

Characteristic properties of indium selenide thin films grown by the successive ionic layer adsorption and reaction method

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Indium selenide thin films were grown by using Successive Ionic Layer Adsorption and Reaction method at room temperature. The band gaps of the films were determined by using optical absorption measurements which were carried out in the temperature range 10-320 K. Influence of the increased cationic precursor's concentration on optical properties of the films was investigated in terms of absorption curves. The films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for crystallographic and surface morphological properties. The electrical characterizations of the films were done by two probe method which was carried out in the temperature range 300-450 K. By using hot probe method the type of electrical conductivity was determined as n-type.

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1. Introduction

III–VI semiconductors which crystallize with a layered structure have been investigated extensively [1,2]. Among them, InSe has been of particular interest also because of its potential applications in photovoltaic devices [3]. In particular, InSe has attracted attention as a candidate for solar cells since it has a low density of dangling bonds on its surfaces. For example, *n*-InSe/Pt Schottky junction solar cells have been fabricated but the energy conversion efficiency of the InSe cells is still relatively low [3,4].

In₂Se₃ is a binary compound, with a direct band gap of 1,7 eV. It is a suitable absorber in CdS/In₂Se₃ or In₂S₃/In₂Se₃ photocells. It forms hexagonal structure and shows very significant properties for photovoltaic and photochemical applications. This is because of its high absorption coefficient associated with an energy band gap in the optimum range for solar energy conversion. Indium chalcogenides have not been investigated as much as other types of semiconductors [5,6,7].

Nowadays a number of chemical and physical methods are being used to growth metal chalcogenide thin films. Most of these methods have very high cost. SILAR method, which is a chemical deposition method, has low cost and it is also known modified chemical bath deposition (M-CBD). In chemical bath deposition (CBD) method, metal and chalcogen ions are replaced in the same container for growth metal chalcogenide thin films. So an undesired precipitation occurs in the solutions and result of this precipitation is wastage of material. In SILAR method, metal and chalcogen ions are replaced in different containers to avoid this precipitation. SILAR method is beside on the immersion of a substrate into separate

cationic and anionic precursor solutions and rinsing after every immersion with deionized water. This rinsing process enables heterogeneous reaction between the solid phase and solvated ions in the solutions [6-10]. This is the other difference between SILAR and CBD methods. SILAR is a simple, versatile and inexpensive chemical deposition method and it does not require complex equipment. Process is carried out at or near room temperature so temperature sensitive substrates can be used. As a low temperature process, it also avoids oxidation and corrosion of the substrate. One SILAR growth cycle involved four steps. At the first step, substrate is immersed into the cationic precursor solution. This solution contains the positive ions of desired compound. During this step, the cations are absorbed on the surface of the substrate. Then, substrate is immersed into the deionized water. At this step, excess cations and other ions are washed away. And then, substrate is immersed into the anionic precursor solution. This solution contains the negative ions of desired compound and this is the third step of SILAR growth cycle. During this step, the anions are reacted with pre-absorbed cations on the surface of the substrate. At the final step of this process, substrate is immersed into the deionized water again to be washed away excess ions. These four steps are a cycle of SILAR. Number of cycles determines the thickness of the films [11].

In this paper, we prepared indium selenide thin films by using SILAR method at room temperature. Crystallographic and surface morphological properties of the films have been determined by using XRD and SEM techniques. Optical and electrical properties of the films were investigated as a function of temperature.

2. Experimental

Indium selenide thin films were deposited from InCl_3 and Na_2SeSO_3 aqueous solutions by SILAR method at room temperature. InCl_3 solution was used as cationic precursor and Na_2SeSO_3 solution as anionic precursor. The Na_2SeSO_3 solution was prepared according to the literature [12]. The concentration of InCl_3 aqueous solution was changed from 0.02 M to 0.1 M by 0.02 M steps. The concentration of Na_2SeSO_3 aqueous solution was adjusted to the value 0.05 M. Thus the effect of cationic precursor's concentration was also investigated. For establish the substrate, different materials such as glass, ITO, quartz, sapphire and cellophane band are tried. The best films were obtained on ordinary transparent cellophane bands at a short time at room temperature. Before deposition, cellophane band substrates were cleaned thoroughly with commercial detergent and rinsed in deionized water of 18 M Ω . For solutions and deionized water 50 ml capacity glass beakers were used. Immersion and rinsing times were chosen experimentally and determined as 25 s for solutions and 50 s for deionized water after many trials. All processes were carried out at room temperature and ambient pressure. The immersion and rinsing of substrates were done manually.

