

**Final Report of the MRP(S)-0659/13-14/
KLKA004/UGC-SWRO dated 28.03.2014**

on

**Optical band gap engineering in zinc selenide thin films
prepared by chemical methods by post thermal
treatment and doping for photovoltaic and luminescent
applications**

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to

University Grants Commission

Declaration

I hereby declare that this report is an authentic record of work carried out by me under UGC Minor Research Project, MRP(S)-0659/13-14/KLKA004/UGC- SWRO dated 28.03.2014 on “Optical band gap engineering in zinc selenide thin films prepared by chemical methods by post thermal treatment and doping for photovoltaic and luminescent applications”.

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Contents

Chapter 1

Introduction to thin film optoelectronics : 4

Chapter 2

Structure and optical properties of zinc selenide : 9

Chapter 3

Thin film deposition and characterization methods : 12

Chapter 4

Effect of annealing on the optical properties of
Chemical bath synthesized ZnSe thin films : 19

Chapter 5

Variation in the band gap due to the effect of
concentration of Na_2SeSO_3 on the properties
of ZnSe thin films : 25

Chapter 6

Effect of annealing on nanocrystalline ZnSe thin films
grown through SILAR technique : 28

Chapter 1

Introduction to thin film optoelectronics

1.1. Introduction

A thin film is a material created by the random nucleation and growth processes of individually condensing or reacting atomic or ionic or molecular species on a substrate. The structural, chemical and physical properties of such materials depend strongly on a number of deposition parameters and thickness. Their properties can be controlled and reproduced by precisely controlling many of the deposition parameters [1]. The thin film processes are in general eco-friendly and can be called as ‘green’ processes.

Some of the semiconductor materials with a tunable band gap allow the solar cell to absorb a larger fraction of the solar energy spectrum. Semiconductor nanocrystals are regarded as useful materials for building hybrid organic–inorganic third-generation solar cells and other optoelectronic devices. This utility is due to the fact that their optical band can be tuned by both material selection and quantum confinement.

Near to the end of the twentieth century, in an effort to increase integration, enhance functionality and reduce energy consumption, the focus of the development of semiconductor devices was on miniaturization. As we enter the twenty-first century, we visualize nanometer-sized semiconductor devices that can directly interact with individual atoms and molecules at the nanometer level like quantum sensors. Like this, the development of advanced crystal and thin-film synthesis technologies capable of realizing high crystalline quality and purity of materials is an enabling step toward making such semiconductor devices a reality [2].

1.2. Optoelectronics

Optoelectronics is the study and application of electronic devices that interact with light, and thus is usually considered a sub-field of photonics. In this context, light often includes invisible forms of radiation such as gamma rays, X-rays, ultraviolet and infrared. Optoelectronics involves the study and application of electronic devices that include Light emitting devices, (e.g. LEDs and laser diodes) Light receiving devices, (e.g. photo detectors and solar cells) Display instruments, (e.g. LCDs and LED display) Data storage instruments, (e.g. optical disks related instruments) Input/output instruments, (e.g. scanner

and digital cameras) Medical instruments,(e.g. lasers related instruments for medical usage) Illumination instruments, (e.g. LED lightings) Extended Systems Optical Communication Systems Solar power system etc.

The ability to control both the shape and size of semiconductor nanocrystals is essential for precise tuning of their optical and electronic properties, as well as their overall functionality, to enable their use in proposed applications [3]. A variety of semiconductor nanostructures with different shapes has been reported in the literature, including nanowires [4], nanotubes [5], and hollow nanospheres [6]. These nanostructures have potential applications in nonlinear optics, solar cell technology, and in the miniaturization of electronic systems leading to novel optoelectronic devices [5].

The extraordinary properties of semiconductor nanoparticles resulting from quantum confinement have drawn considerable interest and are currently undergoing in depth investigation [7]. Semiconductor nanoparticles exhibit size dependent electronic band gap energies, melting temperatures, solid–solid phase transition temperatures and pressures. In addition to these, doped semiconductor nanoparticles have tremendous potential for use in light emitting applications.

These nanoparticles may find applications in nonlinear optical devices, photocatalysis, etc. The challenging search for blue/green laser diodes and light emitting diodes (LEDs) has been ongoing for only a few decades. While the GaAs-based (III-V direct bandgap 1.424 eV) devices dominated the longer wavelength light emitters, the members of II–VI compound semiconductors have immense technological importance in different applied branches of science and technology since many of them are attractive candidates for the realization of blue/green laser diodes and LEDs[8].

In the near past, solar cells have experienced a peak in manufacturing capacities, which was enabled by significant advances in manufacturing technologies [9]. Now, the market is dominated by crystalline Si solar cells but thin film technologies, in particular thin film chalcogenide semiconductor solar cells (Cu(In,Ga)(S,Se)_2 and CdTe), have considerable production volumes. The increased commercialization of the thin film chalcogenide semiconductor solar cells has led to considerable advances in solar cell efficiencies [10]. Both Cu(In,Ga)(S,Se)_2 and CdTe solar cells can be prepared with efficiencies above 20% [11-12]. Both are higher than that of polycrystalline Si.

1.3 Thin film solar cell devices

A solar cell is a junction device formed by placing two electronically dissimilar materials together with a thin electronic barrier in between to separate the charges. The efficiency of the device must ensure high conversion efficiency of solar photons and high collection efficiency of excited charge carriers [13]. Thin film solar cells contain sub-micron thick semiconductor layers. When sunlight is absorbed by the active material it loses electrons which flow through the material to produce electricity. The process of converting light to electricity is termed the photovoltaic effect.

Thin film solar cells consist of layers of different materials in thin film form. Generally the solar cell consists of a substrate to hold on the thin film layers, transparent conducting oxide (TCO) to draw the current to the outer circuit, buffer layer (p or n type) to create the junction with the absorber layer with minimum absorption losses and to drive the generated carries to the electrode, absorber layer (n or p type) for generating carriers on absorption of light with minimal transmission or reflection losses and metal contact layer as the bottom electrode [14].

