Chemical Deposition of Polycrystalline Znse Thin Films from Malonic Acid Solution: Nucleation and Growth Mechanism, Structural, Optical and Electrical Studies

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Abstract: Zinc selenide (ZnSe) polycrystalline semiconductor thin films have been synthesized adopting dip method in malonic acid solution. The formations of nucleus and growth process of this technique have been investigated. The XRD pattern shows a characteristic cubic structure with a (111) crystallographic preferred orientation. SEM studies reveal that grains are uniformly dispersed on the surface of the substrates. The optical energy gap was 2.80 eV. The activation energies are 0.053 and 0.317 eV for low and high temperature region, respectively obtained.

Keywords: Electronic material; Chemical synthesis; Optical properties; Scanning electron microscope.

1 Introduction

Recently, thin chalcogenide films of II-VI, IV-VI, II-IV-VI and I-III-V families have emerged as the potential semiconductors of high performance and low production cost. They are important semiconductor materials because of manipulability of band gap that matches the solar spectral distribution [1-2].

The electronic and optical properties of binary semiconductor compound of group II-VI were widely investigated because of their significant non-linear, luminescent characteristics and quantum dimension effect [3-4]. Polycrystalline electrodes of II-VI compounds with huge area are cost-effectively attractive for solar devices applications. Zinc selenide is one of the important materials as a buffer layer in copper indium selenide based solar gadgets that enhanced traditional values of lattice parameter as well as no toxic character. Moreover, it has been used in different light emitting diodes, photovoltaics, thin-film transistors, photoelectrochemical devices and laser screens [5-13]. In addition, ZnSe is distinct as an infra red coating material because of its wide spectral range of higher transmission between 600 and 20000 nm. Thus, synthesis of high quality ZnSe thin films is still an attractive subject [14-16].

Rusu et al [17-18] addressed the mechanism of electronic transport in polycrystalline ZnSe thin films through applying the

Steo's model [19]. Numerous workers have reported different types of crystal structures for zinc selenide thin films deposited by chemical method [20-21].

Thus, taking into account the practical importance of zinc selenide, thin films have been prepared employing simple chemical method. The kinetics and growth mechanism will also be explored. All films will be characterized using X-ray powder diffraction (XRD) and optical absorption technique. Parameters, such as lattice parameters, optical absorbance, optical band gap, nature of optical transitions, grain size, electrical conductivity and activation energy will be defined.

2 Experimental Details

Analytical grade chemicals have been applied to synthesize of ZnSe thin films. All solutions were prepared in double distilled water. Zinc sulphate octahydrate, Malonic acid, Ammonia, Selenium powder, Anhydrous sodium sulphite and Hydrazine hydrate were used.

The moderately stable source of selenium ion, sodium selenosulphate was prepared adopting the following method. It was prepared by refluxing 5g grey selenium powder with 12g anhydrous sodium sulphite in 200 mL distilled water for nine hr at 363 K. The hot solution was filtered through Whatmann filter paper No. 1 and stored in

air tight bottle. The concentration of the obtained sodium selenosulphate solution was 0.2 M.

To prepare the bath, 10mL (0.2 M) zinc sulphate octahydrate was kept in 100mL container. Another chemical has been applied in the following sequence: 2.5mL (1 M) Malonic acid, 10mL (2.8 M) ammonia, 2.5mL (99%) hydrazine hydrate and 10mL (0.2 M) sodium selenosulphate. The pH of the reactive mixture was 10.38. The total volume was 50 mL with double distilled water. The temperature of the bath was managed at 278 K applying ice bath. The reactive mixture was vigorously stirred before dipping substrates. The substrates kept upright and somewhat slanted in a reactive bath. Then, temperature of the bath slowly increased up was then allowed to increases up to 298 K. 4 hours later the slides were frequently washed with double distilled water. The film was dried out in nature and deposited on both sides of the slides.

3 Results and Discussion

In growth process, no film formation occurs within an hour. This is the induction period required to form nucleation point on the glass slides. Occurrence of induction time suggests ion-by-ion growth mechanism instead of cluster-by-cluster. Fig. 1 shows the thickness against deposition temperature. It shows that in the early stages of growth the deposition directly changes with deposition temperature and then reduced after typical temperature. When temperature gets higher, release rate of Zn^{+2} and Se^{-2} ion gets faster. Hence precipitation occurs instead of film formation.
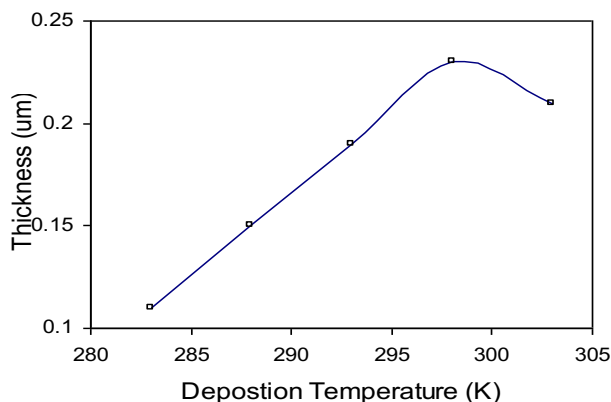

