

## STUDY ON InSe THIN FILM PREPARED IN THE JOURNEY OF Cu(In<sub>1-x</sub>Al<sub>x</sub>)Se<sub>2</sub> THIN FILMS

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InSe thin films were prepared in the journey of CuInAlSe<sub>2</sub> [CIAS] thin films preparation by chemical bath deposition technique and the prepared films were characterized through structural, compositional, morphological and optical analysis. Morphological analysis confirms the elements as InSe. Structural and optical parameters of InSe thin films were evaluated and presented in this paper. The optical analysis confirms that InSe thin film is a suitable absorber layer for photovoltaic cell.

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### 1. Introduction

Indium selenide (InSe) is one of the important III-VI layered compounds which has a low density of dangling bonds [1] [A dangling bond occurs when an atom is missing a neighbor to which it would be able to bind. Such dangling bonds are defects that disrupt the flow of electrons and that are able to collect the electrons. A dangling bond is a broken covalent band. Dangling bonds are found on the surface of most crystalline materials due to the absence of lattice atoms above them] and is a candidate material to form the heterojunction with a very low density of interface states. Being layer-type semiconductors, their two-dimensional structure and their resulting anisotropic properties are of particular interest. In these materials inter-layer interactions are very weak compared to those in a single layer. It is known that semiconductor applications are strongly influenced by the presence in the forbidden gap of the energy levels arising from impurities and structural defects [2]. Indium selenide belongs to III –VI compounds family consisting of covalent bonded units (Se-In-In-Se) held together by Vander Walls forces and is one of the most suitable compound semiconductors for optoelectronic and photovoltaic applications [3]. The band gap (E<sub>g</sub>) of InSe is about 1.3 eV at room temperature [1], which makes it an attractive material for solar energy conversion [3-5]. These have typical characteristics of the layered semiconductors, namely: (A) – the low density of the dangling bonds on the surface because of the almost complete chemical bonds within the layer [6]; (B) – intercalation [7] and (C) – the mechanical weakness due to the weak Vander Walls forces between the layers. Property (A) makes it possible to form heterojunction devices with a low interface density of states. Property (B) allows altering the electrical properties of the semiconductors, which will be convenient in device processing. However, because of the disadvantage (C), it is almost impossible to form devices from layered semiconductor crystals. In order to overcome this disadvantage and to utilize the advantages (A) and (B), epitaxial films of layered semiconductors are needed.

It has been reported that the phases with a major content of In have E<sub>g</sub> values larger than those of the phases with larger content of Se [7]. Therefore by tuning In and Se compositions in InSe thin films, it can be used as an absorber or buffer layer. In the present paper, we report the

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compositional, structural, morphological and optical properties of chemical bath deposited indium selenide thin films prepared towards the journey of CuInAlSe<sub>2</sub> [CIAS] thin films.

## 2. Experimental details

The concentration and volume of the reaction mixture in the chemical bath was varied over a wide range for the preparation of CIAS thin films. The reaction mixture contained 15 ml (0.2 M) CuSO<sub>4</sub> solution, 7.5 ml (0.1 M) trisodium citrate, 6.25 ml (0.1 M) InCl<sub>3</sub> solution, 25 ml (0.05 M) citric acid, 20 ml of selenous acid and 3 ml of Al<sub>2</sub>SO<sub>4</sub> [8]. 15 ml of CuSO<sub>4</sub> solution was taken in a 100 ml beaker, 7.5 ml of trisodium citrate solution is then added drop by drop to it and followed by 20 ml of selenous acid, 6.25 ml of InCl<sub>3</sub> and citric acid as a complexing agent. Finally 3 ml of Al<sub>2</sub>SO<sub>4</sub> is added drop by drop to it. The deposition parameters such as pH, deposition time and temperature have been varied from 9-11, 30-120 minutes, 50-60°C and they are optimized as 10, 30-90 minutes and 50°C respectively. Well-cleaned substrates were immersed in the chemical bath and the films were annealed and employed for analysis.

### 2.1 Characterization

In the present study the structural characterization of CBD InSe thin films has been carried out using Shimadzu (Lab X-6000) x-ray diffractometer with Cu K<sub>α</sub> ( $\lambda = 1.5406 \text{ \AA}$ ) line in  $2\theta$  range from 20 to 60°. The composition of the chemical constituents in the deposited thin films has been confirmed by energy dispersive x-ray analyzer (LEICA.S440i) and scanning electron microscope used in the present investigation was JEOL-JSM-100. JASCO-UV/VIS/NIR(JASCO V-570) double beam spectrophotometer has been used for optical transmittance measurements in the wavelength range 200 to 25000Å.