A heterojunction solar cell has p-n junction between different semiconductors. So the absorber and the buffer layers are made of two different materials which introduce a possibility of using materials having different band gaps. Buffer layer with a wider band gap enhances the amount of light reaching the junction which is the main difficulty in homojunction solar cells. Buffer layer in combination can minimize the interface recombination losses and help to attain large band-bending [15]. The absorbing layer must have a high absorption coefficient in order to be effective in the generation of current and a suitable band gap to provide good voltage.

1.3.1 Thin-film solar cells based on compound semiconductors Solar cells based on CdTe

With a direct optical energy band gap of 1.5 eV and high optical absorption coefficient for photons with energies greater than 1.5 eV, only a few microns of CdTe are needed to absorb most of the incident light. A front contact is provided by depositing a transparent conductive oxide (TCO) onto the glass substrate. The TCO layer has a high optical transparency in the visible and near-infrared regions and high *n*-type conductivity. This is

followed by the deposition of a CdS window layer, the CdTe absorber layer, and finally the back contact.

CdS has been found to be the best material, but alternatives such as ZnS, ZnSe, In₂S₃, (Zn,In)Se, Zn(O,S)[16], and MgZnO [16] can also be used. The buffer layer can be deposited by chemical bath deposition, sputtering, chemical vapor deposition, or evaporation, but the highest efficiencies have been achieved when using a wet process as a result of the presence of Cd²⁺ ions [17].

1.4 The role of the buffer layer in thin film heterojunction solar cells

The basic function of a buffer layer in a heterojunction is to form a junction with the absorber layer and admitting a maximum amount of light to the junction region and absorber layer [18]. In addition, this layer should have minimal absorption losses and should be capable of driving out the photo generated carriers with minimum recombination losses and transporting the photo generated carriers to the outer circuit with minimal electrical resistance. For high optical throughput with minimal resistive loss the band gap of the window layer should be as high as possible and the layer should be as thin as possible to maintain low series resistance.

1.5 Optoelectronic devices -LED

The semiconductor laser diodes operate well in the wavelength range 200nm to 3μm, which can be the optimized wavelength range. The 3–30 μm spectral regions are an excellent range within which there are a wide variety of laser diode active region options to design device and theory concepts to the test.

The II-VI semiconductors become significant owing to their range of band gap energies, including the entire visible spectrum and at the same time enhancing direct band gap transitions. The difficulty in achieving both n- and p- type conduction in a single wide band gap II-VI compound prevented the formation of a p-n junction, the structure at the heart of an electrical injection device. These growth techniques like Molecular Beam Epitaxy, Metal Organic Chemical Vapour Deposition etc. enabled greatly improved material quality in metastable structures and an opportunity to extend the quantum confinement revolution to the II-VI, which had begun in the GaAs family. It was made possible to incorporate suitable impurity into ZnSe to produce useful p-doping levels. Almost simultaneously a p-n junction LED and the p-n junction laser diode were brought in to reality. The latter efforts

have been ongoing to improve the performance and lifetime by addressing a variety of problems including doping, contacts, epitaxial growth and device processing.

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Chapter 2

Structure and optical properties of zinc selenide (ZnSe)

2.1 Introduction

Thin films of group II–VI semiconductor compounds have attracted considerable attention due to their novel physical properties [1-2]. One of the most striking features of wide band gap II–VI semiconductors is the strong influence that point defects can affect electrical and optical properties [3]. These defects can be involved in the formation of energetically favorable compensating centers causing difficulties to achieve a sufficient electron or hole concentration in p–n junction devices or substrates. In other cases, they create shallow levels producing unwanted high background doping. Furthermore, native defects can influence the absorption and luminescence properties dramatically [4-5].

Most II–VI group materials are direct band gap semiconductors with high optical absorption and emission coefficients. Cadmium sulphide, cadmium telluride and zinc selenide are examples. Cadmium telluride (CdTe) is a leading candidate for solar cell applications. But the toxicity of cadmium forms an important challenge in this field. So it is necessary to find out a suitable substitute for CdTe and CdS buffer layer. The possibility of a beneficial chemical modification of the absorber surface for the case of CdS on CuInSe₂ has also been proposed. The interface formed by chemical bath deposition of ZnSe films on CuInS₂ absorbers was studied using different techniques. The composition of the CuInS₂-ZnSe interface with depth resolution was analysed by XPS. At the same time, the electro reflectance technique was used to obtain ‘in-situ’ non-destructive, information of this interface working in the solar cell [6].

Basic requirements of best buffer layer are wider band gap, better lattice match and good conduction band with respect to the absorber layer. High efficiency values in Cu (In, Ga) (S, Se) ₂- based solar cells have been achieved using CdS buffer layers. Due to the toxic nature of CdS layers much attention has been focused on developing Cd-free buffer layers. However for industrial production and for environmental protection, it is necessary to replace CdS by non-toxic alternative buffer material [6]. ZnSe is a promising candidate for the replacement of the toxic CdS material in the buffer layer, which in addition more transparent in blue spectral range. ZnSe is not only environment friendly but have wider band gap as compared to CdS (E_g=2.4 eV). Consequently ZnSe buffer layer may transmit

even higher energy photons to the absorber layer of the solar cell. It possess better lattice match with CIG(S,Se)₂ also. There are reports in the literature that it is possible to fabricate ZnSe based solar cells with efficiency >11% [7-8].

2.2 ZnSe

Zinc selenide has a wide energy band gap at room temperature. ZnSe, an n-type non toxic semiconducting material is a member of IIA–VIB group. It exhibits unique physical properties such as a large and direct optical band gap ($E_g=2.7$ eV for bulk at room temperature), high refractive index, and low optical absorption in the visible and infrared spectral region. Due to its high bandgap, ZnSe has gained considerable attention in the field of blue emitters and blue lasers. The major obstacle to the use of ZnSe as a laser material arises from the ease with which defects are created and propagate into the active medium. The electronic properties of ZnSe, in terms of electron and hole mobilities, are poor, thus gives rise to large resistances [9].

