Optical Characterisation of ZnSe Thin Films by Using Electro Deposition Technique

A. Ayeshamariam1, M. Kashif2, S. Muthu raja3, S.Jagadeswari4, D. Saravanakkumar5, N.M.I Alhaji6, A.Uduman Mohideen7, M. Bououdina8, M.Jayachandran9

1Department of Physics, Khadir Mohideen College, Adirampattinam, 614 701, India
2Nano Biochip Research Group, Institute of Nano Electronic Engineering (INEE), Universiti Malaysia Perlis (UniMAP), 01000 Kangar, Perlis, Malaysia
3MEMS and Sensors Division, SENSE, Vellore Institute of Technology, Vellore, India
46Department of Chemistry, Khadir Mohideen College, Adirampattinam, 614 701, India
5Department of Physics, Devanga Arts College (Auto), Aruppukottai, 626 101, India
6Nanotechnology Centre, University of Bahrain, PO Box 32038, Kingdom of Bahrain
7Department of Physics, College of Science, University of Bahrain, PO Box 32038, Kingdom of Bahrain
8Electrochemical Material Science Division, Central electro Chemical Research Institute, Karaikudi, 630 004, India

Abstract—The basic aim of this research work is to present the synthesis of ZnSe thin film, by varying doping concentration of selenium oxide on ITO plate using a relatively simple and low cost traditional electrodeposition technique. The physical properties obtained are similar to that reported earlier. The compatibility of the room temperature ZnSe thin films for structural, optical properties are investigated by using the techniques, X-ray diffraction (XRD), FTIR, UV-Vis spectroscopy, and morphological studies are analysed by using scanning electron microscope, (SEM). The crystallite size was calculated ranges from 30–40 nm, and band gap values are nearly equal to 2.2 eV, the selenium oxide concentration increases the band gap of the value is also increased to minimum value. The optical band gap is found to be particle size dependent and increases with increasing Se content or it is increasing with decreasing particle size.

Keywords—ITO plate, selenium oxide, band gap

I. INTRODUCTION

World’s energy demands are met from a variety of energy sources, both conventional and non-commercial. In spite of substantial increase during the last many decades in the supply of commercial sources of energy such as coal, oil and electricity, non-commercial sources dominated by fuel wood still meet around half of our energy needs, particularly in the rural areas. Besides, being inefficient in terms of end use, loss of green wood for fuel also results in adverse impact on the environment and pollution control. There exists a substantial potential in non-conventional sources such as solar, wind and tidal energy etc. Considering the factors of continued consumption for long run, it is possible to have sustainable energy by tapping renewable energy sources particularly solar energy which is available in plenty.

Solar energy conversion is mainly classified as solar thermal energy and solar photovoltaics electricity.

The direct conversion of solar energy into electricity by photovoltaic (PV) solar cells was studied for the past 30 years [1, 2]. We are still far from making these sources cost effective. Photovoltaic solar energy conversion offers one of the few ways of producing electricity in urban areas which is free of various emissions and noise. Functional considerations, and in particular efficiency, dominated research and development, when terrestrial PV applications were developed, the same considerations of functionality and efficiency continued to be given priority among them ZnSe, CdSe and doped CdSe thin films are in queues [3]. The present thesis gives a brief account of thin film solar cells.

Thin films of group II–VI semiconductor compounds have attracted considerable attention due to their novel physical properties.[4,5] As a wide band-gap material, ZnSe is a talented candidate showing compatibility for optoelectronic devices based on the thin film technology [5,6]. The substantial interest over the years owing to their wide range of applications in various optoelectronic applications and current developments go hand-in-hand with the explosion of scientific and technological breakthroughs in microelectronics, optics, and nanotechnology [7–9].