Fig. 1: Variation of thickness against deposition temperature of ZnSe thin films.

The period of film preparation the glass slides was investigated. This study revealed that homogenous ZnSe films were synthesized in four hours. Thickness was calculated every hour and plotted against time as shown in Fig.2. This diagram indicates that thickness directly changes with preparation time, but the concentration of the reactive species decreases within certain time. Thickness

remains almost constant. All films were homogenous and well-adherent to the substrate.

For the crystallographic study of ZnSe thin films deposited by chemical method, X-ray diffractrogram of the films was examined in the range from 20^0-80^0. The chalcogenide of zinc normally shows the duality in the crystal structure. The deposited thin film grows both sphalerite (cubic, zinc blend type) and wurtzite (hexagonal type) structure. This depends upon preparative factors, like precursor concentration and deposition temperature [22-24].
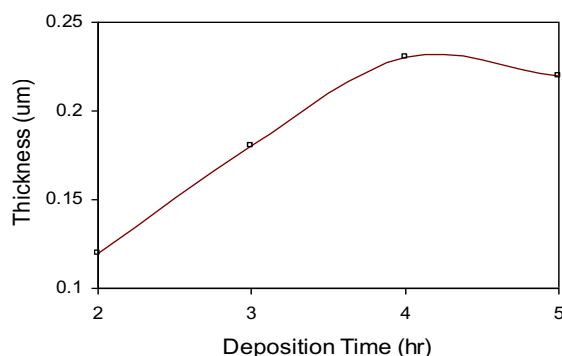

Fig. 2: Variation of thickness with deposition time of ZnSe thin films.

The X-ray diffractrogram of ZnSe thin films coated on glass slides is shown in Fig.3. The abundance of peaks confirms that the samples were polycrystalline in nature. The diffused background occurs because of amorphous glass substrate and some amorphous phase materials.
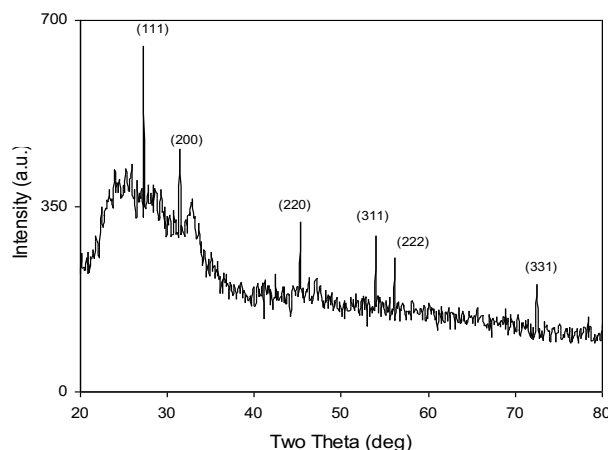

Fig. 3: X-ray diffraction pattern of ZnSe thin films.

The experimental magnitude of interplanar distance for thin film was in good accord with the standard d value taken from JCPDS card No. 1463 (Table 1), which confirmed that zinc selenide exists in the sphalerite (zinc blende type) structure. The XRD spectrum indicates the maximum intensity reflection plane at interplanar distance 3.271 Å (111). Along with (111) plane, (200), (220), (311) (222) (331) peaks were observed. A method that evaluates the

magnitude of the favored orientation parameter (f) for a known plane compared with other planes in thin film is employed [25]. In accordance with this technique the favored orientation parameter 'f' (111) of the (111) plane for the ZnSe thin films has been defined through measuring the ratio of (111) plane intensity over the total of intensities of all remaining peaks. f(111) = 0.2990, f(200) = 0.2096, f(220) = 0.1467, f(311) = 0.1357, f(222) = 0.1165, f(331) = 0.0931.