There are a number of reports on the different structural, optical and electrical properties of ZnSe polycrystalline thin films prepared by various techniques such as chemical vapour deposition, MOCVD, Electrodeposition, Photochemical deposition, chemical bath deposition(CBD), pulsed laser deposition and thermal evaporation [10-18].

2.3 Optical properties

High refractive index materials in multilayer optical coatings have low absorption over a broad wavelength range. They are now widely used for the preparation of semiconducting elements [10].

2.4 Applications of ZnSe

ZnSe films have several potential applications in optoelectronic devices, optical coatings, thin film transistors and heterojunction solar cells [9-10]. It also find very wide applications in areas such as solar energy conversion (as a window material), laser diodes, blue green LEDs and electroluminescence since band gap of ZnSe is direct and large enough for obtaining blue emission at room temperature [19-20]. ZnSe is a suitable candidate for red, light emitting diodes, laser screens, thin film transistors, photo electrochemical cells etc.

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Chapter 3

Thin film deposition and characterization methods

3.1 Introduction

A wide Variety of techniques are available for synthesizing and characterizing nanostructured films. Most of the thin films synthesized have different properties from their corresponding “bulk” material. The techniques utilized to deposit these materials have a large impact on their final properties.

3.2 Methods of deposition

Thin films can be synthesized by either physical or chemical methods.

In physical methods, the material is transferred from the source to the substrate with the help of some external energy. Chemical method involves chemical reaction and the precursors are mostly components undergoing reaction at the substrate surface or near the substrate. Chemical synthesis can be carried out in either the solid, liquid or the gaseous state.

Chemical methods include gas phase chemical processes such as conventional chemical vapour deposition (CVD), Plasma-enhanced chemical vapor deposition (PECVD), laser CVD, metal organo chemical deposition (MOCVD) and plasma enhanced chemical vapour deposition [1]. Techniques like, molecular beam epitaxy[2], chemical bath deposition[3] spray pyrolysis, pulse electrodeposition, electroless deposition, successive ionic layer deposition and reaction (SILAR), chemical bath deposition (CBD), and pulsed laser deposition, sol–gel deposition, photo assisted chemical deposition technique [4-5] etc. also come under chemical deposition of the ZnSe films.

Wet chemical techniques include chemical bath deposition, spray pyrolysis, Successive ionic layer adsorption and reaction (SILAR) [6-7], electrodeposition, electroless deposition, anodization, spin coating, dip coating, hydrothermal method etc. Unlike vapor-phase processes, techniques that use liquids as the deposition medium do not rely on line-of-sight deposition. It does not require high quality substrates with planar surfaces, and the film synthesis can be operated at room temperature without the need for vacuum.

3.2.1 CBD process

Chemical bath techniques are well known for polycrystalline or amorphous thin films. CBD is more advantageous than other methods because it is the conventional method with the

advantages of economy, convenience, ease of scaling up to large area deposition and high degree of direct composition control. Other main advantages of the CBD method are no requirement of sophisticated instrument, low processing temperature and non-polluting properties. CBD is attractive due to its obvious advantages of low-cost, low-temperature operation and environmental friendliness.

Schematic diagram of the experimental set up of CBD technique is shown in Fig.

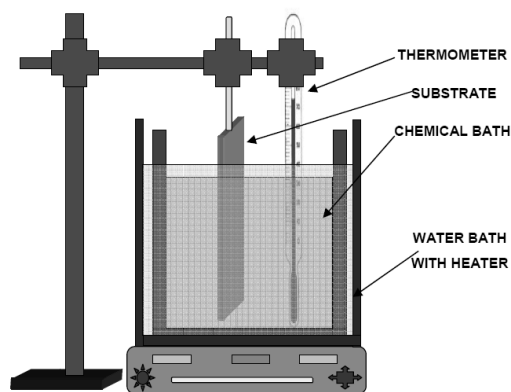


Fig. 3.1: Experimental set up of CBD technique

In this study, by appropriate complexing agents and controlling the bath parameters like pH, temperature of bath etc., good quality ZnSe films were synthesized by CBD on glass substrates with high quality and reproducibility.

3.2.2 SILAR Deposition

The successive ionic layer adsorption and reaction (SILAR) technique was introduced by Ristov et al. [8] and the name was ascribed by Nicolau [9]. Among the different methods for film deposition, the relative simplicity of SILAR method and its potential application for large area deposition make it very attractive. The SILAR method is based on immersion of the substrate into separate cation and anion precursor solutions, and rinsing in between every immersion with ion-exchanged water to avoid homogeneous precipitation [8-11].

Adsorption is a surface phenomenon between ions and surface of substrate which is possible due to attractive force between them. These forces may be cohesive forces, Vander Waals forces or chemical attractive forces. Sequential reaction at the substrate surface followed by rinsing after each stage enables heterogeneous reaction between the solid phase

and the solvated ions in the solution. Easy control on film thickness by adjusting number of deposition cycles is the beauty of this method.

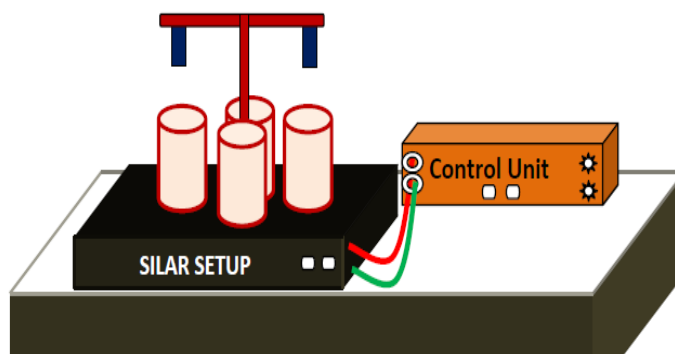


Fig 3.2: Successive Ionic Layer Adsorption and Reaction

In principle it is possible to fabricate thin films layer by layer by the SILAR method. Due to the low deposition temperature, diffusion of ions in the thin film is low; hence SILAR is suitable for growing thin multilayered structures. In this method, concentration and of pH cationic and anionic solution, the duration of adsorption, reaction and rinsing are easily controllable.