## 3. Results and discussion

### 3.1 Compositional analysis

EDAX of the prepared thin films [Fig.1] enabled to conclude the elements present in the prepared thin films as In and Se and absence of Cu and Al. EDAX spectra revealed that the InSe thin films contained 47.7 % In and 52.28 % Se and therefore we have visualized In<sub>0.95</sub>Se<sub>1.05</sub> near stoichiometric thin films in the journey towards CIAS thin films preparation.

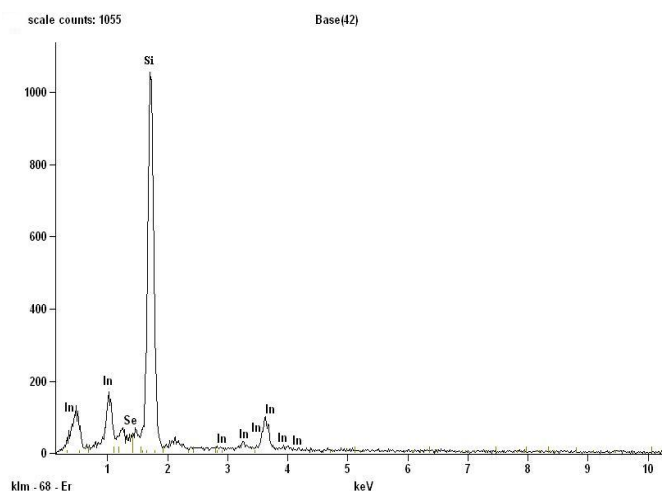


Fig 1 EDAX spectrum of a representative InSe thin films

### 3.2 Structural analysis

Fig. 2 shows the XRD profile of a representative InSe thin film of thickness 510 nm. Possible directions in which the film diffracted the beam of monochromatic x-ray are determined by Bragg condition [9].

The predicted peaks (002), (004) and (101) are reported as identified peaks for InSe thin films by earlier reports [10, 11] and JCPDS file [34-1431]. The spectra exhibit a diffraction pattern typical for a polycrystalline hexagonal structure [12, 13]. The strong diffraction peak at  $2\theta=21.1^\circ$  corresponds to diffraction from the (004) planes while the other peaks at  $2\theta=10.6^\circ$  and  $26.2^\circ$  are the result of diffraction from the (002) and (101) planes respectively. The absence of [(012) and (108)] peaks as well as [(104), (107) and (101)] peaks confirm the absence of rhombohedral InSe and rhombohedra  $\text{In}_2\text{Se}_3$  phases in the prepared InSe thin films in the journey towards CIAS thin films preparation.

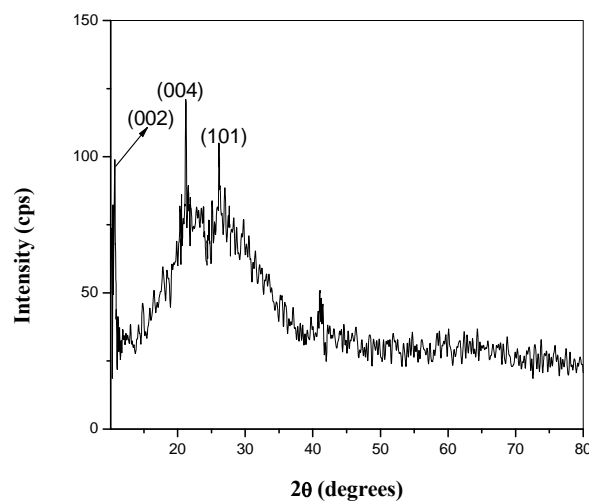


Fig 2 X-ray diffractogram of InSe thin film of thickness 510 nm.

From the observed d-spacing and (hkl) planes the lattice constants a and c, as well as other micro structural parameters like, crystalline size, number of crystallite per unit area, dislocation density and strain were calculated and presented in Table 1 and 2. The lattice constants 'a' and 'c' was observed to be in very good agreement

Table 1. Lattice constants of InSe thin film of 510 nm.

Plane	2θ (degrees)		d-spacing (Å)		Lattice Constants (Å)			
					a		c	
			observed	JCPDS	Observed	JCPDS	Observed	JCPDS
(004)	21.1	21.2	4.13	4.17	3.985	4.005	16.64	16.62
(002)	10.6	10.62	8.14	8.17			16.59	
(101)	26.2	26.1	3.33	3.35			16.72	

Table 2. Microstructural parameters of InSe thin films

Plane	Crystallite size Dc (nm)	Dislocation density $\times 10^{14}$ (lines/m <sup>2</sup> )	No of crystallite per unit area $\times 10^{15}$ m <sup>-2</sup>	Strain $\times 10^{-3}$
(004)	74.5	1.80	1.45	5.03
(002)	73.6	1.85	1.51	5.12
(101)	75.4	1.75	1.39	5.00

with JCPDS [34-1431] value and earlier researchers. The prepared CBD InSe thin films consisted of large crystallized [ $\pm 75$ nm] and hence less number of surface states acting as recombination centers are present [14].

