\alpha h\nu)^2$ vs. hν characteristic is predicted to be a straight line with a photoenergy axis intercept indicative for the band gap. This is illustrated in Fig. 8, where a band gap of 2.35 eV can be obtained. The dark electrical conductivity of In^2Se^3 film on non conducting glass slide was determined by using a dc two probe method, in the temperature range 300−525 K. At room temperature the specific conductance was found to be of the order of 10^{-2} $(\Omega cm)^{-1}$, which agrees well with the earlier reported value [19]. The electrical conductivity with temperature during heating and cooling cycles was found to be different and this shows that the 'as deposited' films undergo an irreversible change due to annealing out of non-equilibrium defects during first heating.

In thermoelectric power measurements, the open circuit thermo voltage generated by the sample, when a temperature gradient is applied across a length of the sample, was measured using a digital microvoltmeter. The temperature difference between the two ends of the samples causes the transport of carriers from the hot to cold end, thus creating an electric field, which gives rise to thermovoltage across the ends. In the case of In^2Se^3 thin film, the negative terminal was connected to the cold end, therefore, the film shows n-type conductivity [20].

5.CONCLUSION

Homogenous and uniform films of indium selenide (In^2Se^3) have been successfully deposited using electro chemical deposition method. The film formation takes place by ion-by-ion growth mechanism. Crystallographic and micrographic studies revealed the polycrystalline nature of the films. Optical studies show that, indium selenide films have high optical absorption coefficient and direct band-to-band type optical transition. Temperature dependence of electrical conductivity showed the semiconducting nature of the film. Thermoelectric power measurement shows n-type conduction for In2Se3 thin film.

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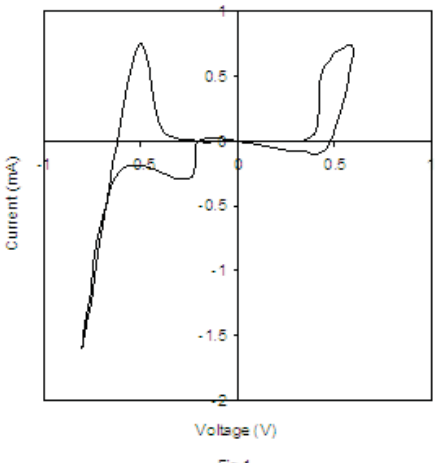
Fig.1: The voltammogram of In2Se3 thin film.

Fig.1: The voltammogram of In2Se3 thin film.
Fig.2: Variation of Isc and Voc with deposition time for the In2Se3 thin film.
Fig.3: Variation of Isc and Voc with bath temperature for the In2Se3 thin film.
Fig.4: Variation of Isc and Voc with pH of the bath for the In2Se3 thin film.
Fig.5: XRD pattern of In2Se3 thin film.
Fig. 6: SEM images of indium selenide thin films
Fig.7: Absorption spectra of In2Se3 thin film.
Fig.8: Direct band gap of In2Se3 semiconducting thin film, $(\alpha h\nu)2$ vs. $h\nu$

Table Captions:

Table.1: Crystallographic data for In2Se3 thin film.