This environmentally benign soft chemical route has been used to synthesize zinc chalcogenide thin films [12-14] with good optical properties. The microprocessor controlled SILAR deposition set up used in this work is shown in Fig. 3.2. In this study SILAR method has been used to deposit pure and doped ZnSe thin films.

A typical SILAR deposition cycle was comprised of four steps. In the first step the substrate was immersed in the cationic precursor solution for a definite time so that the zinc-complex ions are adsorbed on the substrate. In the next step the substrate was rinsed in distilled water for a definite time to remove the loosely held ions. This is followed by dipping of the substrate in the anionic precursor solution with the chalcogenising agent (sodium selenosulphate) during which reaction between cations and anions occurs at the surface of the substrate leading to the formation of ZnSe. Finally the excess unreacted species at the substrate surface was removed by the rinsing in distilled water for the same duration as in the second step.

3.3 Substrate Cleaning

Cleaning the substrate is the process of reduction of surface contamination to an acceptable level for obtaining desirable film properties. Here, chromic–sulfuric acid solution was used

as the reactive cleaning liquid. Cleaning solution prepared using potassium dichromate and sulfuric acid provides free oxygen for cleaning. Commercially available microscopic glass slides of dimension 76 mm × 26 mm × 2 mm were first kept in the detergent solution for 2-3 days and then were boiled in chromic acid for a few hours. The residues left on the surface were then removed by rinsing the substrate very thoroughly with pure distilled water and finally ultrasonically cleaned with distilled water before use. The substrates rinsed in distilled water were dried by blowing hot air and used for film deposition.

3.4 Thin film characterization tools

3.4.1 Thin film thickness

The physical properties of a thin film are highly dependent on their thickness.

The difference in mass of film coated substrate and bare substrate gives the mass of the film. The film thickness (t) can be computed from the data obtained from gravimetric method also using Eq. (3.1).

$$t = \frac{m}{pA} \quad (3.1)$$

Where ' m ' is the mass of the film deposited on area ' A ' and ' p ' is the bulk density of the material.

In this study, thickness of the films determined by gravimetric method was carried out by using an analytical balance (SHIMADZU model AUY 220) of readability 0.1 mg.

3.4.2 Structural characterization

The X-ray diffraction pattern of a pure substance is like a fingerprint of the substance. X-ray diffraction (XRD) studies were carried out to study the crystallographic properties of the thin films.

X-ray diffraction results from the interaction between X-rays and electrons of atoms. Depending on the atomic arrangement, interferences between the scattered rays are constructive when the path difference between two diffracted rays differs by an integral number of wavelengths. This condition is called Bragg's law. This selective condition is described by the Bragg equation given in Eq. (3.2) and is called Bragg's law.

$$n\lambda = 2d\sin\theta \quad (3.2)$$

Where ‘ λ ’ is the wave length, ‘ d ’ is the d -spacing and ‘ θ ’ is the Bragg angle, which is half the angle between incident and reflected beam corresponding to the lattice plane.

For determining the physical and chemical properties of the thin film material, the diffraction patterns of the thin films, which were obtained experimentally, are compared with the standard powder diffraction files in the JCPDS.

Grain size

The mean grain sizes of the films can be determined using the FWHM of the diffraction peaks by the Debye- Scherrer’s equation given by,

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (3.3)$$

where 0.94 is the value of the shape factor[21], ‘ λ ’ is the wavelength of X-rays which is 1.5406 nm for $\text{CuK}\alpha$, ‘ β ’ is the FWHM of diffraction peak measured in radians and ‘ θ ’ is the Bragg’s angle which corresponds to diffraction peak.

3.4.3 Optical studies

Optical properties of thin films are of great importance because they find applications in various optoelectronic devices and there is a considerable deviation of optical parameters of nanostructures from that of a bulk material. The optical properties of a semiconductor thin film can be defined as any property that involves the interaction between electromagnetic radiation and the semiconductor. This includes absorption, transmission, diffraction, polarization, reflection, refraction, and scattering effects. The electromagnetic spectrum gives an overview of the types of measurements and physical processes characteristic of various regions of interest involving the optical properties of semiconductors.

Buffer layer, used near the top of a cell, is beneficial for optical enhancement because of reduced absorption and reflection losses. It assists in improving the cells efficiency by separating the contact, which has high minority-carrier recombination loss from the absorber layer. An effective injection of carriers (between the face electrode and the absorbing layer) and a maximum transmission of light can be attained by using optimum material as the buffer layer. This layer is usually made from high-optical quality, n-type films based on a wide band gap semiconductor compound.

When a semiconductor is illuminated with light, electrons absorb photons and undergo transitions to higher energy levels. If the energy of the incident light ($h\nu$) is greater than

the band gap (E_g) of the semiconductor ($h\nu \geq E_g$), then valence band electrons are excited into the conduction band. Optical absorption resulting from such band-to-band transitions is known as fundamental absorption, and the minimum energy at which such absorption takes place is called the fundamental absorption edge. The fundamental absorption edge energy is determined by the semiconductor band gap.

The percentage of incident light absorbed by a particular semiconductor depends on the transition probability of electrons between the valence and conduction bands.

Hence, the optical energy band gap of a semiconductor can be determined by studying the absorption of incident photons by the material. The optical absorption intensity can be measured experimentally in terms of the absorption coefficient (α). The photon energy dependence of the absorption coefficient for direct allowed and indirect transitions is given by Eq. (3.5) and Eq. (3.6) respectively.

$$\alpha = (A/h\nu) (h\nu - E_g)^{1/2} \quad (3.5)$$

$$\alpha = (A/h\nu) (h\nu - E_g)^2 \quad (3.6)$$

Where, 'A' is the parameter, which depends on the transition probability. The rise of the absorption coefficient at the fundamental absorption edge is steeper due to the higher probability of interband electron transitions in direct band gap semiconductors than in indirect band structures.