### 3.3 Surface morphology

Fig. 3 shows the scanning electron micrographs of InSe thin films. It can be observed that InSe film has uniform, smooth and highly dense compact surface with an average grain size of 0.05 $\mu$ m.

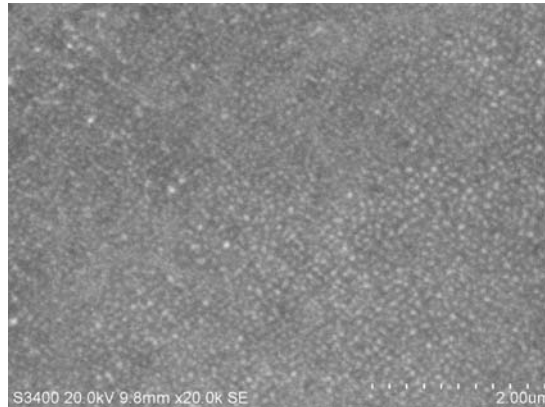


Fig 3 Scanning electron micrographs of InSe thin film of thickness 510nm.

### 3.4. Optical properties

Absorption coefficient was calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relation [15].

Optical absorption coefficient measurements are essential for the understanding the band structure of any semiconducting material. To estimate the value of optical band gap of InSe thin films the optical transmission spectra of the films were recorded in the wavelength range 200 to 2500 nm at room temperature [Fig 4.a]. Fig 4.b shows the plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  of InSe thin films. The straight-line portion is extrapolated to cut the x-axis, which gives the average band gap as 1.48eV. Band gap values are in good agreement with the earlier investigations on InSe thin films [16, 17, 18]. The estimated bandgap enabled to conclude that the deposited InSe thin film is a suitable absorber layer for photovoltaic cell.

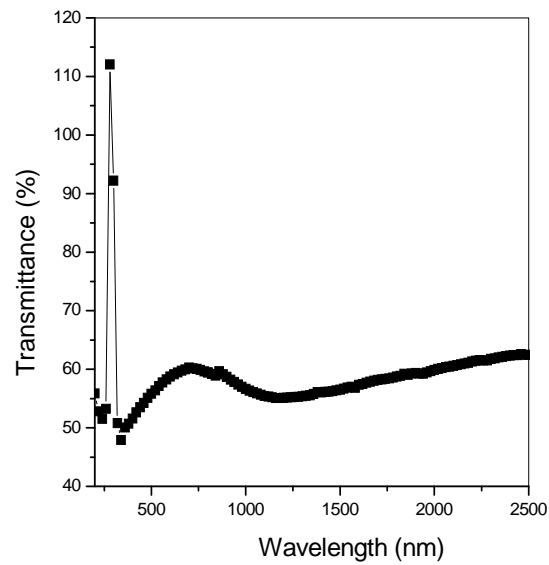


Fig 4.a Transmittance spectra of InSe thin films of thickness 510 nm.

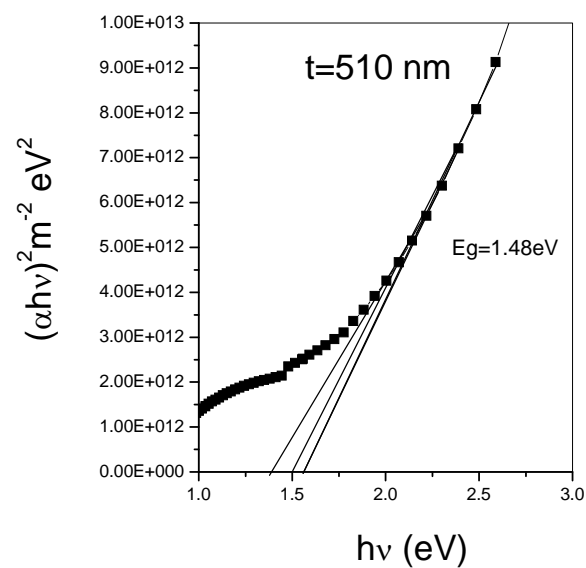


Fig 4.b Plot of  $(\alpha h\nu)^2$  vs  $(h\nu)$  of InSe thin film of thickness 510 nm.

#### 4. Conclusions

InSe thin films had obtained in the journey towards CIAS thin films preparation by chemical bath deposition technique. Compositional analysis confirms the presence of In and Se in near stoichiometric and absence of Cu, Al in the prepared films. Structural analysis confirms that the prepared films were InSe with hexagonal structure and morphological studies shows that the prepared films have grain size around 50 nm. Optical analysis revealed that prepared InSe thin films were direct allowed and it is a suitable absorber layer for photovoltaic cell.

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