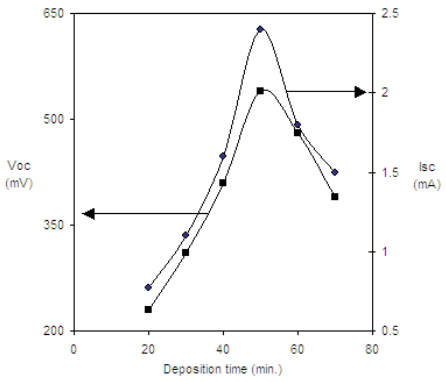


Fig.2

Fig.2

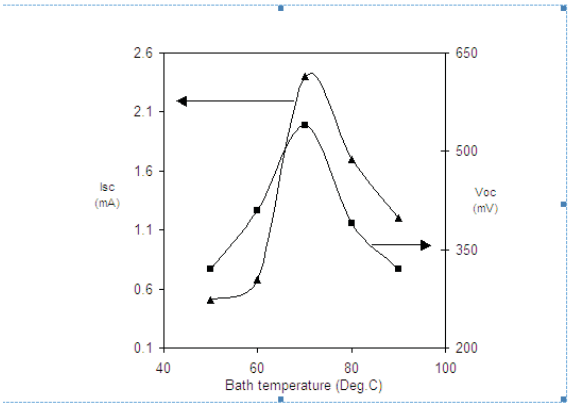
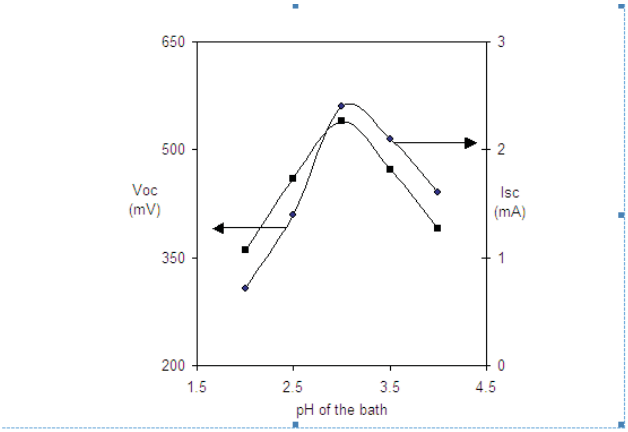
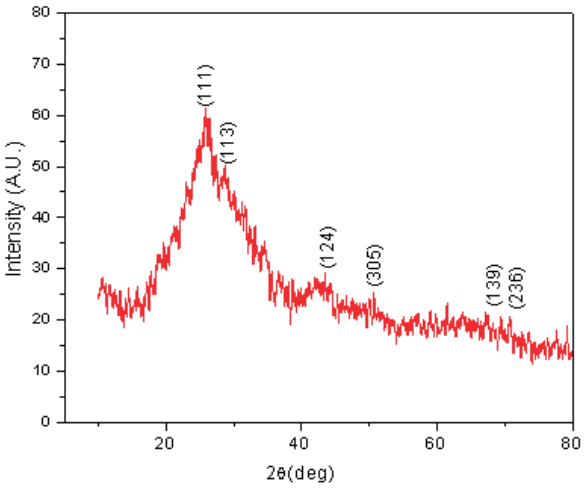
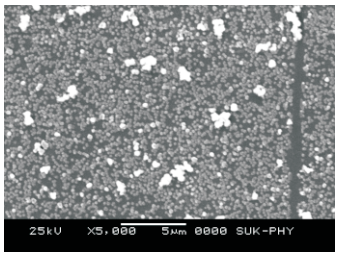

2.6
2.1
1.6
1.1
0.6
0.1
Isc
(mA)
650
500
350
200
Voc
(mV)
40
60
80
100
Bath temperature (Deg.C)

Fig.3


650
500
350
200
Voc
(mV)
3
2
1
0
Isc
(mA)
1.5
2.5
3.5
4.5
pH of the bath


Intensity (A.U.)
(111)
(113)
(124)
(305)
(139)
(236)
2θ(deg)



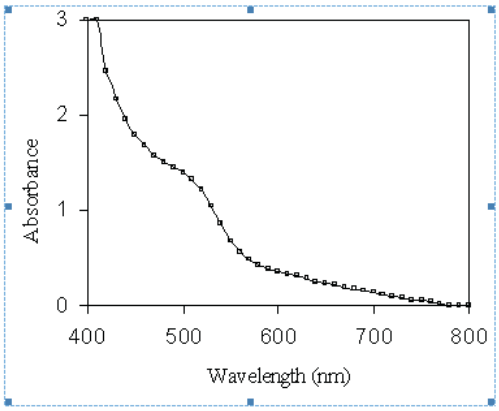


Table. 1: Crystallographic data for In2Se3 thin film.

Composition	d observed (Å)	d standard (Å)	hkl plane	Grain size (Å)	
		In_2Se_3 (Hex)		XRD	SEM
In_2Se_3	3.5001	3.4964	111	210	218
	3.1120	3.1130	113		
	2.0864	2.0970	124		
	1.8131	1.8130	305		
	1.3580	1.3369	139		