The absorption coefficient of the ZnSe films can be deduced from the absorption or transmission spectra using the relation,

$$I = I_0 e^{-\alpha t} \quad (3.7)$$

Where, 'I' is the transmitted intensity and 'I₀' is the incident intensity of the light and 't' is the thickness of the film. In direct transition, $(\alpha h\nu)^2$ varies linearly with $h\nu$ above the optical band gap energy of the films. The optical energy band gap of the films can be determined by plotting $(\alpha h\nu)^2$ against photon energy ($h\nu$). Accordingly, the energy band gap can be obtained by extrapolating the straight-line portion of the curve to the $h\nu$ -axis.

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Chapter 4

Effect of annealing on the optical properties of chemical bath synthesized ZnSe thin films

4.1 Introduction

The role of solution pH on the film properties is also quite important for synthesizing high quality thin films [1]. ZnSe is an important compound in optoelectronics and thin film photovoltaics. Post deposition treatments can modify properties to a greater extent in a favorable way [2-3]. Presently CdS is being extensively used as a buffer layer for higher efficiency in CIGS-based solar cells. Although the CBD-CdS buffer layer provides the above mentioned advantages for outstanding TFSCs performance, the wavelengths of the electromagnetic spectrum lower than 520nm cannot be transmitted through the absorber layer due to the relatively narrow band gap energy of 2.4 eV of CdS [4-6]. This results in a drop of the quantum efficiency in comparison to the theoretical efficiency. Also the toxicity of Cd demands to develop cadmium free eco-friendly buffer layers [7].

Here we report the synthesis of thin films of ZnSe by CBD technique using cationic precursor zinc acetate. Sodium selenosulphate is the chalcogenizing agent and hydrazine hydrate solution is used as the complexing agent [8]. The effects of post deposition treatments such as UV irradiation and annealing on structural, optical and electrical properties of these films have been studied.

4.2 Experimental details

The experimental set up of CBD is shown in Fig.3.1. The zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) was used as the cationic precursor in this study. Prior to the preparation of bath, 0.2M sodium selenosulphate solution was prepared by refluxing 2g selenium powder and 6.2g sodium sulphite in 40ml de-ionized water for 6 hrs at a temperature of 70°C. As this solution is relatively unstable, it must be freshly prepared prior to the thin film deposition process.

Sodium selenosulphate (Na_2SeSO_3) was used as the chalcogenizing agent. The volume and molality of cationic precursors was optimized to 20ml and 0.5 M and that of anionic precursor to 20ml and 0.05M respectively after repeated trials. 80% hydrazine hydrate (HH) was used as complexing agent. The volume of HH was optimized to 5ml to obtain uniform deposits. After addition of complexing agent the mixture was thoroughly stirred

using a magnetic stirrer. This was followed by the addition of 10ml of 0.5M buffer solution. The ammonium acetate salt was used as buffer. The resultant solution has a milky precipitate. Desired amount of ammonia solution was added to dissolve the turbidity of the solution under constant stirring till a clear and transparent solution was obtained. Finally 20ml of 0.05M sodium selenosulphate solution was added and stirred continuously to obtain a homogenous solution.

The deposition was carried out at a constant temperature of 70⁰C for 1.5h. Pre-cleaned soda lime glass substrates were used for deposition. After deposition, the substrates were removed from the bath. The thin films deposited on to the side of the substrate closer to the wall of the beaker were retained for various measurements, and that on the other side was removed by a cotton swab moistened with dilute hydrochloric acid, followed by rinsing with de-ionized water for a few minutes to remove any loosely adhered ZnSe particles on the surfaces, and was finally dried in air. The as synthesized sample was named ZnSe1 and annealed and post deposited UV irradiated films were named ZnSe2 and ZnSe3 respectively.

4.3 Results and discussion

4.3.1 Thickness of the films

The films seem to highly uniform and are pale yellow in colour. The thickness of the films is determined by gravimetric technique using eqn. (3.1). The estimated values are shown in Table 4. 1.

Table 4.1: Variation of thickness of the samples

Sample	Thickness(nm)
ZnSe1	426.876
ZnSe2	347.88
ZnSe3	528.35

4.3.2 Structural studies

Fig 4.1 displays the XRD pattern of the samples deposited. All the samples exhibit nanocrystalline structure with predominant orientation along different directions. The diffraction peaks are indexed and compared with standard values.

The as prepared sample exhibits polycrystalline hexagonal structure [JCPDS Card No.80-0008] with predominant orientations along (101) and (002) directions. The annealed sample

shows same hexagonal polycrystalline structure with directions of orientations along (100), (101) and (102). Only the orientation (101) is preserved and thermal annealing caused the (002) orientation to change to (100) and (102). The UV irradiation after deposition caused no structural change to the ZnSe crystal. It also exhibits hexagonal crystal structure. The direction of orientation (002) is preserved and (101) changes to (100).

The full width at half maximum (FWHM) corresponding to predominant orientation varies from sample to sample indicating variation in the crystallite size. The crystallite size is calculated using Debye-Scherrer's formula given by eqn. (3.2). The crystallite size is tabulated in Table 4.2.

