Physical Properties of Zinc Selenide Thin Films and the Study of Doping Effects

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This thesis submitted to Department of Physics

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Final Approval

It is certified that the work presented in this thesis entitled "Physical Properties of Zinc Selenide Thin Films and the Study of Doping Effects" by **Musarat Abbas, Registration No. 28-FBAS/MSPHY/F10** is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

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بِسْمِ اللهِ الرَّحْمٰنِ الرَّحِيْمِ

In the name of ALLAH, the Beneficent, the Merciful.

In the name of Allah

All praise be to Allah, Lord of all the worlds, most Beneficent, ever merciful, King of the Day of Judgment, You alone we worship, and to you alone we turn for help.

Guide us (O'Allah) to the path that is straight, the path of those you have blessed, not of those who have earned your anger, not those who have gone astray.

Surah-e-Fatiah

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As a partial fulfillment for the award of the degree of

MS Physics

Declaration

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Dedicated to;

Dedicated to my parents & teachers who have given me courage to walk with the pace of life, who has endured my follies, who have rectified them with strong passion of love and who have infused in me the courage of analysis and passion for learning.

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Abstract

Extremely pure 99.99% ZnSe powder was used as evaporant to deposit zinc selenide (ZnSe) polycrystalline thin films by thermal vacuum evaporation method. Substrate temperature was optimized to prepare samples of variety of thickness. Glass coated ZnSe sample was characterized by applying various techniques e.g., XRD, SEM, EDX, AFM, UV Spectroscopy and Hall measurements. XRD technique shows that structures of the prepared samples were polycrystalline in nature with preferred orientation of [111]. Micro structural parameters such as crystallite size, lattice parameter, surface roughness, grain density were determined by the XRD patterns and AFM images of prepared films. The films were optically characterized by using UV-VIS-NIR Spectro-photometer. Direct band-to-band transition was exhibited in optical band gap (Eg=2.62-2.67 eV) as observed from examined absorption spectra. The influences of the deposition conditions and post-deposition heat treatment on the structural and optical features have been investigated. As deposited, annealed and Ag-doped samples were characterized by using UV-VIS-NIR Spectro-photometer in the range of 350–2200 nm. The structure of the films was studied by XRD, SEM, AFM and composition of the films by EDX.

Chapter 1

Introduction

1.1 Zinc Selenide (ZnSe)

Zinc Selenide (ZnSe) as a direct gap II-VI compound semiconductor has significant attention due to its attractive features since last few decades [1]. Its room temperature band gap of ~2.7eV makes it marvelous candidate for the fabrication of blue light emitting devices and lasers [2].

It is one of the most important and leading thin film material for the solar cell fabrication [3-14]. The thin films of ZnSe are very important for micro-electronics industry from the research point of view.

Silver as group I element works as accepter dopant in II –VI semiconductor leading to an increase of electrical conductivity of ZnSe. Works have been reported for low resistivity P-type ZnSe using lithium as the dopant, but doping still remains complex. The electrical conductivity as well as the optical properties are the essential parameters for such applications. On the other hand ion exchange process has been recently developed for II-VI semiconductors doping by copper and silver [12-14].

ZnSe is commonly used in CO_2 focusing lenses, night vision devices, automated trouble reporting prisms and transmission windows for IR Spectroscopy.

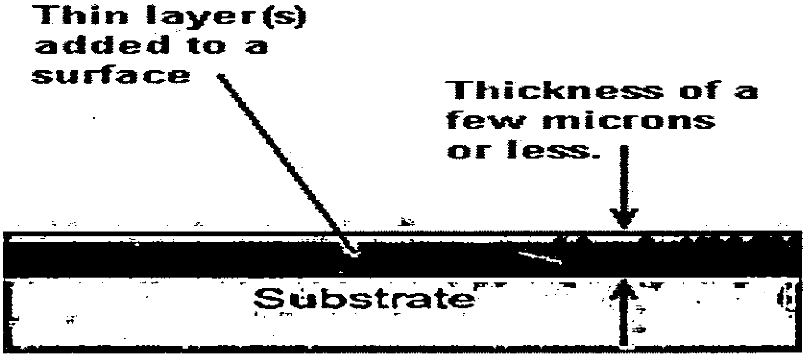
1.1.1 Properties of Zinc Selenide (ZnSe)

➢ Structure	Cubic zinc blended
➢ Appearance	Light yellow solid
➢ Molar mass	144.35 g/mol
➢ Density	5.27 g/cm^3
➢ Dielectric constant	8.976
➢ Thermal conductivity	0.16 W/cm-K
➢ Electron effective mass m^*/m_o	0.21
➢ Energy band gap (Eg) at 295K	2.67eV

- Specific Heat 0.339 J/gK

1.2 Thin films

A thin film is defined as microscopically thin coating of substance ranging from100A°-1μm deposited by various techniques onto a metal, glass substrate(in our case) or semi conducting base. Thin Film has almost two dimensional structures so that it can give bright insight into the structural properties of the material.



1.2.1 Importance of thin films

Production of ZnSe films having high resistivity and transparency is of current interest due to its potential application in various semi conducting devices. Several applications exist for utilizing thin films for their mechanical, chemical and electrical properties. The most widest and demanding application for thin film deposition is the fabrication of electronic components, exceptionally micro electronics integrated circuits and solid-state devices. These thin films distinctively consist of metal, semiconductor, dielectric and insulating materials. Control of conductivity and transparency are important parameter. Thin films have increasing commercial use to store data in compact discs and computer memory application. Thin films are also used for CRT contrast enhancement films, light weight mirrors etc. Thin films technology has been divided into three fundamental groups [14].

- Fabrication
- Characterization
- Applications

The fabrication of electronic devices such as micro integrated circuits and solid state devices, are dependent on the thin films deposition. Electronic components that can be made up from thin films are

- Light Emitting Diode
- Liquid-Crystal Displays
- Plasma displays
- Florescent displays
- Sensors
- Solar cells
- Diodes

1.2.2 Thin Films Fabrication:

- The process engages numeral independent steps:-
- Selection of the substrate.
- Identifying and defining significant properties of the substrate morphology.
- Uncontaminating of suggested substrate.
- Collection of the material and coating composition to generate the film adhesion and necessitated properties of film.
- Preferences of the production procedure to fabricate replicated film properties and extensive strength.

Major focus must be on development of the process parameter, monitoring techniques, parameter limits and fabrication equipment, in the direction of furnishing a high-quality product [15].

1.3 The Purpose of Vacuum

A vacuum is a space from which air or other gases have been removed, or the pressure of the gas in the enclosure has been reduced to less than the atmospheric pressure. In technical terms, the vacuum refers to a given space filled with a gas having a density of molecules less than 2.5×10^{19} molecules/ cm^3 at normal temperature.

In thin films fabrication process a certain level of vacuum helps us

- To avoid collisions
- To remove dissolved gases
- To reduce the energy transfer
- To achieve Pressure difference
- To produce contamination free surfaces
- To remove active atmospheric constituents
- To pull down the boiling points (helps in sublimation as well) etc

The pressure of a gas, defined in terms of gas impingement on a surface is the time rate of change of the normal component of momentum of the impinging gas molecules per unit area of surface (force per unit area) [16].

We speak of low, medium, high and ultra-high vacuum corresponding to the region of lower and lower pressure. These regions are distinguished from the point of view of the relationship in the kinetic theory of gases and according to the kind of gas flow.

1.4 VACUUM GAUGE

Vacuum gauge is a device, which is used to measure the vacuum in a specified range. In any vacuum system, the most important parameter to be measured is gas pressure. There is not a single pump that can achieve the vacuum up to extreme ultra high vacuum range; similarly, no gauge is available that can measure the vacuum of the whole spectrum. As different pumps produce vacuum of different degrees, in the same way, different gauges can measure vacuum within specified ranges as per their design [16, 17].

1.5 Research Objectives:

Following are the main objectives of this research work:

Fabrication of ZnSe thin films for its potential applications in optoelectronic devices in particular with solar cell.

Using close space sublimation technique, the substrate temperature and vacuum level will be optimized for desired thickness of ZnSe thin films

The as deposited thin films will be annealed and doped with Ag to a certain suitable level for solar cell applications. The samples will be electrically, optically and structurally characterized.

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Chapter: 2

Deposition Techniques

2.1 Techniques of thin films deposition:

- Electrolyses or Solution Growth
- Electro-Chemical Deposition (ECD)
- Molecular Beam Deposition
- Vacuum Evaporation
- Close space sublimation

Fabrication of thin films can be categorized into two main methods, which are as follow:

- Chemical Vapor Deposition (CVD)
- Physical Vapor Deposition (PVD)

2.1.1 Chemical Vapor Deposition:

In Chemical vapor deposition (CVD) technique, a fluid after a chemical reaction leaves a solid thin film on the surface of substrate. It requires no vacuum. The deposited material reacts with other gaseous species in the system to give compounds (e.g. oxides, nitrides). In CVD, a wafer is exposed to volatile chemicals which reacts with surface of substrate and deposited thin films. In this process there are also by products produced which can be removed by the flow of gases in the reactive chamber.

2.1.1.1 Types of Chemical Vapor Deposition:

There are six types of CVD which are widely used and are different from each other by chemicals reactions are started and process conditions, which are as follows:

- Ultrahigh vacuum- Chemical Vapor Deposition processes at a very low pressure, usually below 10^{-6} Pa.
- Low-pressure- Chemical Vapor Deposition processes at sub atmospheric pressures.
- Rapid thermal- Chemical Vapor Deposition processes that utilize heating lamps or further techniques to quickly heat the wafer substrate.
- Atmospheric pressure- Chemical Vapor Deposition processes at atmospheric pressure.

- Atomic layer– Chemical Vapor Deposition deposits successive layers of different substances to produce layered crystalline films [1].
- Plasma-Enhanced- Chemical Vapor Deposition processes that consume plasma to improve chemical reaction rates of the precursors.

2.1.2 Physical Vapor Deposition:

PVD is a process of transferring growth species from a source or target and deposit them on a substrate to form a film. The process proceeds atomistically and mostly involves no chemical reactions. Various methods have been developed for the removal of growth species from the source or target. The thickness of the deposits can vary from angstroms to millimeters.

PVD is widely used in the manufacturing of semi-conductor devices and coated cutting tools for metal working.

PVD is divided into two methods:

- Sputtering.
- Vacuum Thermal Evaporation.

2.1.3 Sputtering:

Sputtering relies on a plasma (usually a noble gas, such as Argon) can be used for knocking at some targeted material which will be at low temperature hence the process is not related to evaporation but those deposition techniques which are flexible for such component which were at different level, different component have tendency of evaporation such target is useful [1].

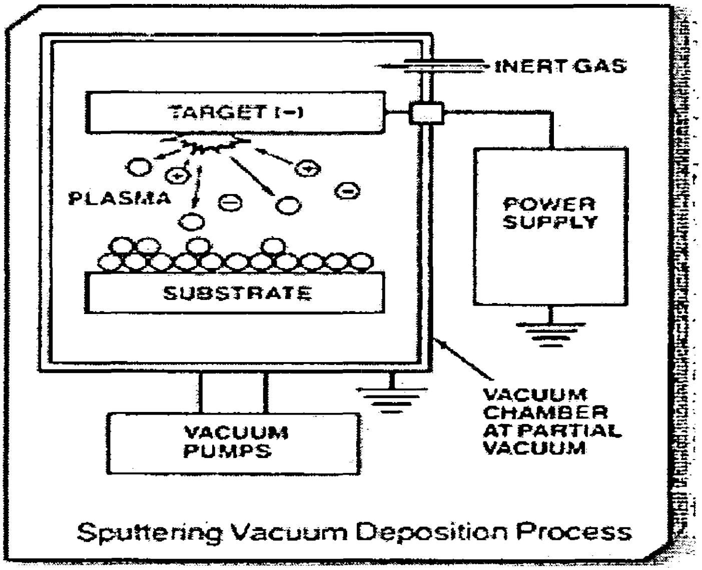

Fig. 2.1: Sputtering Vacuum Deposition Process

The substrate is positioned interested in the vacuum chamber and subsequently vacuum is build up to exist. The sputtering initiates as soon as a negative charge is functional on the way to the target material (material to be deposited), reasoning plasma or radiance discharge. Positive charged gas ions produced inside the plasma state are fascinated in the direction of the negative biased target plate at an extremely elevated speed then accelerating the ions from this plasma into target material [2]. The target material is destroyed gradually(eroded) by the arrival of ions through energy transfer and is emitted or ejected out in the form of neutral particles, which are either single atoms, group of atoms or molecules. The ejected neutral particles will travel in straight lines unless they come into contact with something-other particles or a nearby surface. If we placed a substrate like silicon in the path of ejected neutral particles then silicon is coated by a thin film of target material [3].

2.1.4 Thermal evaporation in Vacuum:

Thermal evaporation method for preparing thin films is becoming very popular since 30 years or so. In this method the pressure of gas in chamber is reduced to value as low as possible, this is called creating vacuum. Generating vacuum properly is very important for the reason that when evaporation is executed during poor vacuum or secure near the atmospheric pressure, the resulting deposition is commonly non-uniform. The purity of deposited films also depends on the control, quality of vacuum and on the source material must be free from contamination of impurities of. Vacuum is created by different pumps for example we have rotary vane pump, oil diffusion pump, in our vacuum coating unit.these pumps create different vacuum ranges, 10^{-3}-10^{-6}mbar. In this vacuum chamber source material is evaporated by heating at suitable temperature for particular time. In this method one must make sure that the evaporation system should be capable to sublimate a material, in regulate to deposit it and also pressure of gas in chamber is low enough so that mean free path of the atoms of evaporated material is larger than source-substrate distance. Thermal evaporation is similar to sputtering because reduced pressure is required for each. The properties of films are dependent on film structure and also on the interaction of film with the substrate.