The major technical importance of semiconductor ZnSe thin films is exhibiting simultaneously high electrical conductivity and optical transparency. For example in solar cells flat panel displays and electronic devices. The nanocrystalline II–VI films are prospective for development of resistive sensors, operating at room temperature.
There also exists interest in inclusion of ternary alloys of II–VI semiconductors in low-dimensional structures [10–13] since they offer possibilities to change their lattice constant and optical properties by changing the composition and this gives them some advantages over binary compounds. For the preparation of ternary ZnSe layers epitaxial techniques [14,15] and electro deposition are most frequently used and even the epitaxial growth methods produce compositionally disordered films.

ZnSe is the most popular material for infrared applications because of its high refractive index (2.417–2.385 at 8–13 nm), low dispersion rate at infrared (IR) wavelengths, and towering transmission band from 0.60 nm to 20 nm. ZnSe is a competitive material compared to the other thin film materials owing its compatibility [16]. Thin films of this material can be deposited by using a variety of methods, including pulsed laser ablation, electron beam deposition, magnetron sputtering, and atomic layer deposition.[17–19] While the we used electro deposition method which offers many advantages compared to the other sophisticated techniques, like reproducibility, simple mechanism, high deposition rate, and economically viability, is one of the fast synthesis methods to produce high quality thin films of large scale.

Moreover, the easy substrate loading, and high deposition rate are its additional advantages. Nevertheless, thin films synthesized at higher temperature have been studied and investigated over the years including ZnSe; however, achieving high quality thin films at room temperature is rather challenging.

Over the last few years, the family of wide bandgap II–VI semiconductors has been widely studied due to their fundamental electronic and optical properties,

1. Among them, ZnSe, with a direct bandgap of 2.67 eV at 300 °K, are attractive materials for various optoelectronic devices, such as: ZnSe: blue-light emitting diodes and lasers; as a window material in heterojunction solarcells, in the place of CdS.

As reviewed elsewhere (2), electrodeposition is a simple and versatile method for preparing thin films of these materials. In this work results on the preparation and characterization of ZnSe thin films obtained by electrodeposition method.

S. Venkatachalam et al. [20] have reported the influence of substrate temperature on the structural, optical and electrical properties of zinc selenide (ZnSe) thin films. Zinc selenide (ZnSe) thin films were deposited onto well cleaned silicon (100) and glass substrates at different substrate temperature (483 – 589 K) using vacuum evaporation method under a vacuum of 4 x 10⁻³ Pa.

The compositions of the deposited films were determined by Rutherford backscattering spectrometry and the percentage of iodine concentration is calculated as \((\text{ZnSe})_0.008\). The X-ray diffractograms reveal the cubic structure of the film oriented along the (111) direction. In optical studies, the transition of the deposited film is found to be a direct allowed transition. The optical energy gaps of the deposited films are found to be in the range from 2.72 to 2.60 eV. ZnSe/Silicon Schottky diodes were fabricated. From the current-voltage measurement the ideality factor was found to be in the range 2.01 – 3.51. From the capacitançe-voltage studies, the built in potential was found to be 1.51 V. The values of effective carrier concentration \((N_A)\) and the barrier height are calculated as 4.37 x 10¹¹ cm⁻³ and 1.95 eV, respectively.

T. W. Kim et al. [21] have reported the effect of a ZnSe buffer layer on the surface, structural, and optical properties of the ZnTe/ZnSe/GaAs heterostructures. Lattice-mismatched ZnTe epilayers on GaAs (100) substrates with and without ZnSe buffer layers were grown by using molecular beam epitaxy.

AFM, XRD and TEM measurements were performed to investigate the surface and structural properties of the ZnTe thin films. Photoluminescence, Raman scattering and TEM measurements showed that the crystallinity of a ZnTe epilayer grown on a GaAs substrate was remarkably improved by using a ZnSe buffer layer. Photoreflectance measurements showed that the strain of the ZnTe layer with the ZnSe buffer layer was smaller than that without the ZnSe buffer layer. These results indicate that ZnTe epitaxial films grown on GaAs substrates with ZnSe buffer layers hold promise for potential applications in optoelectronic devices operating in the blue-green spectral region.