Table 4.2: Variation in grain size of the samples

Sample	Grain size(nm)
ZnSe1	48.95
ZnSe2	56.76
ZnSe3	46.44

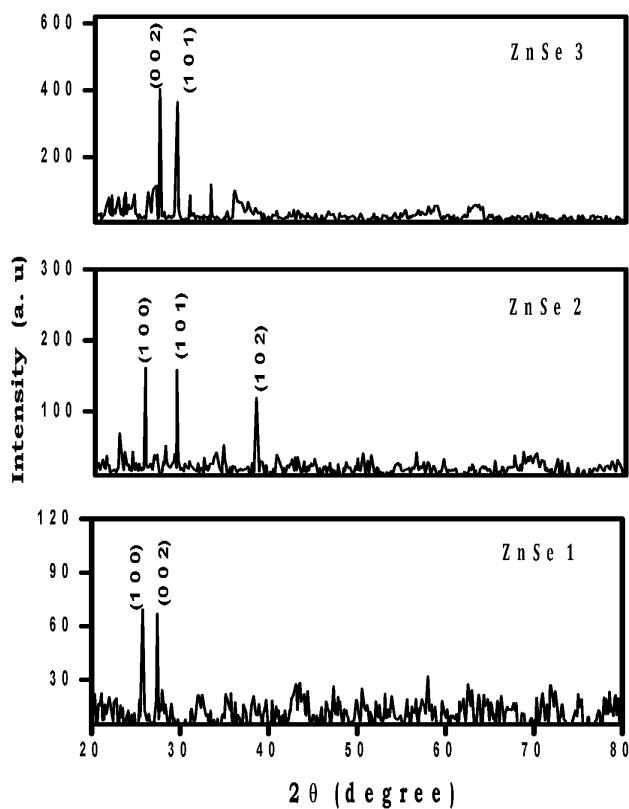


Fig 4.1 XRD patterns of the ZnSe samples

4.3. 3 Optical studies

The optical properties like absorption and transmission spectra were taken using a Varian Carry 5000 UV-Vis-NIR spectrophotometer in the range 200-2000nm. The optical transmittance in the spectral range 300-900 nm of as synthesized zinc selenide films is shown in Fig.4.2. The percentage of transmittance varies for samples synthesized with different post deposition treatments. All the samples exhibit good transmittance in the visible region, confirming their suitability for TFSC buffer layers and comparatively higher transmittance in the wavelength region greater than 750 nm. It is observed that transmittance is enhanced by post deposition treatments. Figure shows that the uniform transmittance is increased slightly by UV irradiation where as thermal treatment of the film increases the transmittance considerably.

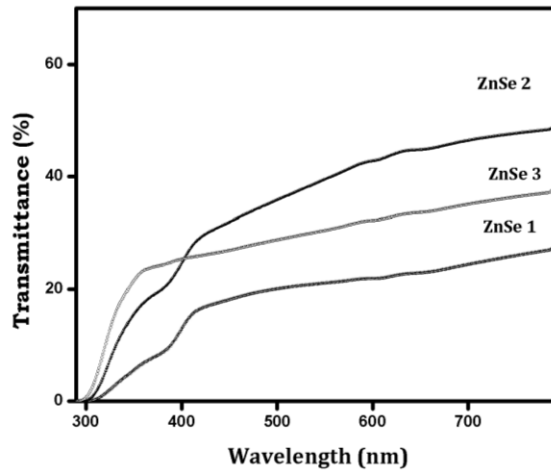


Fig. 4.2: Transmittance spectra of ZnSe samples

Fig. 4.3 and fig. 4.4 shows the reflectance and absorption spectra of ZnSe thin films as synthesized and undergone post deposition treatments. Reflectance of the films lies in the range 8-20%. The films with high refractive index have excellent light harvesting capability.

The optical band gap of the samples is obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ vs $h\nu$ plot to energy axis. It is observed that the as synthesized film has minimum band gap energy and the annealed film has maximum band gap energy. The band gap obtained from the graph is given in Table 4.3.

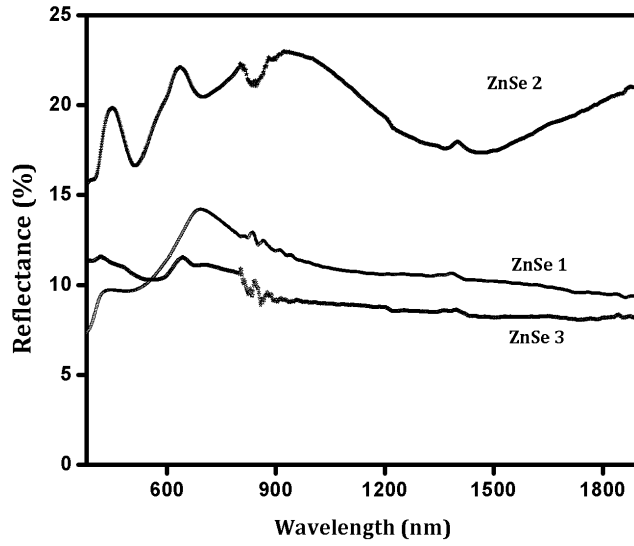


Fig. 4.3 Reflectance spectra of ZnSe thin films

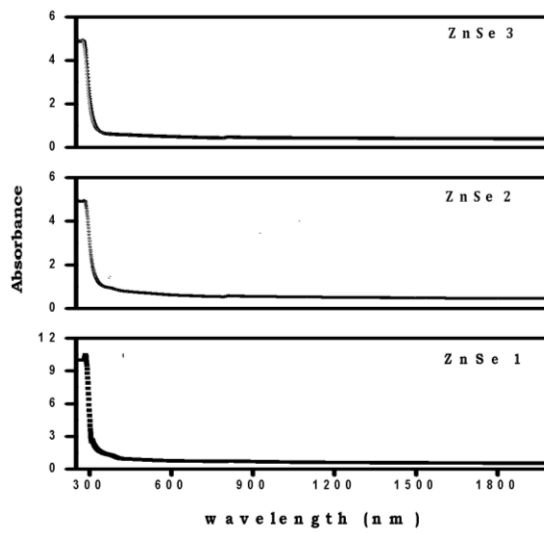


Fig 4.4 : Absorption spectra of ZnSe samples

Table.4.3: Optical band gap of ZnSe thin films

Sample	Band gap(eV)
ZnSe 1	2.743
ZnSe 2	2.82
ZnSe 3	2.84

4.4 Conclusion

After suitable time of deposition uniform and homogenous films got deposited on the substrate. The as prepared samples were undergone post deposition treatments such as post deposition UV irradiation and annealing which enhanced the physical properties of the ZnSe thin films. The changes in the values of the band gap reveal the significance of post deposition treatments in the optical band gap engineering.