The lattice factor of ZnSe cubic phase is estimated through applying the following relation:

$$a = d\ (h^2+k^2+l^2)^{1/2}\ \text{-----------------}1$$

The lattice parameter 'a' of ZnSe film is 5.665 Å. The crystallite size of zinc selenide thin films was calculated using Scherrer's formula:

$$D = k\lambda/\beta cos\theta\text{-----------------------}2$$

Wherein D is the particle dimension (Å), λ is nothing but the wavelength of X-ray used (Å), β is the full width at half maximum, θ is the Bragg's angle and k is constant. The crystallite size was 85.40 nm. The unit cell volume can be calculated using equation [26];

$$V= a^3\ \text{-----------------------}3$$

The unit cell volume was 181.8 (Å)^3 The microstrain (ε) generated in the films has been estimated using equation [27]

$$\varepsilon = \beta cos\theta/4\text{----------------------}4$$

The microstrain was 4.058 x 10^{-4}. The dislocation density was calculated using equation [28];

$$\delta = n/D^2\ \text{----------------------}5$$

Wherein n is the parameter that is up to unity for the smallest amount of dislocation density. The value was 1.371x 10^{14} m^{-2}.

The optical spectrum of ZnSe thin films prepared onto glass substrate was studied at room temperature in the wavelength of 400-600 nm. The optical absorption spectra of films are shown in Fig. 4. The spectra were utilized to estimate absorptivity (α), type of transition involved and optical band gap (E$_g$). The study shows the existence of absorption edge of exponential form, i.e. a characteristic of II-VI compound. It occurs because of homogeneity of the deposited sample and normal band arrangement.
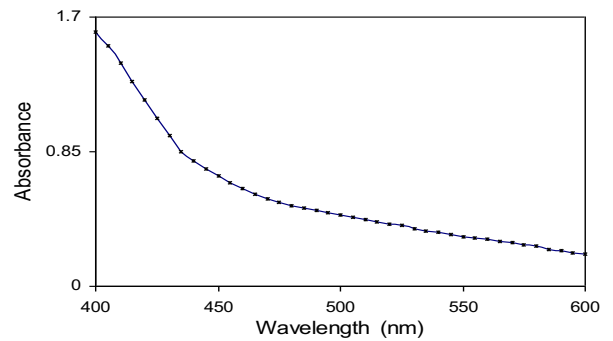

Fig. 4: Absorption spectrum of ZnSe thin films.

The spectrum reveals two regions, one for higher wavelength with practically lower absorbance and the other for lower wavelength in that absorption increases steeply. The graph also shows sharp nature of curve, indicative of good homogeneity in the nature and dimension of the granule and lower imperfection density close to the band edge. The calculation suggests that the films are extremely absorptive with a direct type of transition. (α x10^{4}cm^{-1}). The composition of the thin film and incident radiation energy defines the magnitude of absorptivity. The obtained information was examined in the surrounding area of the absorption edge on the basis of three-dimensional form. The explanation of the outcome may be simply drawn with the help of formula derived for three-dimensional crystal. The easiest structure of the equation adopted close to and beyond absorption edge is [29];

$$\alpha h\upsilon =A(h\upsilon-Eg)^n\ \text{----------------------}6$$

Wherein α is absorptivity (cm^{-1}), hυ is the photon energy (eV). A and n are constants. A is a complex parameter related to phonon energies, photon energy and temperature. The n values are 0.5 and 1.5 for allowed and forbidden direct transition. While 2 and 3 indicate allowed and forbidden indirect transition, respectively [30]. Eg is the direct band optical gap. A graph of (αhυ)^2 against photon energy must be a straight line whose intercept to the x-axis gives the optical band gap. This plot is revealed in Fig. 5. The linear nature of plot shows that the existence of the direct kind of transitions. Cutting off the straight line on the photon energy axis gives the optical band gap, which is about 2.80 eV. The value of the obtained band gap is consistent with the results of previously reported ZnSe using chemical bath deposition method [31]. The observed value is greater than standard band gap (2.7 eV) of the ZnSe material [32], showing a 'blue shift' of 0.10 eV. This is ascribed to the occurrence of size-quantization. This is observed because of the localization of electrons and holes in the limited amount of the semiconductor materials.
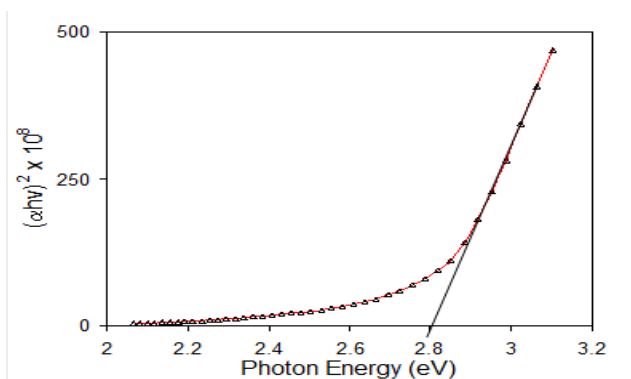
Fig. 5: Determination of band gap of ZnSe thin films.