Vapor deposition process is mostly used to build material of good properties. The materials which are manufactured by evaporation technique show well defined preferred orientation.

Thermal evaporation is divided into following categories:

- Resistive heating
- Electron beam heating
- Close space sublimation
- Two source simultaneous evaporation

2.1.5 Resistive Heating:

Metal layers for all semi conductor technologies are formed by evaporation. Although now a days, sputtering process is widely used for deposition of thin films.

The wafers are loaded into high vacuum chamber that is commonly pumped into low pressure by combination of two pumps, a rotary vane pump to pump down from atmospheric pressure to a pressure of 10^{-2} Torr. From 10^{-2} Torr to 10^{-7} Torr, pressure another pump either diffusion pump or a cryogenic pump or a turbo molecular pump are required.

Vacuum systems with oil diffusion pump commonly required a cold trapped to prevent the back streaming of pumped oil to chamber. The material to be deposited is loaded into container called crucible or boat. The boat is commonly made up one of refractory material such as Mo, Ta, and Ti. All these materials of boats have very high melting temperatures greater than 2500 °C. The boat or crucible are sometimes called filament.

These boats/filaments are heated by passing a very high current through power supplies. As Mo/Ta/Ti is very resistive, so they become red hot when current passes through them. This type of heating process is called Heat Resistive Process.

2.1.6 Close Space Sublimation (CSS):

Close space sublimation is a type of thermal evaporation technique. We have to employed CSS technique for the fabrication of zinc selenide (ZnSe) thin films in our present research work. Advantage of CSS process is simplified deposition and at moderate temperatures, high transport efficiency is able to be conducted under low vacuum conditions.

In CSS technique, a graphite boat is used to carry out the desired source material in powder structure inside a graphite boat and afterward heated by means of halogen lamps. The substrate is placed in a mica sheet, which acts as a thermal gradient between the source and the substrate. The material starts to sublimate and deposit on substrate. The source must be retained on higher temperature than substrate. The deposited film presents a better crystallographic point of reference and sufficient opto-electrical properties intended for photovoltaic functions.

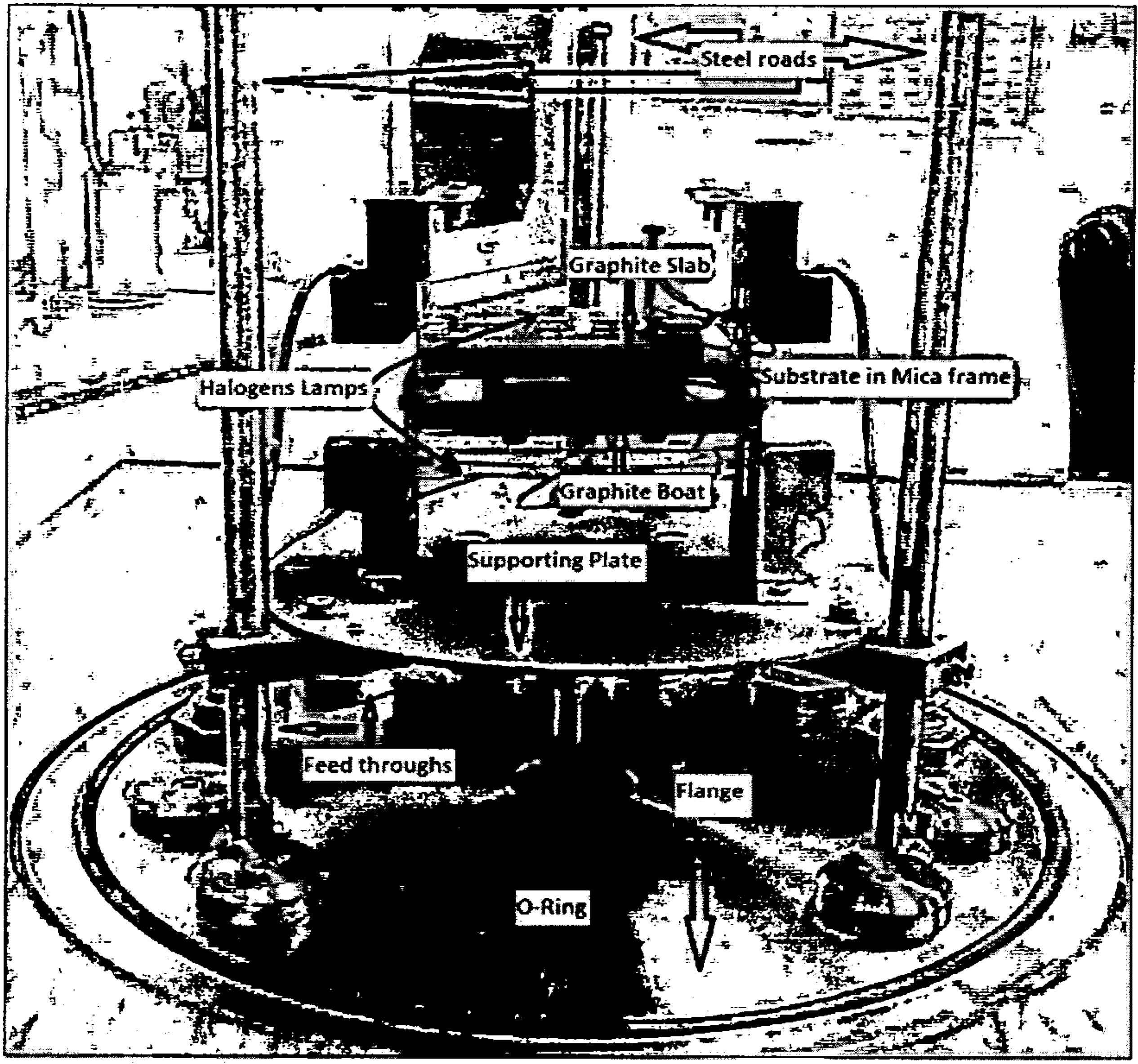

Fig2.2. Internal view of CSS equipment

2.1.6.1 Theory:

Sublimation illustrates the direct phase transition between a solid and gas state. A close space sublimation deposition is dependent on following [4].

- The sublimation process at the surface of the source,
- The transport of the gas from the source to the substrate surface,
- The sublimation process at the surface of the substrate

In this technique, the substrate is placed just above a graphite boat in closed vicinity. Source and substrate are then heated simultaneously by using halogen lamps, maintaining a constant temperature difference between source and substrate. This whole process is carried out in vacuum environment.

The main advantage of CSS over other processes is its high deposition rate. Based on a detailed investigation of close space sublimation, it is found that the material transport and hence growth depend on the following parameters

- The spacing between the source and substrate.
- Source and substrate temperature.
- Vacuum (10^{-6} mbr)
- Composition of the source material
- Deposition time [5].

2.1.6.2 The spacing between Source and Substrate:

The spacing involving the source as well as the substrate must be kept at an optimum affordable minimum (approximately 5mm). By reducing the space in between source and substrate not only we increase the deposition rate but also reduce the material consumption per deposition. It is desirable that nearly all the material consumed for the source is deposited on the substrate [6].

2.1.6.3 Source and Substrate Temperature:

Work by Nagayoshi and Suzuki [7] observed that the deposition rate is increased as the source temperature increased for a deposition under vacuum, in agreement with a sublimation limited case. An increase in substrate temperature leads to a decrease in the resistivity. With increasing substrate temperature, the grain size of film emerges to boost because we have less grain boundaries due to which resistance decreases. Since the surface mobility of the depositing species increases leading to less nucleation sites and therefore larger grains [8].

2.1.6.4 Vacuum:

In vacuum, transportation of molecules from source to substrate is significantly enhanced and larger growth rates were obtained due to larger mean free path.

2.1.6.5 Composition of the Source Material:

Material to be deposited, (ZnSe 99.99% pure in our case) must be in pure and powder form. Pure and small particle size powder of material is sublimated at low temperature as compared to agglomerated and impure powder.

2.1.6.6 Deposition Time:

By varying the deposition time we can attain different thickness of films. Less the deposition time, the thickness would be thin and greater the deposition time the more thick and denser films we obtain.

2.1.6.7 Substrate Cleaning:

The cleaning of substrate is very necessary before the fabrication of thin films. To protect our film from contaminations, impurities we insert our glass substrate in a beaker filled with acetone or IPA (Iso-propanol alcohol) organic compound with the formula ($(CH_3)_2$ CO) and placed it in the ultrasonic bath for half an hour.

Fig. 2.3 Ultrasonic Cleaner

2.1.6.8 Deposition of Thin films by Close Space Sublimation:

Powder of a material (to be deposited) is poured and dispersed uniformly in the graphite boat. Mica sheet is used as a substrate holder and thermal insulator sandwiched between source as well as substrate. The space among the evaporant (source material) as well as substrate can be changed without any difficulty permitting optimal distance, in order to get required deposition rate and better uniform films. The substrate temperature is raised till the sublimation temperature under vacuum (10^{-2}-10^{-3} mbar), which is being attained in this chamber with the help of a rotary pump. To attain higher vacuum of (10^{-4}-10^{-5} mbar) we use oil diffusion pump, the source temperature is adjusted lower than the substrate temperature so the vapors may travel from source to substrate. Temperature controllers have been attached with help of k-type thermo couples to observe the temperature of source as well as substrate. Films of different thickness are obtained by CSS, as thickness monitor can't be installed in this apparatus, due to narrow space between source as well as substrate.

2.1.6.9 Advantages:

- The evaporant (source material) as well as substrate are heated directly by halogen lambs and temperature is controlled with temperature controllers.
- The evaporant (source material) as well as substrate are taken apart in the course of a mica sheet of about 1-3 mm. In this way source vapors are confined to closed space, lead to less wastage of evaporated material as compared to other techniques.
- The mica sheet keeps the source and substrate at different temperatures, due to which the evaporating material will constantly, comprises enhanced access to the substrate.
- The films deposited by this method; the deposited film presents a better crystallographic point of reference and sufficient opto-electrical properties intended for photovoltaic functions.
- The system is very simple and easy to use.
- At moderate temperatures, high transport efficiency is able to be conducted under low vacuum conditions.

2.1.6.10 Limitations:

- The main limitation of CSS deposition system is that there is no quartz crystal to monitor the growth rate and thickness of the film deposited.
- This method can only be used for limited number of materials i.e. materials which can be sublimated at moderate temperatures [9].

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Chapter: 3

Physical Characterization

To prepare defect free film by any method is not possible. Such prepared thin films contain impurities, defect, unwanted phases and in-homogeneities. To study physical effect and morphologies of thin films, we use different characterization techniques.

To measure the electrical, optical as well as structural properties of the thin films, I use different characterization technique; include Hall Effect measurement for electrical properties, x-ray diffraction (XRD) for structural properties, UV visible spectrometry for optical properties, and scanning electron microscopy (SEM) for surface and elemental information's.

Short description of these techniques is given below:

3.1 X-Ray Diffraction (XRD):

XRD can be considered as a non-destructive system and it is used to measure structural properties of thin films. XRD give us information on structure, phases, and other structural parameters like crystal defects, average grain size and crystallinity.

X-ray diffraction is a multipurpose technique so as to provide us comprehensive information regarding the crystallographic arrangement and elemental composition and of assembled along with natural materials. The energy of the photons in the electromagnetic radiation is of the range of 100 eV to 100 KeV and short wavelengths are used for diffraction applications .The x-rays of high energy goes deep into the material and give us information about the bulk structures.

A focused beam of x-ray that falls upon a crystal is scattered in all direction. According to the arrangement of the atoms, in directions the scattered waves constructively interfere with one another while in others they interfere destructively. Constructive interference taken place only between those scattered rays which satisfy the Bragg's law:

$$2d_{hkl} Sin\,\theta = n\lambda \tag{3.1}$$

Wherever, λ denotes the wavelength of the X-ray beam incident upon a crystal at angle θ with the planes whose spacing is d. 'n' is the order of reflection.

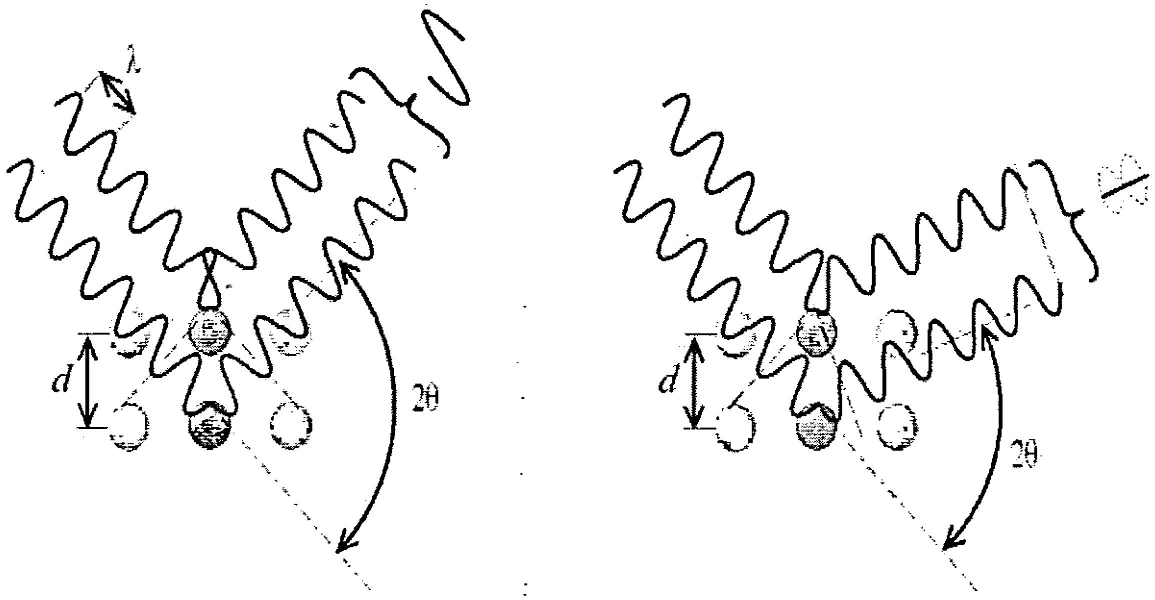


Fig. 3.1 Diffraction of X-Rays at an angle of 2θ

In case of the rotating-crystal method, a crystal is mounted with one of its axes, or some important crystallographic directions, normal to monochromatic x-ray beam. As crystal rotates a particular set of lattice planes will make correct Bragg's angle for reflection of the monochromatic incident beam.