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Chapter 5

Variation in the band gap due to the effect of concentration of Na_2SeSO_3 on the properties of ZnSe thin films

5.1. Introduction

Zinc selenide is an n type semiconducting material with wide band gap of 2.7eV. It has unique physical properties such as high refractive index, low optical absorption in the visible and infra red spectral region. Polycrystalline or amorphous ZnSe thin films have been grown by chemical bath deposition (CBD) method. [1-3]. It is simple inexpensive and an easy application for coating large surface. Generally, ZnSe films have been grown on glass [4-7], indium tin oxide (ITO) /glass and tin oxide (SnO_2) /glass substrates. In this work, ZnSe thin films were deposited on glass substrate by CBD method. The concentration of anionic solution varied and the effect on the structural, optical and electrical properties of the films have been investigated and discussed.

5.2. Experimental details.

Sodium selenosulphate is the anionic source and is prepared via refluxing. Freshly prepared sodium selenosulphate was added in to the chemical bath containing Zinc acetate, ammonia, hydrazine hydrate, and sodium hydroxide. Well cleaned soda lime microscopic glass slides were used as substrates.

5.3. Results and discussion

The films were appeared to be light yellow in colour. The sample prepared by 0.1M sodium selenosulphate was named as ZnSe1, with 0.15M was named as ZnSe2 and 0.2M was named as ZnSe3.

5.3.1 Structural studies

Fig 5.1 shows x-ray diffractograms of ZnSe thin films of different anionic concentration which are annealed at 343 K for 30 minutes. The observed 2θ values are well coinciding with the standard JCPDS Card No.15-0105 which corresponds to hexagonal wurtzite structure. On decreasing the concentration of anionic precursor, films became polycrystalline. For ZnSe1 peaks are at 2θ values 37.34, 50.49 and 53.14 identified as (1 0 2), (1 0 3), and (1 1 2) planes respectively. The average crystallite size was estimated using Debye Scherrer's formula given by eqn. (3.3). The average grain size was 44 nm for ZnSe1, 37 nm for ZnSe 2, and 32 nm for ZnSe3.

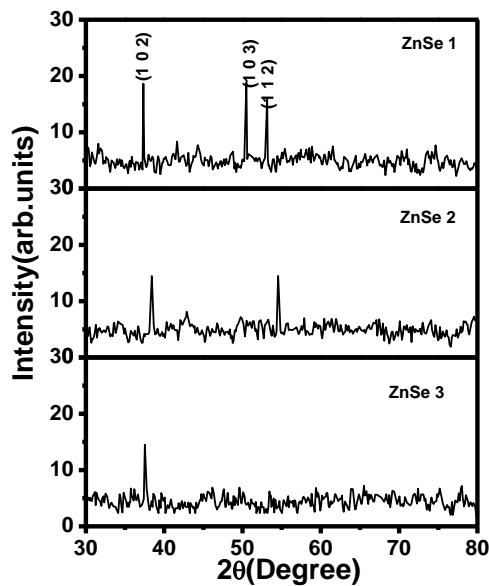


Fig. 5.1: XRD patterns of ZnSe films of different anionic concentration

5.3.2. Optical studies

Fig.5.2 shows the transmission spectra of ZnSe films with various anionic concentrations.

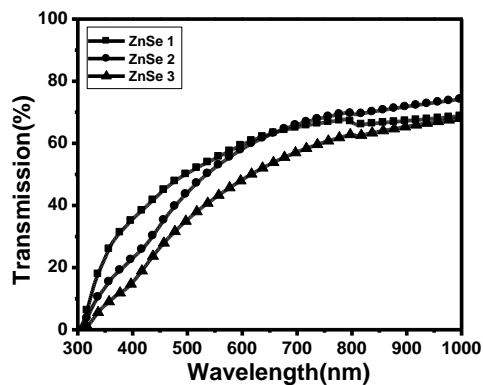


Fig 5.2. Transmission spectra of the films

Optical transmittance increases with the decrease in the anionic concentration. This may be due to the increasing crystallinity of the films. The absorbance of the films decreases with the increase in the concentration of the anionic precursor and the band gap energy was calculated from $h\nu$ versus $(\alpha h\nu)^2$ plot and the estimated values are tabulated in Table5.1

Table 5.1: Band gap of the samples

Sample	Band gap (eV)
ZnSe1	2.72
ZnSe2	2.76
ZnSe3	2.78

5.4 Conclusion

ZnSe thin films deposited by CBD method developed polycrystalline hexagonal wurtzite structure. The crystalline quality of the film found to increase with decreasing concentration of anionic solution. The band gap estimated was in good agreement with theoretical value. It is clear that the band gap can be engineered by varying the concentration of the anionic precursor.

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Chapter 6

Effect of annealing on nanocrystalline ZnSe thin films grown through SILAR technique

6.1 Introduction

The II–VI group compound semiconductor films have figured prominently for many years in a wide variety of commercial electronic applications [1]. They have played an important role in the development of semiconductor devices also. ZnSe meets this requirement because it has a wide band gap (direct band gap, $E_g = 2.7$ eV) and has potential applications in the blue green region of the visible spectrum in light emitting diodes [2-3]. ZnSe buffer layer may transmit even higher energy photons to the absorber layer of the solar cell with high optical transparency (90%) [4]. ZnSe is also suitable as a window layer for thin film solar cells [5].

6.2 Materials and methods

ZnSe thin films were deposited on glass substrates by the SILAR deposition method. Zinc acetate was used as the cationic precursor. The anionic precursor sodium selenosulphate solution was prepared by refluxing 2g Selenium powder and 6.2 g sodium sulphite in 40 ml double distilled water for 6 h at 343 K. Commercially available soda lime microscopic glass slides with a dimension of 7.5 x 2.5cm were used as substrates, which degreased thoroughly in detergent solution and kept overnight in chromic acid. Then they were ultrasonically cleaned in distilled water and dried in hot air.

80 ml 0.2 M zinc acetate solution was prepared under continuous stirring served as cationic precursor. Sufficient amount of ammonia solution was added to make the pH of the solution 9.5. The anionic precursor contains 80ml of 0.1 M sodium selenosulphate solution. Each dipping in precursor was followed by rinsing in double distilled water two times so that the loosely held particles were removed from film surface. The dipping time was optimized to be 15 seconds and uniformly deposited ZnSe films were obtained for 50 cycles. The samples prepared were annealed at 373 K and 573 K and were named Z1 and Z2.