A. R. de Moraes et al. [22] have reported the growth and properties of electrodeposited ZnSe-Fc and ZnSe-Co granular films. The growth process as well as optical and magnetic properties of the ZnSe-Fc and ZnSe-Co granular films deposited electrochemically has been investigated. The ferromagnetic nanoscaled particles with multidomain structure are embedded in a ZnSe matrix with a polycrystalline structure exhibiting semiconductor behaviour at room temperature have been demonstrated.

Dori Gal et al. [23] have reported the electrochemical deposition of ZnSe and (Zn, Cd) Se films from nanoaqueous solutions. The composition of the mixed selenides could be controlled by variation of the deposition current density, utilizing diffusion control of the low concentrations of Cd(ClO₄)₂.
The film composition was measured by X-ray photoelectron spectroscopy and compared with the measured bandgap values extracted from optical transmission spectra. Photoelectrochemical photocurrent spectroscopy and contact potential difference (Kelvin Probe) measurements both showed changes in apparent conductivity type with Zn concentration in the electrolyte from “n-type” (low Zn) concentration to “p-type” (high Zn).

X. H. Wang et al. [24] have reported the growth and characterization of ZnSe films prepared on ZnO/Si (111) templates. It was found that the as-deposited ZnSe films are highly oriented with Zinc blende structure, and the preferred crystal orientation is (111). The small X-ray diffraction (XRD) full-wide-half-maximum (FWHM) also suggests that the crystal quality of the deposited ZnSe films is reasonably good. From temperature dependent photoluminescence (PL) measurements, it was found that exciton binding energy, $E_{\text{B}}$, equals 25.6 m eV for the as-prepared ZnSe/ZnO/Si(111) samples.

P. Reiss et al. [25] have reported the luminescent ZnSe nanocrystals of high color purity. A new synthesis method of colloidal ZnSe nanocrystals exhibiting size–dependent optical properties is reported.

The ZnSe quantum dots are prepared in a non-coordinating solvent (octadecane) via direct reaction of zinc stearate with selenium dissolved in trioctylphosphine. ie, without the use of pyrophoric reagents. The photoluminescence of the resulting nanocrystals can be tuned in the spectral range 390-440 nm with constant emission line widths of the order of 15 nm.

Biljana Pejova et al. [26] have reported the three dimensional confinement effect in semiconducting zinc selenide quantum dots deposited in thin film form.

Experimentally measured bandgap shifts with respect to the bulk value for quantum dot thin films with various average nanocrystal sizes are compared with the predictions of the effective mass approximation model (i.e., Brus model) the hyperbolic band model, as well as of the Nosaka’s approach. It is found that the original Brus model fails to predict correctly the $\Delta E_g$ ($R$) dependence, the deviations from experimental data being largest for the smallest nano-crystals. However, using the Brus equations with a single modified parameter—the relative dielectric constant of the material, leads to an excellent agreement with the experimental observations. On the other hand, application of the hyperbolic band model leads to only a moderate improvement of the agreement with the experimental data in comparison to the Brus model.

This conclusion is drawn on the basis of excellent agreement of the predicted $\Delta E_g$ ($R$) dependence according to Nosaka’s approach with our experimental data for chemically deposited ZnSe quantum dots in thin film form. Zinc selenide (ZnSe) II-VI compound semiconductor with cubic Zinc blende structure and a direct band gap of 2.7 eV is found to be a very promising material for optoelectronics devices. It has either a saphalerite structure with lattice parameters $a = 3.820 \, \text{Å}$ and $c = 6.626 \, \text{Å}$.

II. MATERIAL METHODS

Electrodeposition technique was adopted for the preparation of Zinc selenide (ZnSe) thin films. The chemicals used for the preparation were analytical reagent grade (99 % purity, E-Merck). The electrochemical experiments were performed using a PAR scanning potentiostat (Model 362, EG&G) employing a three-electrode configuration, with the indium doped tin oxide coated conducting glass substrate as cathode, graphite plate as anode and saturated calomel electrode (SCE) as reference electrode. Before use, indium doped tin oxide substrates were treated for 15 min with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The saturated calomel electrode was introduced into the solution by lug gin capillary whose tip was placed as close as possible to the working electrode. All the experimental potentials are referred to this electrode.