3.2 Scanning Electron Microscope:

SEM is a basic tool for material characterization especially micro structural/morphological properties. SEM gives highly magnified images of surface. It is a versatile tool for the surface analysis. The scanning electron microscope works on the momentum transfer principle, electrons from the source comes and strike with the surface of target and penetrate and knock out the electrons of material.

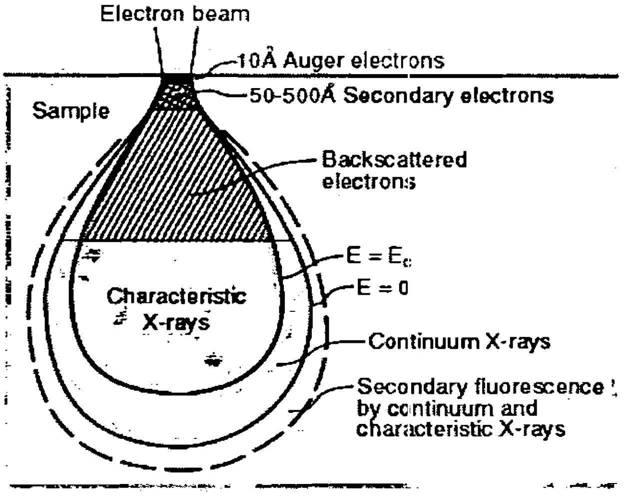


Fig. 3.2 The interaction of electrons with surface

A number of interactions occur when an electron penetrates into the surface which results in the emission of electrons or photons from the surface figure 3.2. The electrons which emits from the surface of specimen can be collected by appropriate detectors. If the amplitude of the saw-tooth voltage applied to the x- and y-deflection amplifiers in the SEM is reduced by some factor while the CRT saw-tooth voltage is kept fixed at the level necessary to produce a full screen display, the magnification, as viewed on the screen, will be increased by the same factor.

There are three types of images produced by SEM

- Secondary electron images
- Backscattered electron images
- Elemental X-ray maps

Conventionally secondary and backscattered electrons are divided according to their energies. There are different mechanisms by which they can be produced. When a high-energy electron interacts with an atom, the two types of scattering are occurred, inelastic scattering with atomic electrons and elastic scattering with the atomic nucleus.

Some amount of energy is transferred to the other electron in an inelastic collision with an electron. The emitted electron will not have enough energy to exit the surface if the energy transfer is very small. The emitted electron will leave the solid if the energy transferred exceeds the work function of the material.

Conservatively it is referred to as a secondary electron (SE) or simply a secondary when the energy of the emitted electron is less than about 50 eV. A lot of the emitted secondaries are produced within the first few nm of the surface. These SE produced inelastic collisions much deeper in to the material which lower their energy and trap them in the interior of the solid [1].

The primary electrons have higher energy that have been scattered elastically by the nucleus of an atom. Backscattered electrons (BSEs) are considered to be the electrons that leave the specimen with an energy greater than 50 eV, including Auger electrons.

However a lot of BSEs have energies comparable to the energies of the primary beam electrons. The backscattering will occur when higher the atomic number of a material. Thus as a beam passes from an area of low atomic number to a high atomic number, the signal owing to backscattering, and as a result the brightness of image will increase. There is a built in contrast caused by elemental differences.

The main features of the instrument are the electron column containing the electron source (i.e., the gun), the magnetic focusing lenses, the sample vacuum chamber and stage region (at the bottom of the column) and the electronics console containing the control panel, the electronic power supplies and the scanning modules. A solid state EDS X-ray detector is usually attached to the column and protrudes into the area immediately above the stage; the electronics for the detector are in separate modules, but there has been a recent trend toward integration into the SEM system architecture.

The overall function of the electron gun is to produce a source of electrons emanating from as small a "spot" as possible. The lenses act to demagnify this spot and focus it onto a sample. The gun itself produces electron emission from a small area and then demagnifies it initially before presenting it to the lens stack. The actual emission area might be a few nm in diameter and will be focused eventually into a spot as small as 1 or 2 nm on the specimen [2]. The two following detectors are used in Scanning Electron Microscope for the detection of elements.

- Energy Dispersive X-Ray Detector
- Wavelength Dispersive X-Ray Detector

The detectors produce an output signal that is proportional to the number of X-ray photons in the area under electron bombardment. With an Energy Dispersive Spectroscopy (EDS) the output is displayed as a histogram of counts versus X-ray energy. The data usually can be quantified through the use of appropriate elemental standards and well-established computational algorithms.

3.3 ATOMIC FORCE MICROSCOPE (AFM)

To examine insulating surfaces Gerd Binnig and Christoph Gerbeused used the cantilever in the fall of 1985. Atomic Force Microscope has high resolution and it is a type of a scanning probe microscope. There is a fine tip termed as the cantilever. Typically Si_3N_4 or Si are used to make the tip and extended down from the end of a cantilever. A beam of laser falls onto the back of cantilever and reflects back as shown in figure 3.3. This laser beam directly goes into an element photodiode that is attached with the cantilever. As the tip of cantilever scans the surface of the sample, it moves up and down with the surface [3]. This photo detector investigates the difference in light intensities owing to the rough surface of the sample.

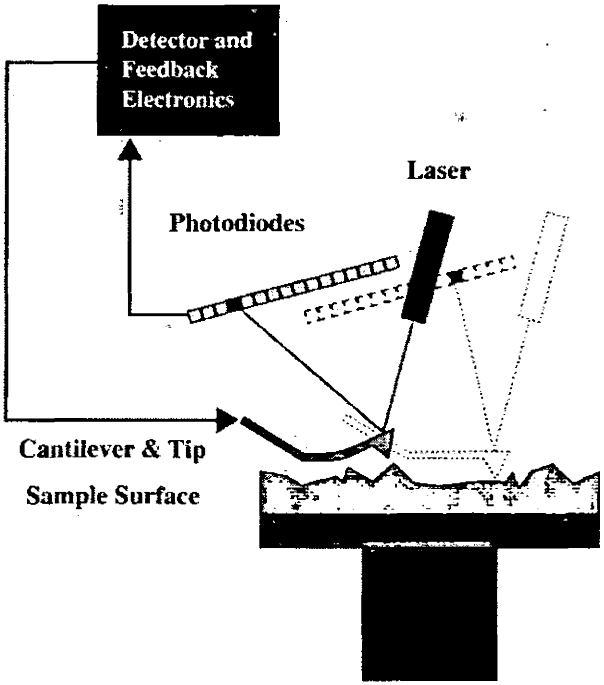


Fig. 3.3 Atomic Force Microscope (AFM)

There are three modes of working

- Contact Mode

- Non-Contact Mode
- Taping Mode

3.3.1 CONTACT MODE

The first mode of AFM is contact mode and it is used widely to examine the surface. In the contact mode, the tip of cantilever examines the surface with in contact of the surface. The forces involved in the contact mode have repulsive nature. The attractive forces can snap into the surface. The tip of cantilever is placed at a constant distance above the surface of the sample. As the tip has a hard contact with the surface of the sample, the stiffness of the tip should be small [4].

There is chance of damage for the samples in the contact mode. This damage depends upon the force with which the tip moves on the surface. The static charges can be produced on the surface of the sample during the scanning. These charges produced the attractive forces between the probe and sample. These attractive forces can damage the surface of the sample.

3.3.2 NON-CONTACT MODE

In the non-contact mode, the tip of cantilever oscillates on the surface but do not touch the surface. Van der Waals forces on the surface of the sample change the frequency of oscillating cantilever. The change in the frequency of cantilever can be measured and a topographic image of the surface of the sample has been generated.

The forces involved in non-contact mode are weak in nature. The non-contact mode is better to use for the soft samples rather than contact mode. The frequency and amplitude modulation are used for the detection of the position of cantilever. In the frequency modulation, the change in the frequency of oscillating cantilever gives us information about the interaction of surface and tip. In amplitude modulation, the change in the amplitude of cantilever has been measured for imaging.

3.3.3 TAPING MODE

It is difficult to the image of sample surface which are easily damaged. Tapping mode has higher resolution than the other modes. The problems regarding the scanning of the surface of sample like friction, adhesion, and electrostatic forces in AFM can be reduced with the help of tapping mode.

In the ambient conditions, there is a risk of water contamination on the surface of sample due to which the tip can be stuck with the surface it is therefore dynamic mode is used to avoid the contamination.

A more general term is used for the tapping mode is Dynamic Force Mode (DFM). The cantilever should have large stiffness as it sticks at the water contamination. In the tapping mode the cantilever lifts off after touching at the different points of the surface of sample. This mode is used for the soft samples to take high resolution images [5].

3.4 UV-VIS-NIR Spectroscopy

The optical characterizations have some major parameters such as refractive index, transmittance, reflectance, and band gap and absorption coefficient. It is promising to find out the optical constants conveniently by means of the reflection, transmission and interferometric properties [6]. When a light is applied resting on the electronic arrangement of solids then the thin films optical phenomena of the absorption studies will be led. Films are characterized by refractive index. The spectrophotometer is a device to measure the optical properties of a material. To measure the optical properties, the substrate should be a transparent.

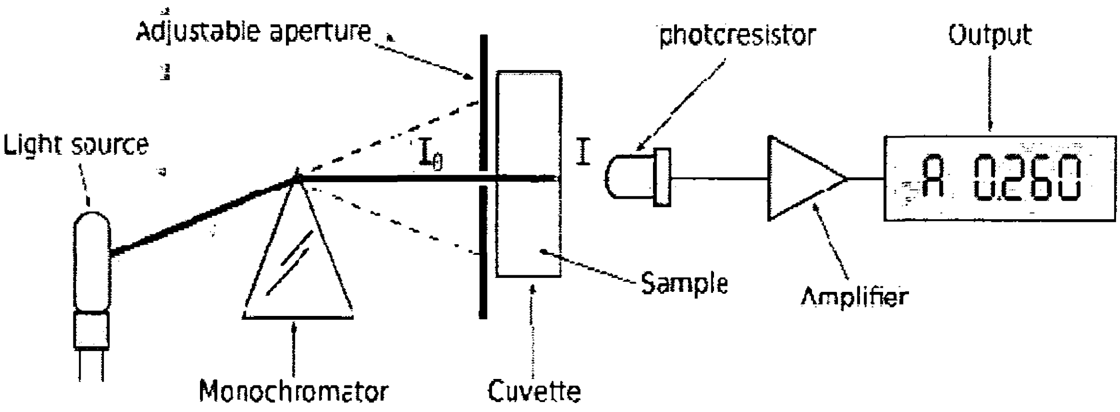
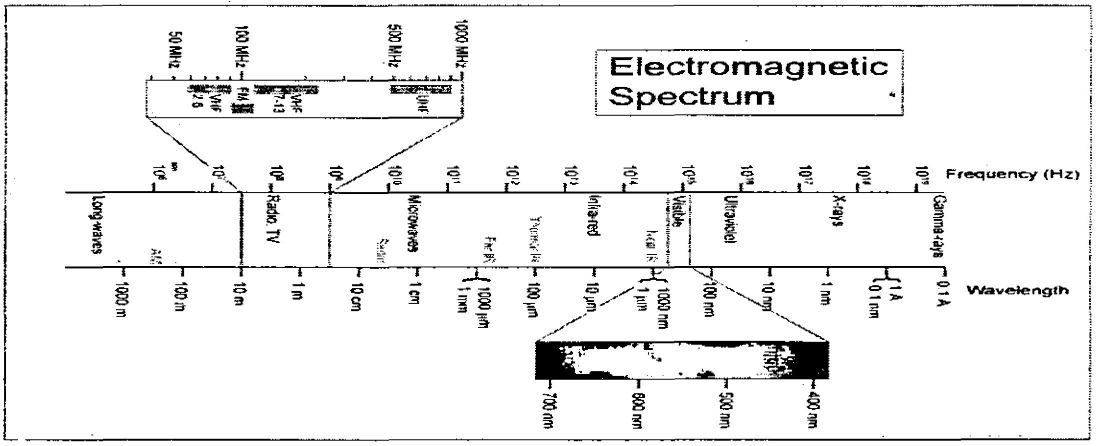


Fig 3.4 Spectrophotometer

The spectrophotometer consists of a light source, a sample holder, a device to measure light intensity as shown in figure 3.4. In short, the sequence of parts of a spectrophotometer is as follows:

- ➢ The light source shines into a monochromator
- ➢ A particular output wavelength is selected and beamed at the sample.
- ➢ The sample absorbs light

The technique which is discussed is the UV-VIS-NIR spectroscopy which refers to absorption spectroscopy in the near infrared spectral region and ultraviolet visible. In this technique, it make use of the light inside the visible and adjacent (near-UV and near-infrared (NIR)) ranges. It lastingly influences the recognized color of the chemicals which are involved by the absorption within the visible range. The expanse of electromagnetic spectrum, molecules went through electronic transitions.