A digital balance, which has 0.00001 g sensitive, was used for to weigh of the chemical materials. The thicknesses of the films were measured by the optical interference method. For this aim, the films were replaced two thick glass plaques and these glass plaques were illuminated by monochrome light. Thus an interference pattern was obtained.

The optical properties of the films were studied via optical absorption spectra as a function of temperature with Perkin-Elmer UV/VIS Lambda 2S spectrometer which wavelength resolution better than $\pm 3\text{nm}$ in the wavelength 400-800 nm and a closed cycle He cryostat was used. Optical measurements were done in the temperature range 10-320 K with 10 K steps and in every temperature values, we waited 5 minutes for temperature stabilization. For determining the optical absorption coefficient $\alpha = \text{absorption}/\text{thickness}$ formula was used. The optical band gap values of the films were determined from the extrapolation of the straight line section of the curve α^2 versus $h\nu$ estimation from the optical transmission curve [13]. The structural characterization of the samples was carried out by X-ray diffractometer using Cu K α radiation and SEM was used for surface morphological studies. The electrical resistivity of the films were determined using two probe method in the temperature range of 300-450 K. For ohmic contacts, silver paste was applied [14]. The type of electrical conductivity of the indium selenide thin films was determined from the polarity of thermally generated voltage.

3. Results and discussion

By making several trials the preparative conditions were optimized. Table 1 shows the optimized preparative conditions for deposition of indium selenide thin films.

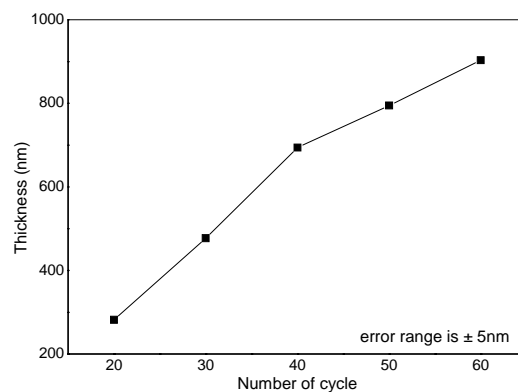


Fig.1. Thickness values of the indium selenide films which were prepared using 0,1 M InCl_3 aqueous solution..

Table 1. Deposition conditions of In_2Se_3 films.

Precursor	InCl_3	Na_2SeSO_3
Concentration (M)	0.01-0.1	0.05
Immersion time (s)	25	25
Number of circles	20-60	20-60
Deposition temperature (K)	300	300

The thicknesses of the films, for each number of deposition cycles, were calculated by using optical interference method. The films thicknesses which were prepared by using 0.1 M concentration of InCl_3 solution are shown in Figure 1 and it is seen that the thicknesses are increasing with number of SILAR deposition cycles. Besides, the thicknesses of the films were also determined for the samples which were prepared by using different InCl_3 aqueous solution concentration. But it was observed that the variations with InCl_3 concentration were about in the error limits (± 5 nm).

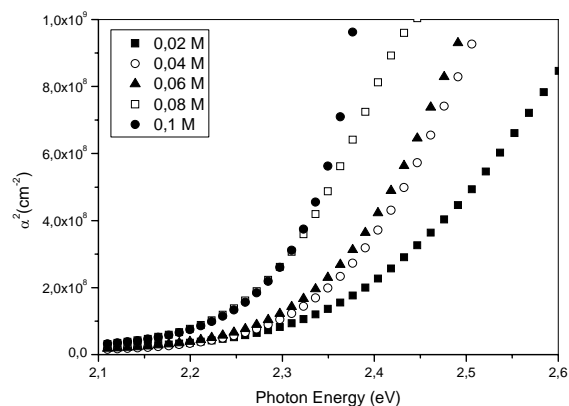


Fig.2. The absorption coefficient changing with photon energy at different concentration.

Fig. 2 shows the optical absorption of the indium selenide thin films which were grown with using different concentration of InCl_3 solutions. It is observed that the absorption curves are improving with increasing InCl_3 quantity of the solutions. So, it is seen from the figure that, better indium selenide thin films can be obtained when the concentration of InCl_3 solution is two times as much as the concentration of Na_2SeSO_3 solution is.