An aqueous electrolytic bath containing 250 mM of ZnSO$_4$, and 2.5 mM of SeO$_2$ are nearly stoichiometric. When the ZnSO$_4$ concentration is kept below 200 mM there is no incorporation of Zn ions in the film. If the concentration of ZnSO$_4$ is increase above 250 mM there is an excess of Zn content in the films. It was observed that a very low pH<3.5 value the films grow spontaneously at high current densities making the process uncontrollable. The rapid growth of films followed by its peeling out from the substrate is observed.

At pH>3.5, precipitation of ZnSO$_4$ occurs in the deposition bath. At pH value around 2.5±0.1, there is controllable growth of films with current density around 10 mAcm$^{-2}$. Hence, the optimum value of pH for all depositions was fixed at 2.5±0.1. Deposition period was 30 minutes, as which uniform and adherent films were obtained. After 30 minutes there is a rapid growth of films followed by peeling out from the substrate. The potential of the electrolytic bath was increased or decreased from -750 mV to -650 mV. When the potential is increased -750 mV and decreased below -650 mV, there is a rapid growth of the film followed by peeling out from the substrate itself.
The potential was fixed at -700 mV versus SCE for all depositions. The optimum condition to synthesize ZnSe thin films are identified as:
(i) electrolyte concentration: 250 mM of ZnSO₄, 2.5 mM of SeO₂ and various concentrations of ZnSO₄;
(ii) solution pH: 3.0±0.1;
(iii) deposition potential: -700 mV versus SCE;
(iv) bath temperature: 75 ºC and
(v) deposition time: 30 min.

Thickness of the deposited films was estimated using 'stylus profilometer'. X-ray diffraction data of the electrodeposited undoped ZnSe sample was recorded with the help of Phase purity, crystal structure and the crystallinity of the samples were analyzed by recording the X-ray diffraction (XRD) pattern using X-ray diffractometer (PANalytical X′Pert Pro) engaging Cu-Kα radiation (λ =1.54056 Å). The surface morphology of the samples was investigated by scanning electron microscopy, SEM, (Hitachi S-3400N, Japan) respectively. Optical transmittance spectrum was recorded using a JASCO-V-570 spectrophotometer.

III. RESULTS AND DISCUSSION

Structural Characterisation XRD

All diffraction peaks are well assigned to cubic crystalline phase of ZnSe. From Figure 1, it is noted that the intensity of the Zn peaks decreases with doping of Se content and the full-width at half-maximum (FWHM) widths of the peaks changes with respect to Se content, as well indicates that crystalline size of the thin film equal to 44 nm. The diffraction pattern corresponds to 100, 110, 112, 202 and 203 of hexagonal ZnSe. All the particle sizes were calculated using the Scherrer equation from the average of three strongest peaks.

The strongest peaks can be classified as 100, 110 reflections of ZnSe. The broadening of the peaks indicates that the particles are on the nanometer scale.

The crystallite size was determined by means of the X-ray line broadening method using the Scherer equation [27]
\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

Where λ is the wavelength of CuKα radiation (λ= 0.154056 nm), is the full width at half β maximum (FWHM) of the (hkl) peak at the diffracting angle hkl 2θ, the (110) peak is used to calculate the crystalline size D.

The presence of single sharp peak in the figure confirms the polycrystalline nature of the ZnSe thin film with high periodicity and crystallinity. The preferential orientation of the crystal plane (110) corresponds to the Bragg’s reflection at 2θ = 39.08° instead at 2θ = 45.37°, it may be due to the deposition of ZnSe thin film on indium tin oxide plate.