There are two types of Energy gaps (E_g) in semiconductors.

- ➢ Direct energy gap
- ➢ Indirect energy gap

3.4.1 Direct energy gap

The minimum of the conduction band and valance band occur at the same values of k. The electrons are transferred vertically without any change in the momentum between the two bands where absorption begins at $h\nu = E_g$.

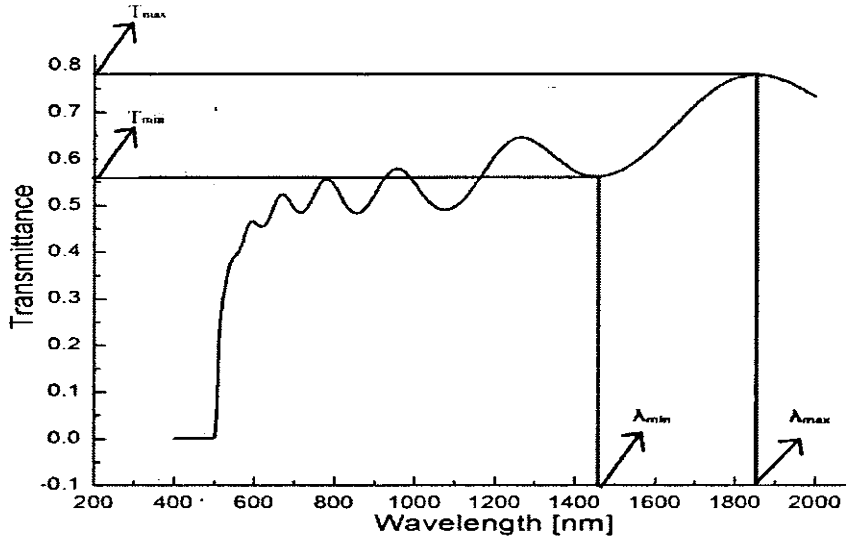
3.4.2 Indirect energy gap

In semiconductor the minima of conduction band and the maxima of the valance band takes places at different values of k. The participation of the phonons in the order to conserve momentum which is require by the transition from the valance band to the conduction band because there is a change in the wave vector. Phonon is emitted as well as absorbed.

Thickness of the film is determined by the following formula:

$$\frac{\lambda_{max}\lambda_{min}}{4n(\lambda_{max}-\lambda_{min})}$$

λ_{max}, λ_{min} be the significances of wavelengths communicating to maximum and minimum transmission respectively as shown in the figure.



Transmission spectrum used to measure the thickness.

3.5 HALL EFFECT:

The phenomena of the Hall Effect are to producing difference in the potential across an electrical conductor in the presence of magnetic field. This potential difference is well-known as Hall voltage. Because current and magnetic field is perpendicular to the direction of hall voltage as shown in Figure3.5.

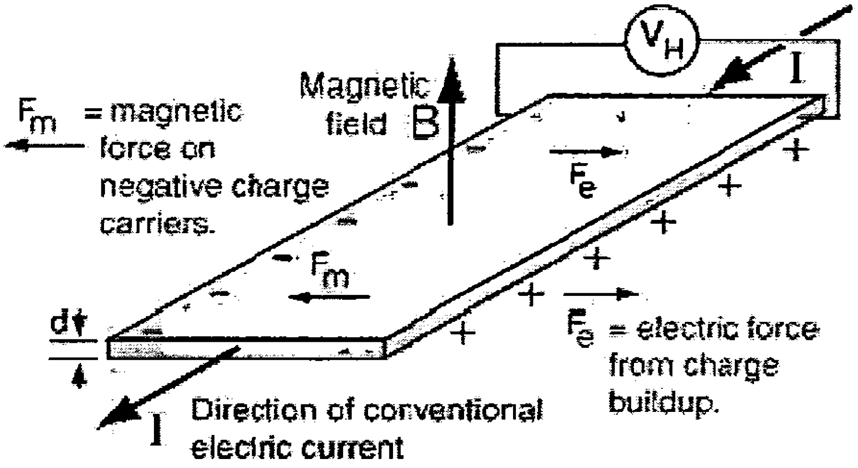


Fig 3.5 The schematic diagram showing Hall voltage across the sides of conductor in presence of magnetic field.

By the following equation we determine Hall voltage.

$$V_H = \frac{-IB}{dne} \tag{3.2}$$

Where, B is magnetic field, I is current across the conducting plate, e is electron charge, d denotes the depth of the plate, and n denotes the charge carrier density (number of charge carriers per unit volume).

The Hall coefficient is described at the same time as

$$R_H = \frac{E_y}{j_x B} \tag{3.3}$$

3.5.1 Hall mobility (μ)

Hall mobility is described like the resultant product of the conductivity (σ) and the Hall coefficient (R_H)

$$\mu = R_H \sigma \tag{3.4}$$

The expression for Hall coefficient is defined over, wherever as resistivity (ρ) is the converse of conductivity (σ). Resistivity is given by Equation 3.5.

$$\rho = R\frac{A}{l} \tag{3.5}$$

Where, A is area, l is length and R is electrical resistance of the samples.

There are two type of doping (p-type or n-type) which can also be tested by Hall Effect. It can be tested by the sign of Hall voltage, if the material is positive then it is p-type and if the material is negative then it is n-type.

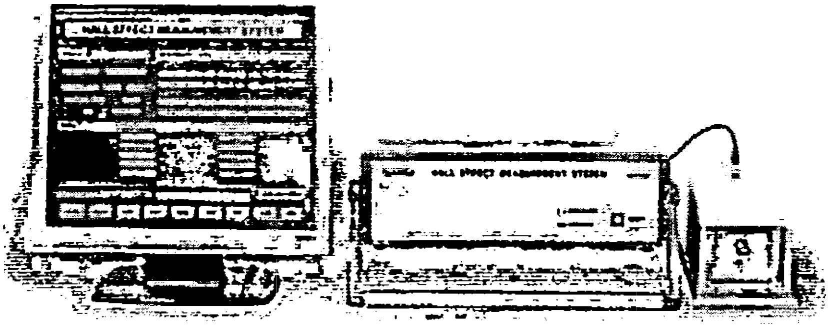
3.5.2 Electrical Resistivity

The electrical resistivity is defines as the resistance (R) of rectangular shape of thin film (measured in direction parallel to the film surface) at constant temperature is given by

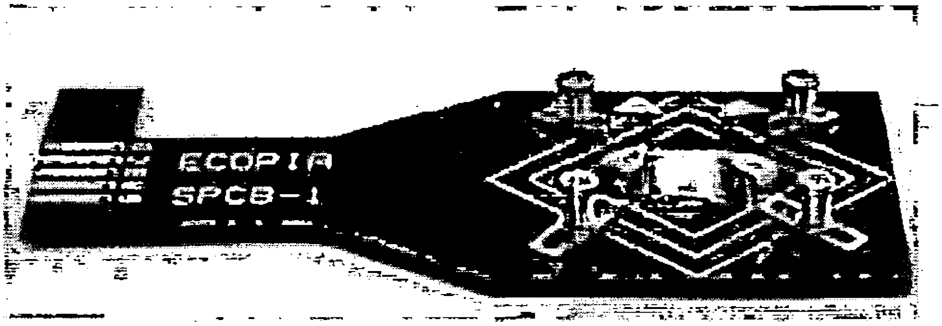
$$R = \frac{\rho}{d}\frac{l}{b} \tag{3.6}$$

Where ρ the resistivity, d denotes the thickness, *l* and b denotes the length and width of the rectangular profile film.

Measuring the resistivity of the samples is known as Vander Pauw method [7] which is one of the commonly used methods. Some of the following conditions are applied to knowing the pattern of the current and the specific resistivity of a plane sample of arbitrary profile can be determined.



Hall Measurements by Ecopia HMS-3000:



PCB with a thin film sample to measure its resistivity and Hall parameters

References:

[1] E. Reithmeier,T ,T. Vynnyk ,T. Schultheis, Appl.Math.Comput, **10** (2010) 1016.

[2] I. Müllerova, I. Konvalina, Collection of secondary electrons in scanning electron microscopes, Journal of Microscopy (2009).

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[4] H. J. Butt, B. Cappella, M.Kappl, Surface Science Reports **59** (2005) 1.

[5] St. Fahlbusch, S. Mazerolle,J. M. Breguet, A. Steinecker, J. Agnus d , J. Michler, J. M. P. Technology, **167** (2005) 371.

[6] http://en.wikipedia.org/wiki/Chemical_vapor_deposition

[7] http://en.wikipedia.org/wiki/Hall_effect

Chapter: 4

Experimental Work

4.1 Experimental Setup

4.1.1 Coating Unit

The schematic diagram of thin film coating unit used in this study is shown in figure 4.1.

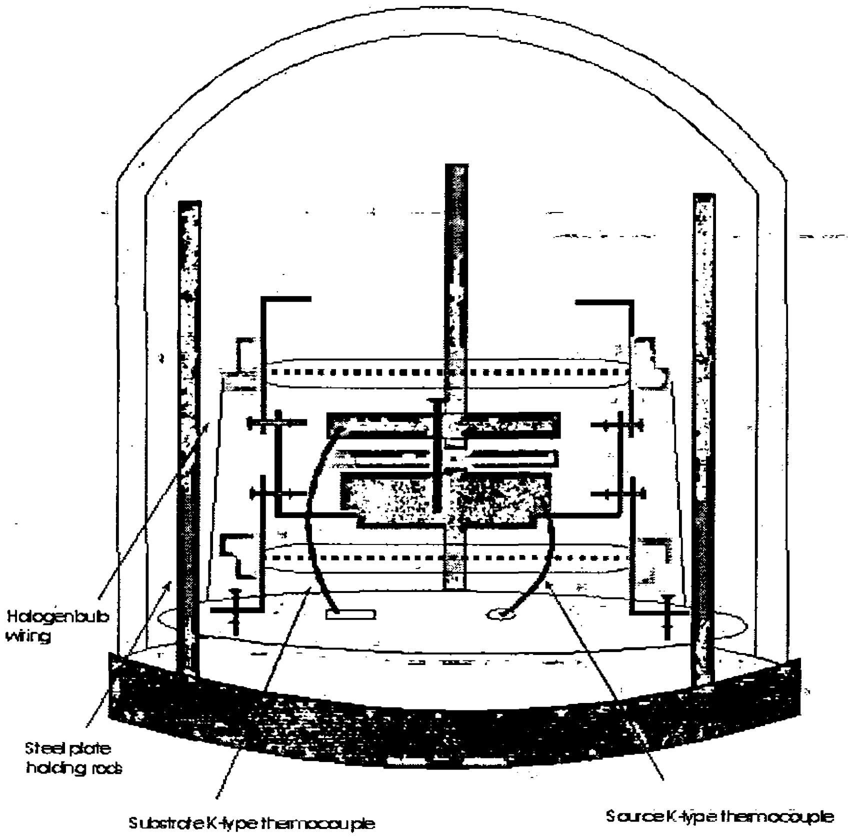

Fig. 4.1: Schematic diagram of thin film coating unit

The detail of the (Close Space Sublimation) assembly is given as:-

- Vacuum enclosure (ball jar)
- Pumping system
- Source holders with temperature controlling system
- Substrate holders with temperature controlling system

An overall view of complete assembly is given in figure 4.2.

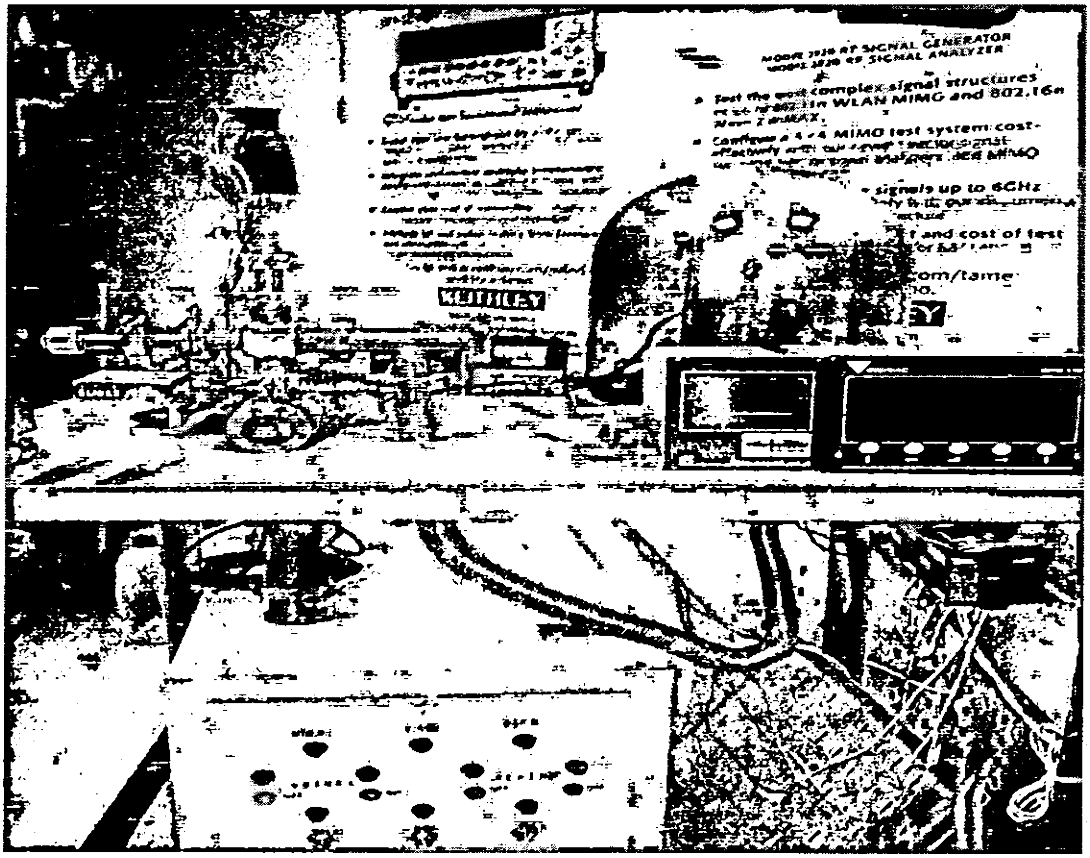

Fig. 4.2: an overall view of CSS complete assembly

Different parts of CSS unit are described as follows

4.1.2 Vacuum Enclosure

The vacuum enclosure can be of different types, shape and material which could withstand high temperature and pressure conditions. In our system, a special type of thick glass with dome shaped mounted on the metal base plate has been used, which can attain high vacuum 10^{-7} mbr and temperature 1200°C.