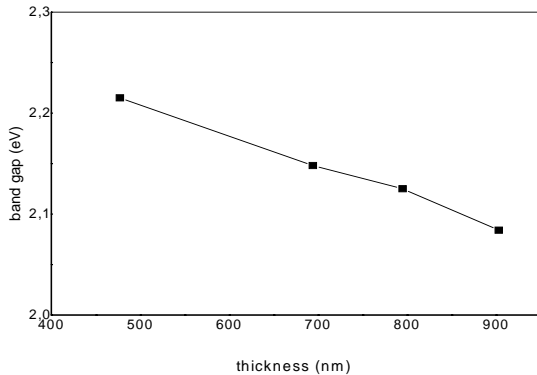


Fig. 3. Variation of band gap values of the films with thickness at room temperature.

Variation of band gap values of the films with different thicknesses can be seen in Fig. 3. It is clear from the figure that, the band gap values of the samples are decreasing with increasing thickness and the variation is about linear. There are two reasons of this behavior which are given in literature as quantum size effect and impurity levels [15-16]. As a result of quantum size effect increasing the particle size with thickness causes decreasing the band gap values. It is known that quantum effects can be observed clearly for small particles. The second reason is insulating the impurity levels with conductivity band. During growth process some impurity levels form the edge of conductivity band and these levels can insulate with conductivity band when the thickness increased. For the samples which have 280 nm or smaller thickness, the intensities of the absorption curves were not enough to determine the band gap.

Optical absorption of the films for different temperatures is shown in Fig. 4. With the help of optical absorption measurements band gap energies of the indium selenide thin films were determined as 2.208 eV and 2.08 eV at 10 K and 320 K respectively. It's evident from the figure that the value of band gap energy is decreasing with increasing temperature depending on the increasing lattice parameters.

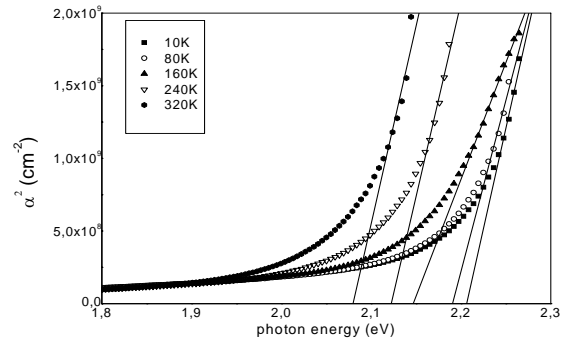


Fig.4. Variation of optical absorption values of the indium selenide films with temperature.

X-ray diffraction studies were carried out on samples to analyze the microstructure using an X-ray diffractometer. X-ray diffraction pattern of indium selenide film which has a thickness of 795 nm, is shown in Figure 5. It is seen from the XRD pattern that, In_2Se_3 formed with InSe and the structure is polycrystalline [6,7,12,16,17]. It is also indicated in the figure that the crystallization of the film is low.

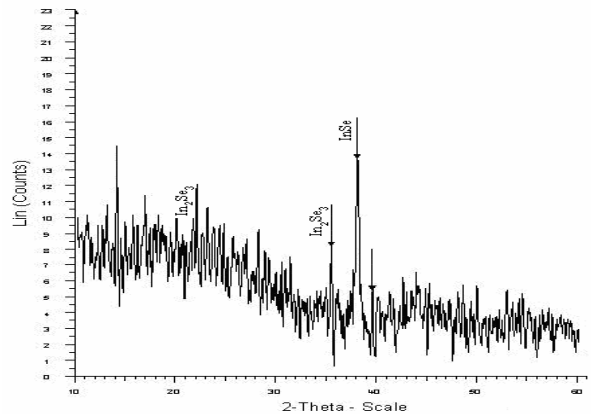


Fig.5. XRD pattern of the film which was prepared using 0,1 M InCl_3 aqueous solution.

SEM images of the indium selenide films for different thicknesses are shown in Fig. 6a and Fig. 6b. It is observed that the surface of the films are about uniform and when the thickness is increased from 280 nm to 903 nm, small grain decreased in number and the larger grains increased in size. It's also seen that clusters have formed with increasing thickness.