![Figure 1 XRD structure of ZnSe thin films after annealing 300°C for an hour for 1%, 3% and 5% of selenium oxide](image)

The lattice parameter c of the as-deposited room temperature ZnSe thin film is calculated using the formula for the hexagonal crystal structure. For the hexagonal crystal system, the lattice parameter c is related to d with the following equation
\[ \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \]  \hspace{1cm} (2)

\[ 2d_{hkl} \sin(\theta) = m \lambda \]  \hspace{1cm} (3)

Where h, k, and l are all integers, (hkl) is the lattice plane index, a and c are lattice constants, d_{hkl} is distance between two consecutive planes (m=1) with lattice plane index (hkl).

The lattice parameter c and the interplanar distance d calculated from the XRD patterns are a = 3.805 Å and c = 6.123 Å, respectively. But according to JCPDS file number 150105 expected results of a = 3.996 and c= 6.55 for 110 plane.

By utilizing the average grain size D, the dislocation density δ is calculated using the following Relation, [28]
\[ \delta = \frac{1}{D^2} \text{ lines/m}^2 \]  \hspace{1cm} (4)
Where \( D \) is crystallite size of ZnSe thin film in units of nm. The value calculated is 5.014 x 10\(^{15}\) linesm\(^{-2}\). This is in agreement with the other experimental results and research reports. After annealing the film to 300°C for an hour we get the well crystalline peak of ZnSe this for 5% of doping of selenium oxide.

Figure 1 shows the spectrum of different selenium oxide concentration of 1%, 3% and 5% were coated on ITO plates at annealing temperature 300°C. From the spectrums of figures 1, it can be observed that the XRD pattern shows a prominent peak at 27.2 degrees of 5% of concentration, corresponding to the diffraction from the (111) plane and shifted to 30.1 for 3% and 32.9 for 1%. No other XRD peak is evident in the scanned angular range of 20-80°. The lattice parameter ‘a’ is determined for a cubic structure by the following expression (1):

\[
\text{By considering that } h, k, l = 1, 1, 1 \text{ for the ZnSe film, a lattice parameter value } a = 5.6627 \text{Å} \text{is obtained. This result is close to the reported data JCPDS card No 88-2345. The full width at half maximum (FWHM) of the observed XRD peak is about 0.2175° for 5% and 0.2207° for 3% and 0.2230° for 1% and used to calculate the average crystalline size } D, \text{ from the Debye–Scherer formula [2]. The calculated } D \text{ value is 37.59 nm for 5%, 37.29 nm and 1%, 37.16 nm. Therefore, the ZnSe film is well crystalline and oriented along (111) direction with Face centered cubic structure on ITO substrate. The absence of any of the strong reflections confirms the formation of single-phase ZnSe films on ITO substrate [2]. In figure (2) a,b,c shows the XRD patterns of the ZnSe thin films of different selenium oxide concentrations deposited on ITO substrates respectively.}

The XRD results of both films exhibit cubic phases. Therefore, the films coated on ITO substrates required some thermal curing to obtain single phase ZnSe films. Thickness of the films were measured by using stylus profilometer and the values are tabulated. From the XRD spectrum, the various parameters are calculated and tabulated below. The peak widths indicate a good grain size. All the peaks identified are from ZnSe, and no additional lines corresponding to Zn or other oxides are present. This indicates that the electrodeposition method could also be useful for the preparation of crystalline ZnSe thin films.

**UV-Studies**

The samples are transparent in a large range of wavelength (bigger 350 nm). In order to calculate the optical band gap we used the Tauc relation,

\[
\alpha \ h \nu = B \ (h \nu - E_g)^n \quad (5)
\]

Where \( \alpha \) is the absorption coefficient, \( B \) is a constant, \( \nu \) energy of incident photons and Exponent \( n \) depends on the type of the transition, \( n \) may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively [29].