The need of this Vacuum enclosure is to provide contamination free environment without disturbing experimental condition.

4.1.3 Pumping system

A double – stage rotary vane pump is used for producing intermediate level vacuum inside the enclosure. Diffusion pump is used to direct gas molecules in the pump throat by using a high speed jet of vapor down into the bottom of the pump and out the exhaust. Diffusion pump is a type of vacuum pump designed to achieve higher vacuum (lower pressure) than possible by use of mechanical pumps alone.

4.1.4 Substrate Holder and Heating Arrangement

The substrate is fixed on mica sheet, which serves as dual purpose and is prepared according to the size of the substrate. It is also used as an insulator to avoid the substrate from direct contact to the source holder so that the temperature gradient between source and substrate can be maintained. There is a rectangular hole in the centre of the mica sheet, which is the only gateway for species to evaporate for deposition.

A smooth graphite block is kept on the substrate with heating arrangement which is further connected to the temperature controller in order to maintain the required temperature of the substrate.

4.1.5 Source Holder and Heating Arrangement

The material is placed on the source holder in order to provide required heating. To choose the material of source holder is critical because there might be a chance of contamination. The material for the holder must tolerate a high temperature. In our system, a source holder is specially designed from the graphite block, which is heated by radiation from the halogen lamp. A hole is drilled on one side of the source holder for keeping thermocouple inside which is further connected to temperature controller.

4.1.6 Substrate

The glass slides are used as substrate, which have very high transparency in the range required for optical studies. There is a wide range of substrates available that can be used according to the requirement of application or experimental conditions. The properties of the deposited thin film also depend upon the substrate. To fabricate a good film, substrate must have a list of properties approaching to an ideal substrate, although it is not possible. The desired properties in the ideal substrate may be formulated as follow

Desired Properties	**Reasons**
Mechanical strength	To Prevent breakage
Atomically smooth surface	To Provide film uniform
No porosity	To Prevent excessive out gassing
High thermal conductivity	To Prevent heating of circuit component
Matching of thermal coefficient of expansion to that of deposited film	To Prevents film stress
Resistive to thermal shock	To Prevent damage during processing
High electrical resistance	Provides insulation of circuit components
Thermal stability	Permits heating during processing
Chemical stability	Permits the unlimited use of process reagents
Low cost	Permits commercial application

Table 4.1 Ideal substrate

4.1.7 Fabrication of Zinc Selenide thin films by the CSS technique

Transparent Light yellow colored thin films were obtained by close space sublimation unit (installed at TFTR Laboratory @ CIIT, Islamabad). Soda lime glass was used as a substrate to deposit ZnSe thin films on it. Before the fabrication of thin film, glass substrate was ultrasonically cleaned in IPA bath. ZnSe powder (99.99% pure) was used to sublimate from a graphite boat. Mica sheet is used as a substrate holder and thermal insulator sandwiched between source as well as substrate. The space between the evaporant and substrate can be changed without any difficulty permitting to get optimized distance, in order to get required deposition rate and better uniform films. The evaporant as well as the substrate are taken apart in the course of a mica sheet of about 1-3 mm. In this way source vapors are confined in a closed space, leading to less wastage of evaporated material as compared to other techniques. There is no thickness monitor installed in this apparatus to control the thickness. Films had good adhesion with the glass substrate as tested by squash tape test.

Chapter: 5

Results and discussions

The prepared samples were characterized in various aspects including morphological, elemental composition, structural, optical and electrical characterizations. The results will be compared with the existing data and are reported in this chapter.

5.1 STRUCTURAL ANALYSIS

The XRD analysis of the fabricated samples of ZnSe thin films was carried out on XRD system "Panalytical Xpert' Pro (Holland)" (installed at applied thermal physics laboratory @ CIIT, Islamabad).

The important parameters of the XRD system are as under:

- X-Rays $Cu_{k\alpha}$
- Wavelength 1.5406Å
- Diffraction angle 2θ varies from 20° to 80°

The XRD traces of the as-deposited sample are shown in Fig.5.1. Peaks relating to ZnSe are identified by using standard card.

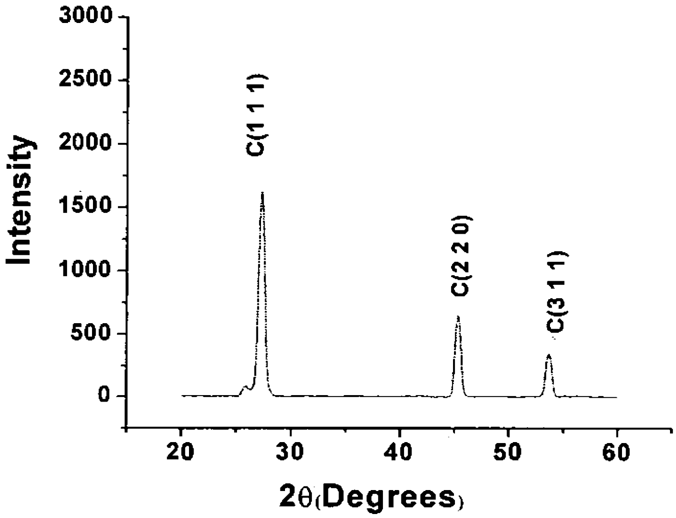

Fig. 5.1: X-ray diffraction traces of as deposited ZnSe thin film

According to the Scherer formula, full width at half maximum (FWHM) is inversely proportional to the crystallite size (C.S). The crystallite size can be calculated as

$$CS = \frac{(0.9)\lambda}{\beta \cos\theta} \tag{5.1}$$

Where

λ = wave length of X-Rays

θ = angle of diffraction

β =FWHM

Values of strain (ε) were calculated by means of the following relation [1].

$$\varepsilon = \frac{\beta Cos\theta}{4} \tag{5.2}$$

Values of dislocation density (δ) calculated by means of the following relation [2].

$$\delta = \frac{n}{D^2} \tag{5.3}$$

Where n is a constant having value ≈1 [3] and D is crystallite size.

The normal internal stress built inside the films is computed by applying the relation [4].

$$S = \frac{E}{2\gamma} \frac{a - a_o}{a_o} \tag{5.4}$$

Using the observed value of lattice constant a, in the calculation, standard value of lattice constant (a_0=5.667Å), Young's modulus (E =67.2×109 dyne/cm^2) and Poisson's ratio (γ=0.28) for bulk material. The negative value of average stress indicates the compressive stress and the positive sign of the stress indicates the tensile stress [5].

XRD is considered as a non-destructive system and is used to measure structural properties of thin films. XRD give us information on structure, phases, and other structural parameters like crystal defects, average grain size, lattice parameter (a), dislocation density (δ) and average internal stress and crystallinity.

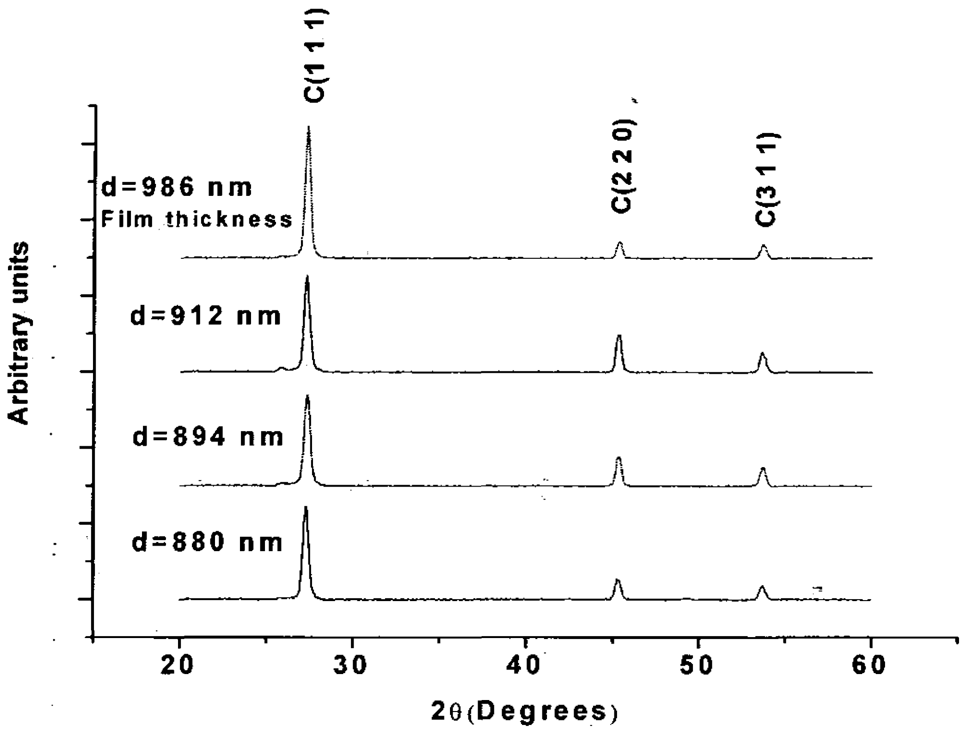

Fig. 5.2: X-ray diffraction pattern of as deposited ZnSe thin films

Fig. 5.2 shows that the intensity and width of the peak (1 1 1) gradually increases with increasing the film thickness. This may be due to the improvement of particle size at higher film thickness. As the film thickness increases, the intensity increases due to the improvement in the structure of the materials incorporated in the diffraction process [6].

The crystallite size (D), strain (ε), lattice parameter (a), dislocation density (δ) and the average internal stress were calculated and presented in Table 5.1. It is observed that the dislocation density (δ) as well as strain (ε) decreases with increase in film thickness. In contrast grain size (D), average internal stress and lattice parameter increases with increase in film thickness. The grain sizes in the films are seen to be almost uniform.

Thickness (nm)	2θ (deg.)	h k l	Lattice spacing (A°)	Lattice parameter a (A°)	Grain size D (nm)	Strain $\epsilon \times 10^{-3}$ ($lin^{-2}m^{-4}$)	Dislocation Density $\delta \times 10^{15}$ ($linm^{-2}$)	Stress $S \times 10^{8}$ (Nm^{-2})
880	27.3199	(111)	3.264	5.654	44.8	0.809	0.499	-1.53
894	27.2159	(111)	3.277	5.675	48.6	0.745	0.423	1.01
912	27.1982	(111)	3.279	5.679	51	0.709	0.384	1.45
986	27.1627	(111)	3.283	5.686	53.8	0.673	0.346	2.32

Table 5.1: Micro structural parameters of ZnSe thin films

The silver-doping in ZnSe thin films by ion exchange process is a new doping process which gives encouraging results. In figure 5.3, the XRD trace of silver doped ZnSe thin films is presented. As the thin films of ZnSe were immersed in Silver nitrate solution, the Silver diffused in it.

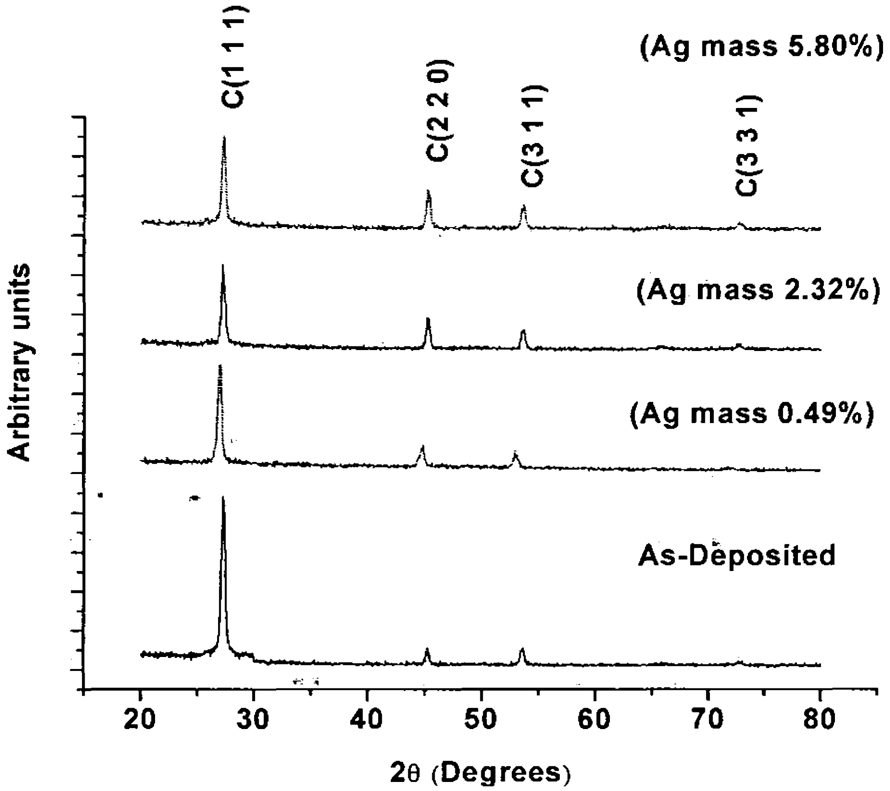

Fig. 5.3: XRD pattern of as deposited and Ag-doped ZnSe thin films

X-ray pattern in figure 5.2, show that the as deposited films have a preferred orientation along (111) direction and cubic in structure. While the films which were treated by $AgNO_3$ solution and post heated were less oriented in (111) direction, the loss in the texture of the ZnSe thin film is exhibited by the treatment of silver nitrate solution followed by heat treatment in vacuum at 400 °C for one hour. The intensities of (220) and (311) peaks are lower than the intensity of (111) peak in as deposited film, whereas (220) and (311) peaks in immersed and heat treated films have grown, implying that the films are losing (111) texture. No peak corresponds to silver or silver compound, which might be due to the minute quantity of silver in the films [7].