6.3. Results and discussion

6.3.1. Thickness of the films

The films seem to highly uniform and are pale yellow in colour. The thicknesses of the films are determined by gravimetric technique using eqn. (3.1). The calculated values are 421.7 and 300 nm respectively.

6.3.2. Structural studies

Fig 6.1 displays the XRD pattern of the samples deposited. The sample annealed at 373 K exhibits polycrystalline hexagonal structure [JCPDS Card No.80-0008] with predominant orientations along (101), (102) and (222) directions. The annealed sample shows same cubic polycrystalline structure [JCPDS Card No.80-0021] with directions of orientations along (111), (200), (222) and (420). The high temperature annealing causes the structure to change from hexagonal to cubic structure of ZnSe crystal.

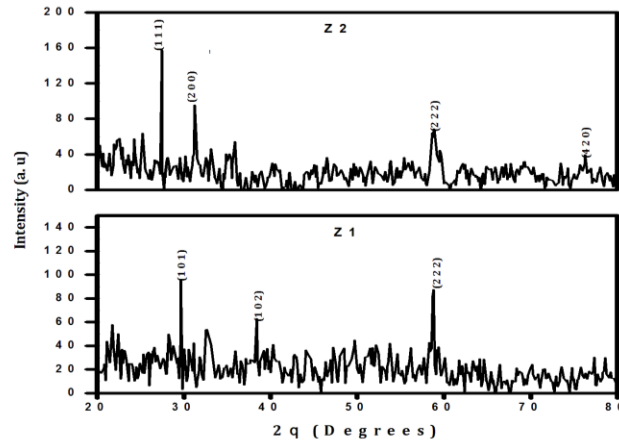


Fig.6.1: XRD pattern of the ZnSe samples

6.3. 3. Optical studies

The optical properties like absorption and transmission spectra were taken using a UV-Vis-NIR spectrophotometer in the range 200-2000nm. The optical transmittance in the spectral range 300-2000 nm of zinc selenide thin films are shown in Fig. 6.2.

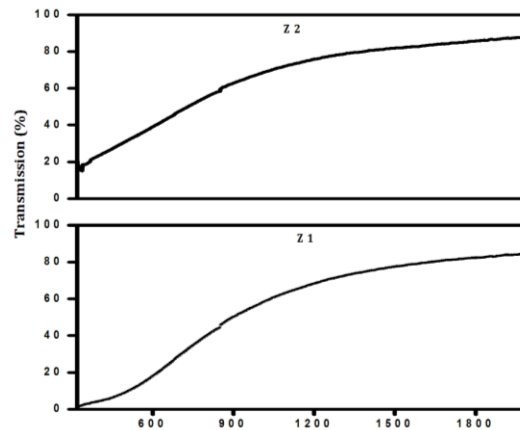


Fig.6.2: Transmission spectra of ZnSe samples

The percentage of transmittance varies for samples annealed at different temperatures. All the samples exhibit good transmittance in the visible region, confirming their suitability for TFSC buffer layers and comparatively higher transmittance in the wavelength region greater than 750 nm. This high transmission of ZnSe material is effective for infrared applications due to its extreme low bulk losses, high resistance to thermal shock and good stability.

Fig. 6.3 shows the absorption spectra of ZnSe thin films which undergone post deposition treatments.

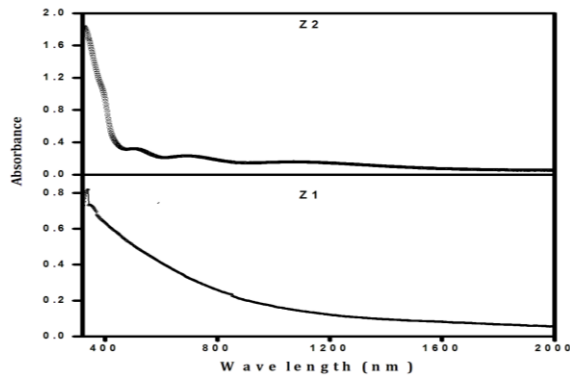


Fig.6.3: Absorption spectra of ZnSe samples

The optical band gap of the samples is obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ vs $h\nu$ plot (Fig.6.4) to energy axis. It is observed that increase in annealing temperature causes a reduction in band gap energy. The band gap obtained from the graph is given in Table 6.2.

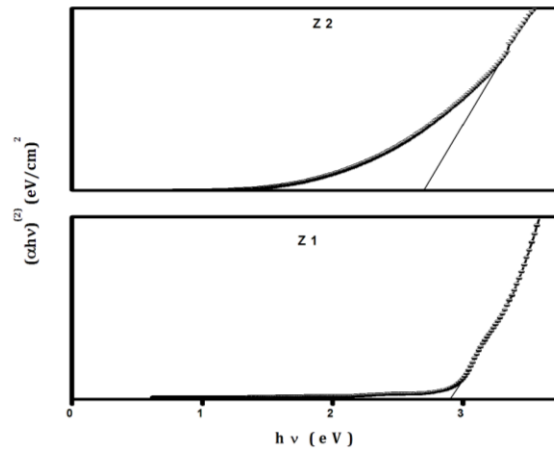


Fig.6.4: $(\alpha h\nu)^2$ vs $h\nu$ plot of ZnSe thin films

Table.6.2: Optical properties of ZnSe samples

Sample	Band gap(eV)	Transmittance (%) at 600 nm	Transmittance (%) at 1500 nm
Z1	2.87	18.1	77.9
Z2	2.67	39.3	82.33

6.4 Conclusion

ZnSe thin films deposited by SILAR method developed polycrystalline hexagonal and cubic structures. The optical absorption studies showed that the ZnSe has an optical band gap decreases with increasing annealing temperature. After annealing the decrease of 0.2 eV was observed in the band gap energy. Optical transmission also is increased and became more uniform. ZnSe films therefore have several potential applications in electro-optical devices, optical coatings, thin film transistors and solar cells.

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