**Bandgap Values**

Since \( \alpha \) and transmittance \( T \) are correlated as,

\[
T = \exp(-\alpha L) \quad \text{(6)}
\]

\[
\alpha = -(\ln T)/L \quad \text{(7)}
\]

Where \( L \) is the thickness of the sample, for direct allowed transition \( n=1/2 \) we have,

\[
(h \nu \ln T)^2 = B^2 L^2 (h \nu - E_g) \quad \text{(7)}
\]

The exact value of the optical band gap is determined by extrapolating the straight-line portion of \( (h \nu \ln T)^2 \) vs. \( h \nu \) graph to the \( h \nu \) axis (Figure 4). The values of the optical band gap are equal to 2.78 eV. The optical band gap values are higher than the bulk value of ZnSe (2.2 eV) for the deposited film annealed at 300°C [30], the optical band gap is found to be particle size dependent and decreases with increasing Se content.

**Figure 2 shows optical transmittance spectra of the samples (a) 1% (b) 3% and (c) 5%**

**Figure 3 Transmittance spectrum of ZnSe films on different selenium content (a) 1% (b) 3% and (c) 5%**

**PL Studies of ZnSe thin films**

All the spectra measured at room temperature contain two characteristic regions. The narrow PL band centered at 2.7 eV is apparently caused by near-band-edge (NBE) radiative recombination, while the broad photoemission band in the vicinity of 1.9 eV is caused by the optical transitions involving deep levels in the band gap. In ZnSe and ZnSe, annealing in results in enhancement of the low energy part of the composite band while the emission in the high energy side of the band is suppressed.
On the contrary, the annealing of ZnSe has no significant effect on its PL spectrum shape. Since the emission enhancement by annealing is so effective in the increase of deep-level-related emission efficiency in all samples under study, thereafter in this paper, we present only the results obtained on the samples annealed in Zn ion.

**Figure 4**: Bandgap values of ZnSe thin films for (a) 1% (b) 3% and (c) 5%

**Figure 5**: Photoluminescence studies of ZnSe thin films (a) 1% (b) 3% and (c) 5%

**Figure 6**: FTIR spectrum of the ZnSe films deposited on ITO substrate in the wavelength range from 400 to 4000 cm$^{-1}$ were taken. The broad absorption peaks at 2600 to 3500 cm$^{-1}$ and 2350 cm$^{-1}$ are attributed to the stretching vibration of the O-H bond from water molecules and C=O bond stretching vibration of CO$_2$ molecules present in the atmosphere. The peaks observed at lower frequencies (finger print region) at 560, 546 and 530 cm$^{-1}$ corresponds to the inorganic molecules which are of interest (ZnSe).

**Morphological Studies**

Scanning electron microscopy (SEM) was used for morphology and size distribution investigations of the thin films. Figure 7 shows the grain morphological pictures of ZnSe films respectively. All the as-prepared powders show uniformly spherical grains. Each spherical grain is composed of very minute crystallites of nano dimension with the increase of temperature, spherical grains fused together and form bigger grains but with good contact between each grain boundary.

**IV. CONCLUSION**

In a summary ZnSe thin film are successfully deposited by electrodeposition method. The as-deposited crystals are well crystallised having hexagonal and cubic structure and crystallite sizes within the range of 44 nm. This method is used for simple and appears to be suitable for the production of larger amounts of ZnSe crystals. The microstructural characterization reveals the device quality nature of these films. Optical studies show the presence of nanocrystalline particles whose size is nearly 44 nm. A direct optical band gap of 2.78 eV was found for the investigated films. Surface morphology results show that the device quality nature of ZnSe films deposited at 75 °C with a thickness of about 52 nm were supported by other optical data.

The ZnSe thin films were prepared using Electrodeposition technique on different substrate at room temperature. In the XRD analysis the structure of the film deposited on ITO substrate is found to be cubic and well crystallined, are exhibiting mixed cubic and hexagonal structure.
The optical band gap energy found in UV visible absorption spectrum indicates, the optical band gap energy of ZnSe nano crystalline thin films on different substrates (2.75, 2.78 and 2.82 eV) is larger than the value of 2.7 eV for the bulk. It is known that the optical band gap of nano crystalline ZnSe semiconducting thin films can be higher than that of bulk ZnSe (2.82 eV) due to quantum size effects. PL studies confirm the ZnSe film coated on ITO substrate is well moderate crystalline and defects free.

REFERENCES