5.2 SURFACE STUDY

The scanning electron microscope (SEM) is one of the best available techniques for the surface studies. It can resolve up to 3 nm with magnifying power of 300000. The scanning electron microscope images of as-deposited ZnSe samples are shown in figure 5.4.

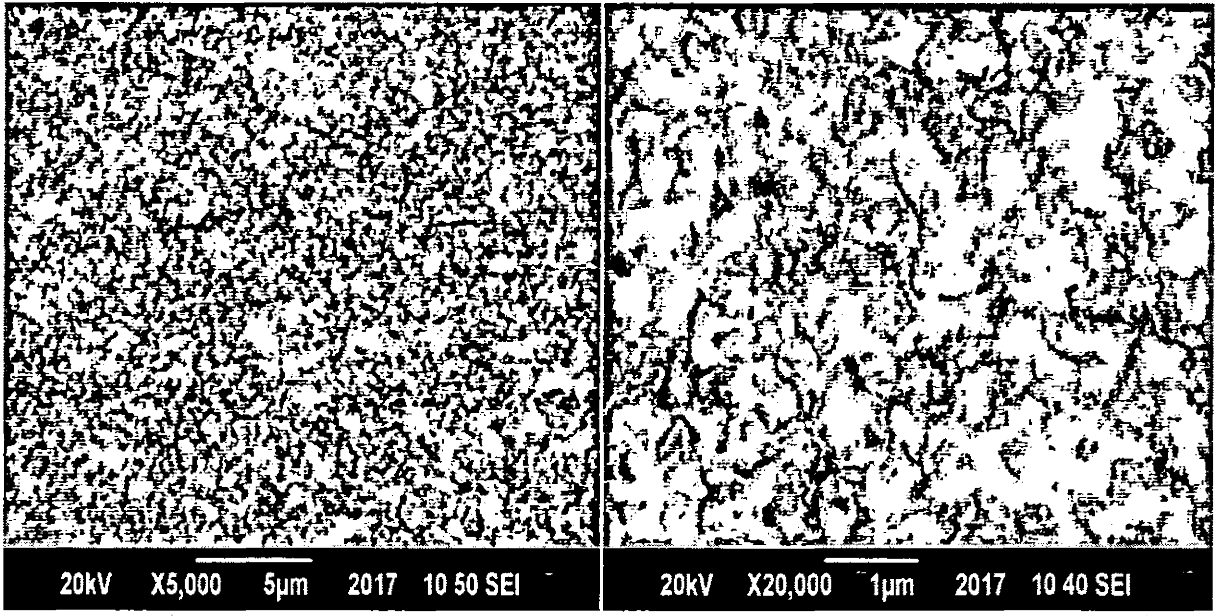

Fig. 5.4: SEM images of as deposited ZnSe thin film

The grain size of as-deposited ZnSe samples calculated from Scherer formula is much less than that taken by SEM. This is explained as agglomeration of particles [8]. The as-deposited ZnSe samples were immersed into the silver nitrate solution, the SEM images of silver deposited on the ZnSe surface is shown in figure 5.5. SEM analysis of ZnSe samples before and after immersion into the silver nitrate solution shows that size of grains has increased after the heat treatment. Before heat treatment average grain size was approximately 0.25 μm and after immersion into the silver nitrate solution followed by annealing of the above mentioned samples at the temperature of 400 °C, the average grain size has been increased up to (0.35-0.4) μm. This analysis shows that it is a very efficient treatment for recrystallization and increase of grain size.

After annealing of the above mentioned samples at the temperature of 400 °C, the process of diffusion of silver into sample was done and it is clear that there was the increase in grain size of Ag doped samples. The annealing temperature is useful for the diffusion of silver and it is also useful in the reorientation of the structure.

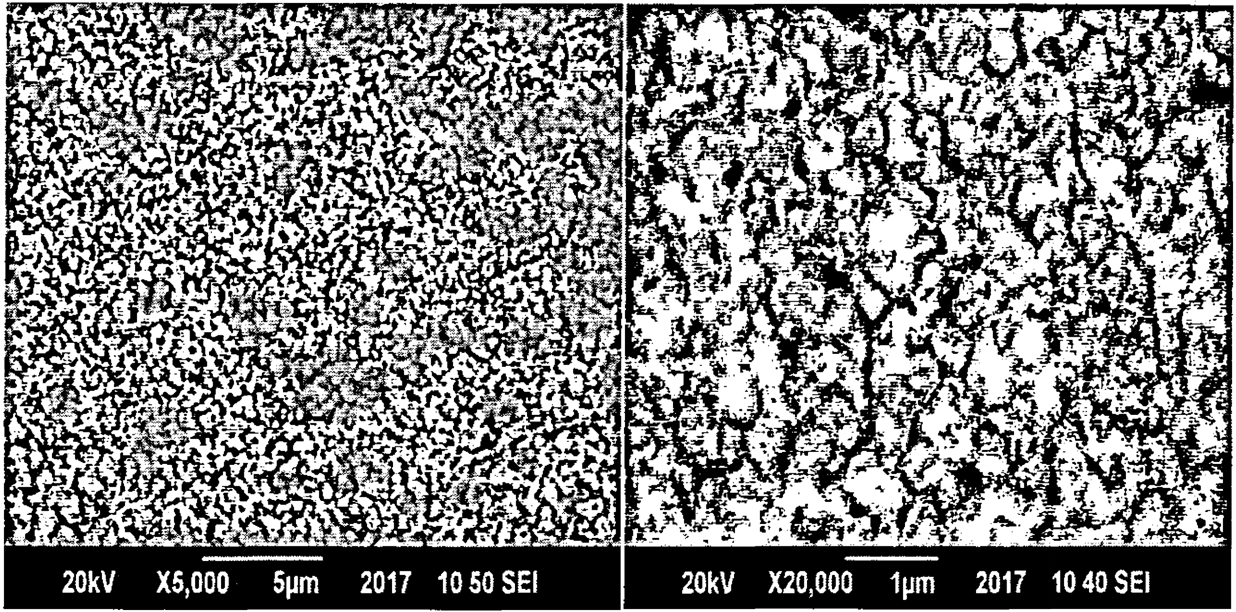

Fig. 5.5: SEM images of Ag doped (%mass 5.80%) ZnSe thin films after annealing 400 °C

The Energy Dispersive X-ray (EDX) provides the compositional analysis.

The quantitative compositional analyses of as-deposited and silver doped ZnSe thin films were carried out by EDX (Energy Dispersive X-ray Analysis) attached with the scanning electron microscope (SEM). Typical EDX results show the atomic contents of elements present in the samples.

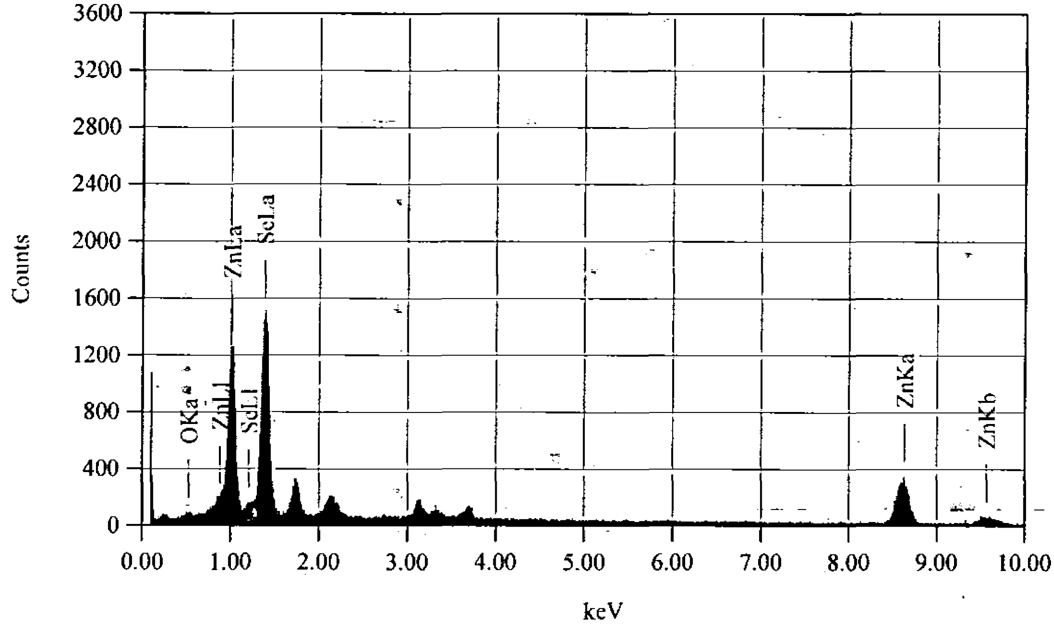

Fig. 5.6: Energy Dispersive Spectroscopy of as deposited ZnSe thin film

The as-deposited samples are Selenide enriched. After immersion in the solution of '$AgNO_3$'and annealing at 400°C, the composition was significantly changed.

Compositional Measurements	Zinc Mass%	Selenide Mass%	Silver Mass%
As-Deposited sample	38.37	59.51	0%
(30min) Ag-doped sample	38.16	55.34	5.80%

Table: 5.2: Composition of as-deposited and Ag-doped ZnSe thin films

In Table 5.2, the compositional comparison is shown between the as-deposited and silver doped ZnSe thin films. Figure 5.7 shows EDX of Ag-doped ZnSe thin films.

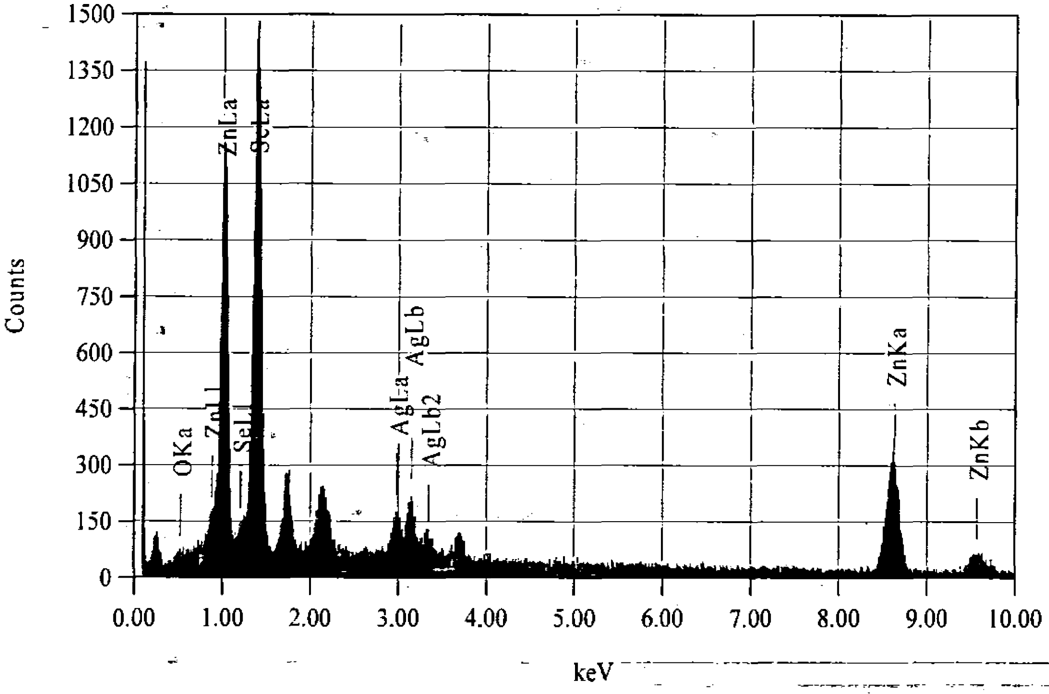

Fig. 5.7: Energy Dispersive Spectroscopy of Ag-doped ZnSe thin film

Doping Time (minutes)	**Silver composition (Mass %)**
10	0.49%
20	2.32%
30	5.80%

Table 5.3: The change in silver composition with immersion time

The concentration of silver atoms increases with increasing immersion time, presented in the Table 5.3. The concentration of Selenide decreases after Ag-doping showing replacement of Se-atoms by Ag-atoms and Selenide goes into the solution.

The atomic force microscope is surface investigation tool, providing two dimensional as well as three dimensional images of the surface. The roughness of the surface of thin films can also be calculated with this tool. The atomic force 3-D images [9] of as-deposited samples are presented in figure 5.8 along with the data.