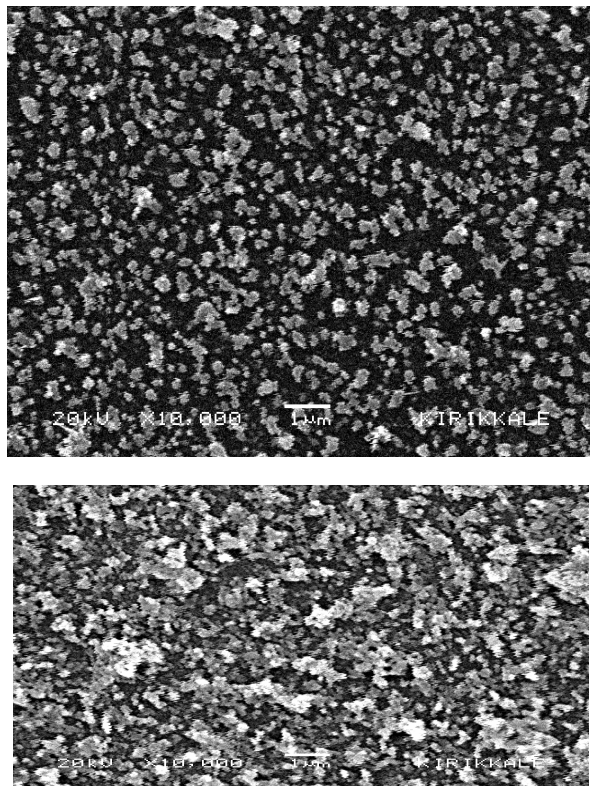


Fig. 6. SEM images of the films (a) 282 nm (b) 903 nm thickness.

Variation of resistivity with temperature is shown in Fig.7. From the figure, it is evident that the resistivity is decreasing with increasing temperature and this is confirming the semiconducting behavior and this variation is non-linear. Consisting of the film with discontinuous clusters [6] and ionizing the impurity levels are two reasons of this non-linear behavior.

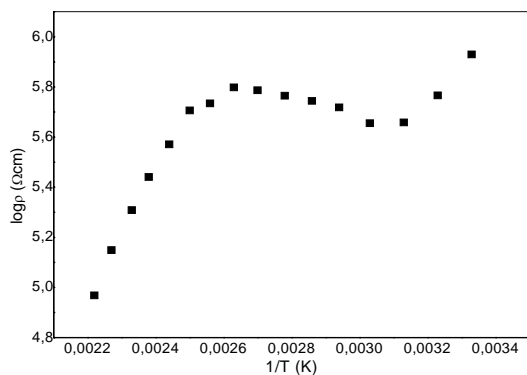


Fig.7. Variation of resistivity of the film, which was prepared by using 0,1 M InCl_3 aqueous solution, with temperature.

Resistivity values of the films were calculated for different temperature and the values were given in Table 2.

These high resistance values (about $10^6 \Omega \text{ cm}$) are due to the low crystallization which can be seen in Fig. 3.

Table 2. Variation of resistivity values of the In_2Se_3 films with temperature.

Temperature(K)	Resistivity (Ωcm)
300	1.37×10^6
350	0.93×10^6
400	0.29×10^6
450	0.14×10^6

By establishing a temperature gradient between the two ends of the films, a thermoeff measurement was carried out and n-type conductivity was found from the polarity of thermoeff.

4. Conclusions

The SILAR method was applied to prepare indium selenide thin films. The best films were obtained on cellophane band at a short time at room temperature. The films thicknesses were calculated by using optical interference method. The effect of cationic precursor's concentration was studied and it was found that the absorption curves were improving with increasing InCl_3 cationic precursor's concentration. The best films were obtained when the concentration of InCl_3 solution is two times as much as the concentration of Na_2SeSO_3 solution. The optical band gap energy is found to be decreasing with increasing temperature. The prepared films consist of In_2Se_3 and InSe phases with low crystallization and it was confirmed by XRD. Indium selenide layers were detected by SEM and it was observed the surface of the film was about uniform and consists of discontinuous clusters. The resistivity at room temperature (300 K) was found about $10^6 \Omega \text{ cm}$. Consequently we can say that, SILAR is suitable method to deposit indium selenide thin films.

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