The morphology of deposited films was examined applying scanning electron microscope (Fig. 6). In the optimized situation, the film surface is smooth confirming that granule covers the substrate. The view of ZnSe film does not show the presence of any voids or pinholes. The grains were small with non-uniform and no well-defined grain boundaries. The average grain size was 90.67nm.
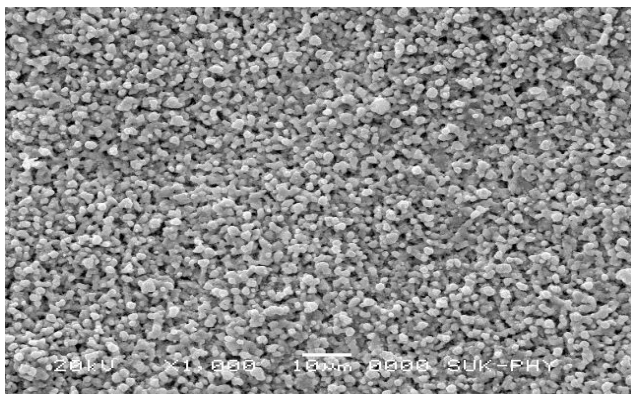

Fig. 6: Scanning electron micrograph of ZnSe thin films.

The electrical transportation properties play a significant role in maintaining the quality as well as applications of the semiconductor tools. Such characteristics were mostly prejudiced by their structural characteristics, purity, nature, and concentration of the impurities [33-35].

The electrical conductivity of prepared ZnSe thin film on amorphous glass slide was defined using a two probe technique, in the temperature limit 300-525 K. A plot of log (conductivity) versus inverse absolute temperature for the cooling curve is shown in the Fig. 7.
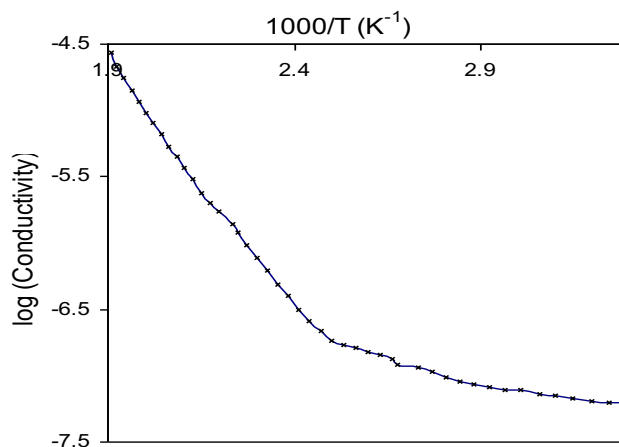

Fig. 7: Electrical conductivity for ZnSe thin films.

It is found that the conductivity during heating and cooling cycles is dissimilar suggesting that the synthesized films undergo an irreversible transformation due to annealing out imperfection throughout initial heating. At 300 K, the specific conductance of the film was found to be of order $10^{-8}(\Omega\ cm)^{-1}$, agrees well with the earlier reported value [36]. The low value of conductivity may occur due to low crystallinity and smaller thickness of the sample. It also occurs because of granule boundary discontinuities and presence of surface states. Therefore, the internuclear gap effectively raises and increases the height of the grain periphery potential. Thus, it decreases in carrier density as well as mobility. Consequently, the electrical resistivity rises. The electrical conductivity of filmhas direct correlation with rise in temperature indicating a sign of the semiconducting nature of the film. A plot shows that electrical conductivity has two regions: an intrinsic area setting at low temperature and indicated by lower slope as well as a higher temperature area related with extrinsic conduction because of the occurrence of donor states. The activation energy is estimated using exponential form of Arrehenius equation;

$$\sigma = \sigma^0\ exp\ (-Ea/RT)\text{-----------}7$$

The activation energies are 0.053 and 0.317 eV for low and high temperature region, respectively.

4 Conclusion

It was promising to develop ZnSe thin films using reactive solution through the appropriate selection of the growth parameters. The obtained films show an outstanding adherence and comparatively good morphological and crystalline properties as inferred from SEM and XRD analysis. The absorbance abruptly gets reduced to be than band gap energy. The films are semiconducting in nature with room temperature electrical conductivity of 6.13 x 10^{-8} $(\Omega\ cm)^{-1}$.

Acknowledgement

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