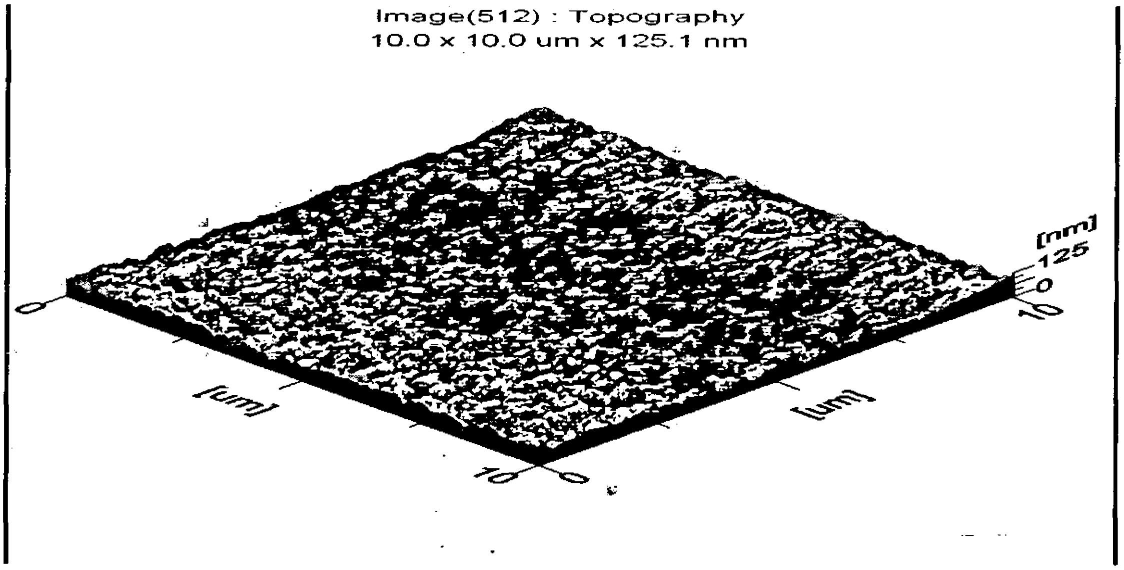

Fig. 5.8: Atomic force microscopy of as deposited ZnSe thin film

By silver doping in ZnSe thin films, the color of the surface changes and a dark region emerges showing the diffusion of silver.

The number of grains decreases, due to the diffusion of silver impurity in the ZnSe films. The AFM images confirm that the change occurred after silver doping in ZnSe samples.

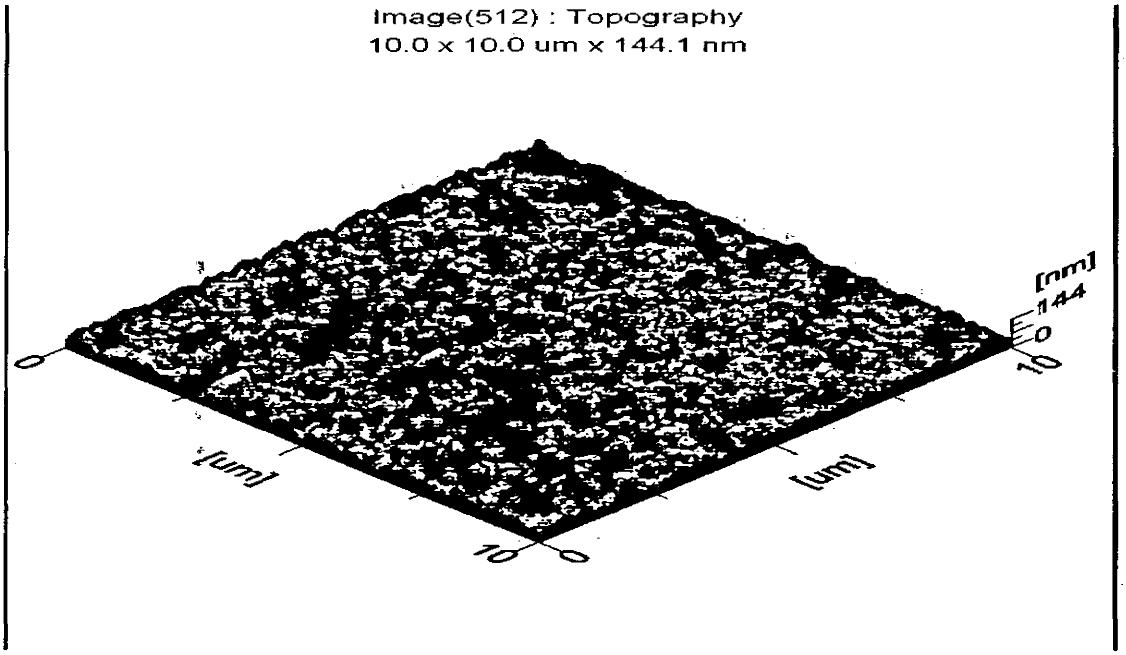

Fig: 5.9 (a): Atomic force microscopy of (10min) Ag-doped sample

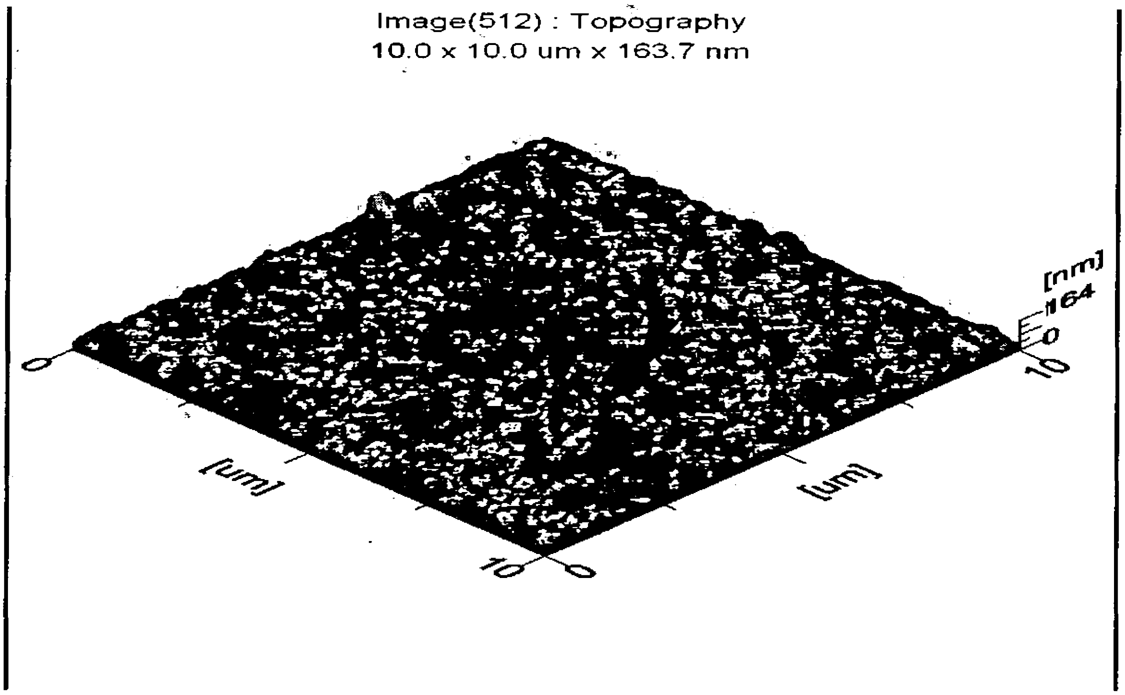

Fig: 5.9 (b): Atomic force microscopy of (20min) Ag-doped sample

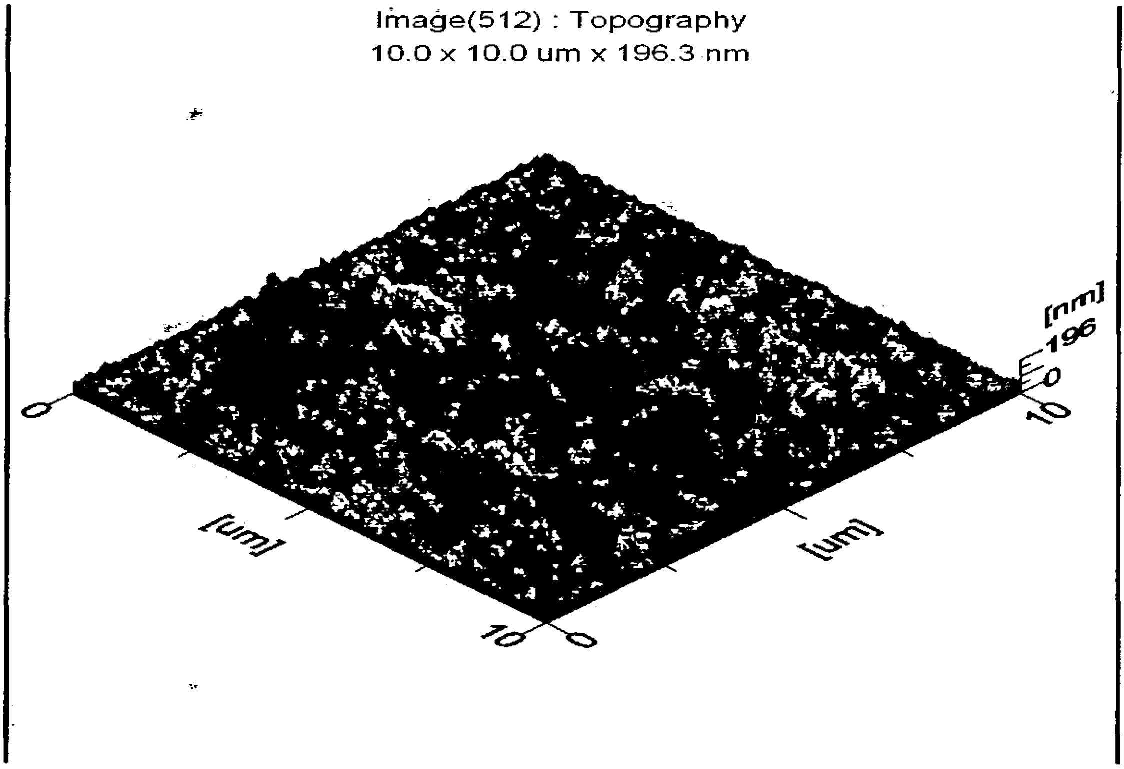

Fig: 5.9 (c): Atomic force microscopy of (30min) Ag-doped sample

Fig. 5.9: Atomic force microscopy of Ag doped ZnSe thin film

Doping Time (minutes)	Silver composition(Mass%)	Surface roughness (nm)
0	0%	14.5
10	0.49%	9.84
20	2.32%	10.6
30	5.80%	11.9

Table 5.4: Effects of Ag doping on surface roughness of ZnSe samples

Table 5.4 shows that surface roughness of Ag doped ZnSe samples increases due to increase in silver composition.

5.3 Optical Results (UV-VIS NIR range)

The percent transmittance of all the films have been measured in the wavelength ranging from 250 nm to 3300 nm using Perkin Elmer UV –VIS-NIR spectrometer model LAMBDA 950. Transmittance is the only property which is obtained directly from the film and the rest are inferred from the transmission spectra.

Thickness of the film is determined by the following formula:

$$d = \frac{1}{4n}\left[\frac{\lambda_m \lambda_M}{\lambda_M - \lambda_m}\right], \qquad (5.5)$$

Where λ_{max} and λ_{min} represent the wavelengths of maximum and minimum transmission respectively

The transmittance decreases with increasing thickness as the distance of light travel through the film increases. As-deposited samples transmitted the light of wavelength above 500 nm. The ultraviolet rays and x-rays are absorbed as these have more energy than the energy band gap of ZnSe. On the other hand the entire wavelength of visible and near infrared region is transmitted. So the ZnSe can be used as a window material for the visible region as well as for infrared region. %T in the visible and IR region is (~70%-90%).

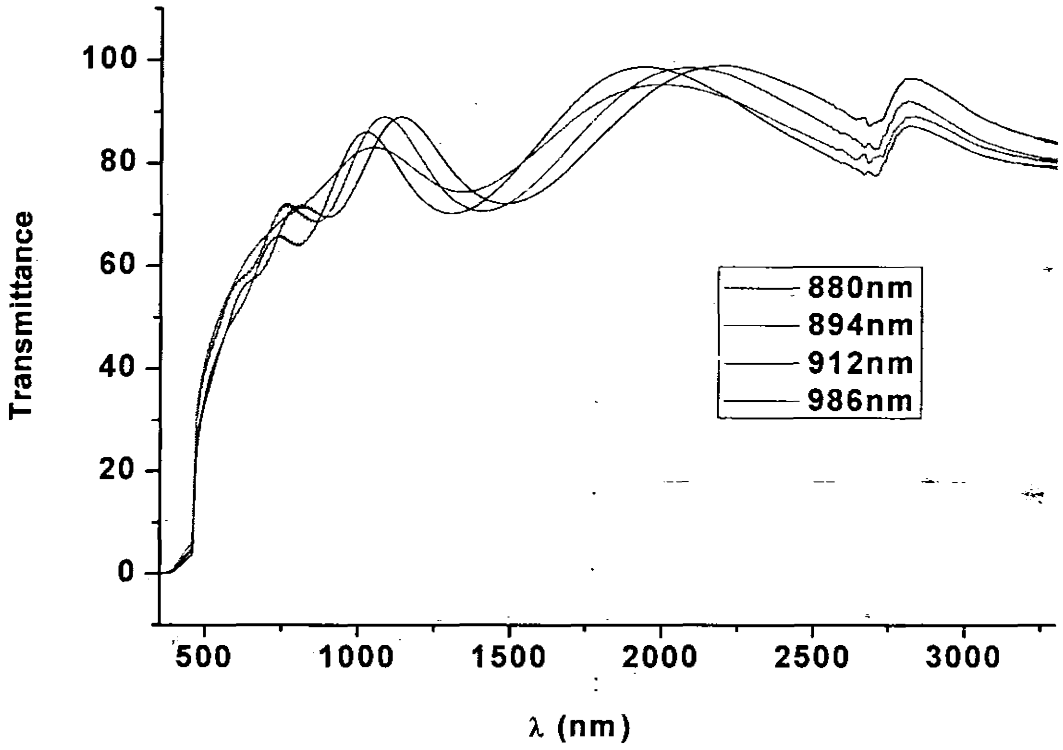

Fig. 5.10: Optical transmission of as-deposited samples of various thicknesses

The most important result obtained from figure 5.10 is that; as the thickness of the films is increasing, transmission is decreasing. As the thickness is increased, there are more chances for scattering and absorption of light while transmitting through the material. This is one of the main reasons for decreasing transmission with increasing thickness.

Transmittance shows decreasing pattern shown in figure 5.10. The comparison of UV-VIS-NIR Transmission of films deposited at different thicknesses.

The transmission spectra and Energy gap Eg changes with Ag-doping [10].

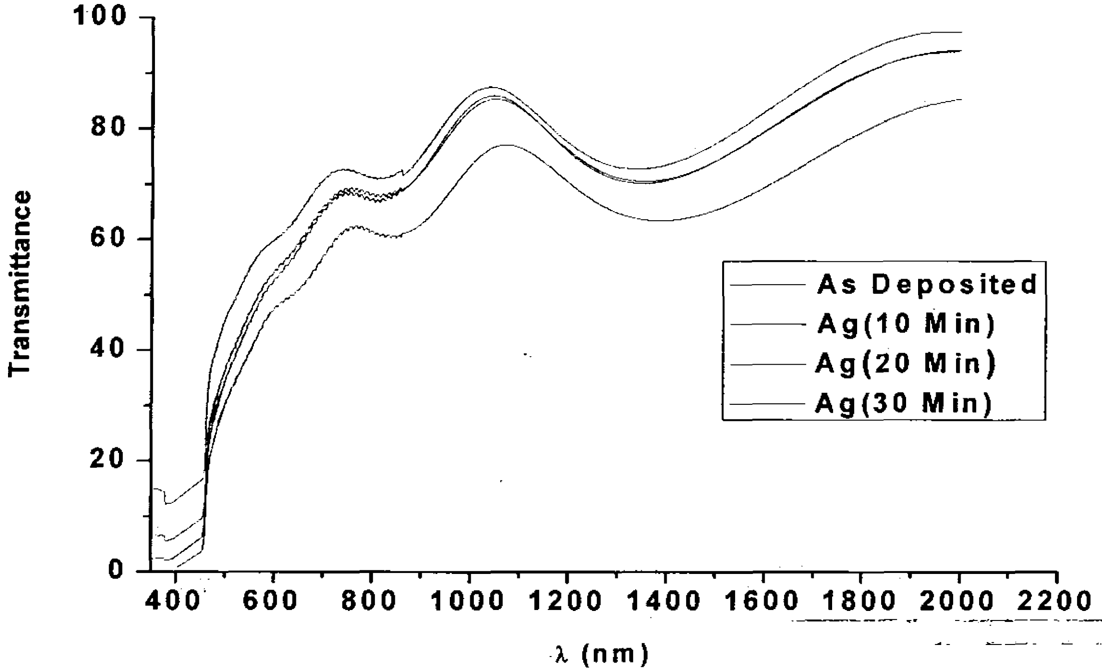

Fig. 5.11: Plot between transmission and wavelength for different films of Silver doped ZnSe.

The energy gap of the deposited thin film can be calculated with the help of the following equation [11]

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^{N/2} \tag{5.6}$$

Where A is a constant, hυ is the photon energy, E_g is the energy gap and N depends on the nature of transition. The absorption co-efficient can be calculated as

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \tag{5.7}$$

Where d is the thickness and T is the transmittance.

Several factors affect the energy gap, including structural parameters, lattice stance, carrier concentration, grain size, etc. The energy gap decreases with increase of thickness [12]. There comes minute change in energy gap with increasing thickness in our case which might be due to lattice strain.

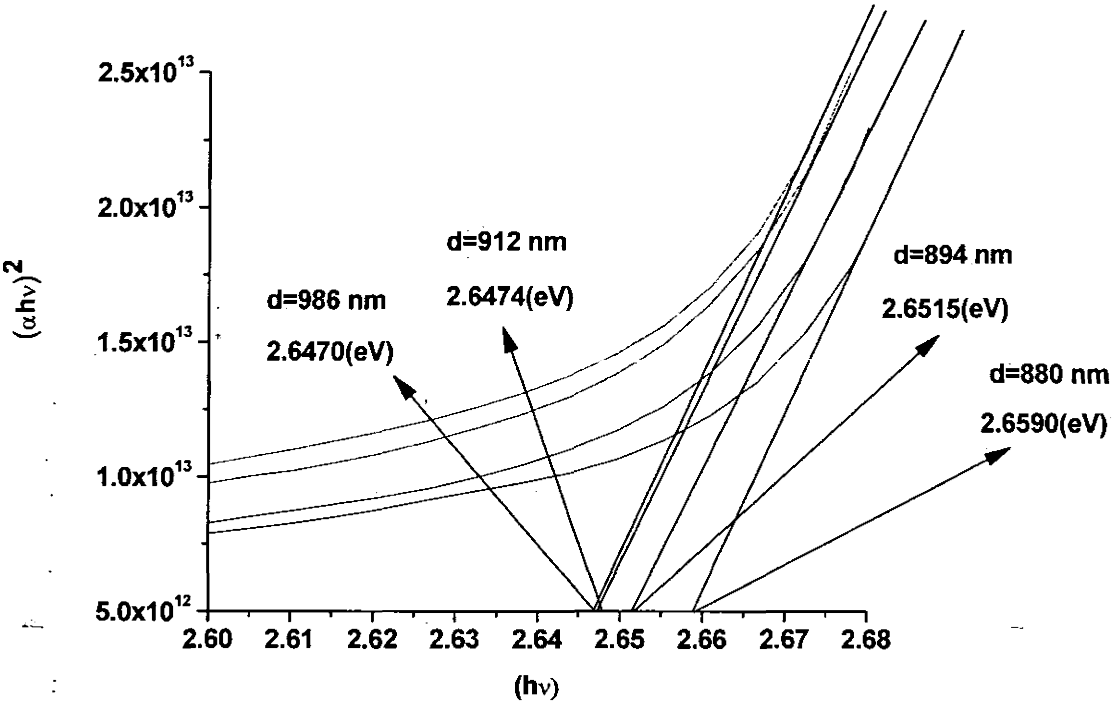

Fig. 5.12: Determination of band gap of as-deposited ZnSe thin films with different thicknesses by extrapolating $(\alpha h\nu)^2$ vs. (hν)

By extrapolating $(\alpha h\upsilon)^2$ versus the incident photon energy (hυ), energy band gap of thin film can be calculated. The energy gap of as-deposited ZnSe thin films was about 2.659 eV and the energy gap for Ag-doped was found 2.625 eV for 5.8% Ag (30 minutes doping time). Although there is a minute change in energy gap, this decrease relates to the higher Silver concentration. This shrinkage of energy gap is due to the larger number of overlapping energy levels which were created due to the Silver diffusion.

Energy gap Eg of all the Ag-doped samples are given in Table 5.5 showing decreasing trend in figure 5.13 with increase of silver composition.

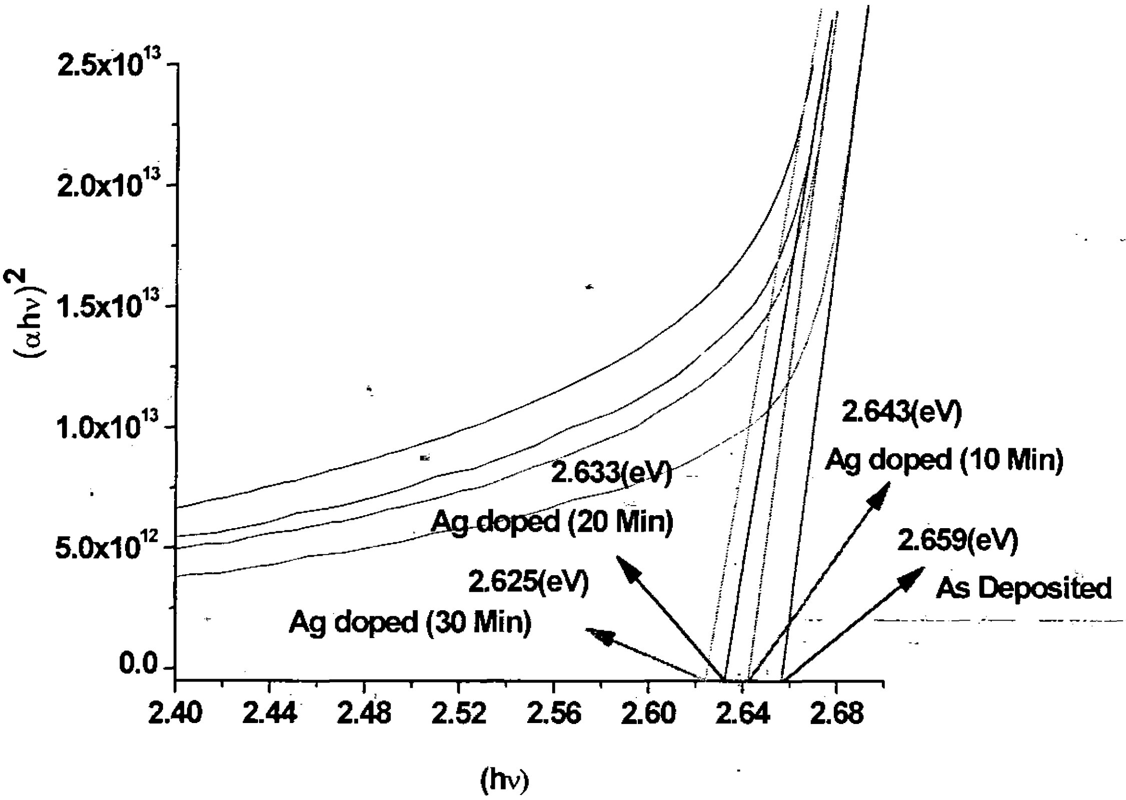

Fig. 5.13: Effect of Ag-doping on energy gap of ZnSe thin films

Doping Time (minutes)	Silver composition (Mass%)	(Energy Gap eV) ±Error
0	0%	2.659±0.01
10	0.49%	2.643±0.01
20	2.32%	2.633±0.01
30	5.80%	2.625±0.01

Table 5.5: Effects of Ag doping on energy gap of ZnSe samples

5.4 Electrical Properties

Electrical properties of material such as resistivity, mobility, sheet concentration etc are discussed in this section. The Hall Measurement system (Ecopia HMS 3000), which gives an accurate and precise measurement is available in the thermal transport physics laboratory @ NUST, Islamabad.

The electrical properties of as-deposited and Ag doped ZnSe samples are measured at 1 nA and 300 K temperature, given in Table 5.6.The ZnSe samples are immersed in the silver nitrate solution for the different time periods as discussed earlier.

Doping Time (minutes)	Resistivity (Ω cm)
0	1.069×10^8
10	4.460×10^6
20	1.169×10^4
30	2.353×10^1
40	1.395

Table 5.6: Variation in resistivity with the increasing doping time

As the doping time of as-deposited ZnSe samples increases, the silver concentration also increases. The lowest resistivity achieved after Ag-doping is 1.395Ω-cm, which was found before doping to be 1.069 × 10^8Ω-cm. With the silver doping, decrease in resistivity was observed by several orders of magnitude, as shown in figure 5.14.

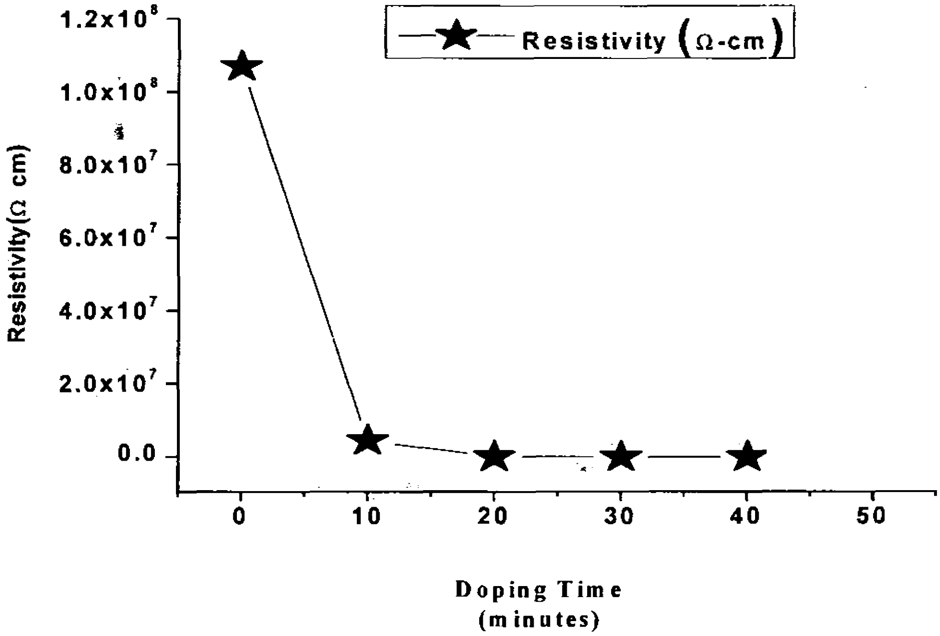

Fig. 5.14: Variation in resistivity with the increase in doping time

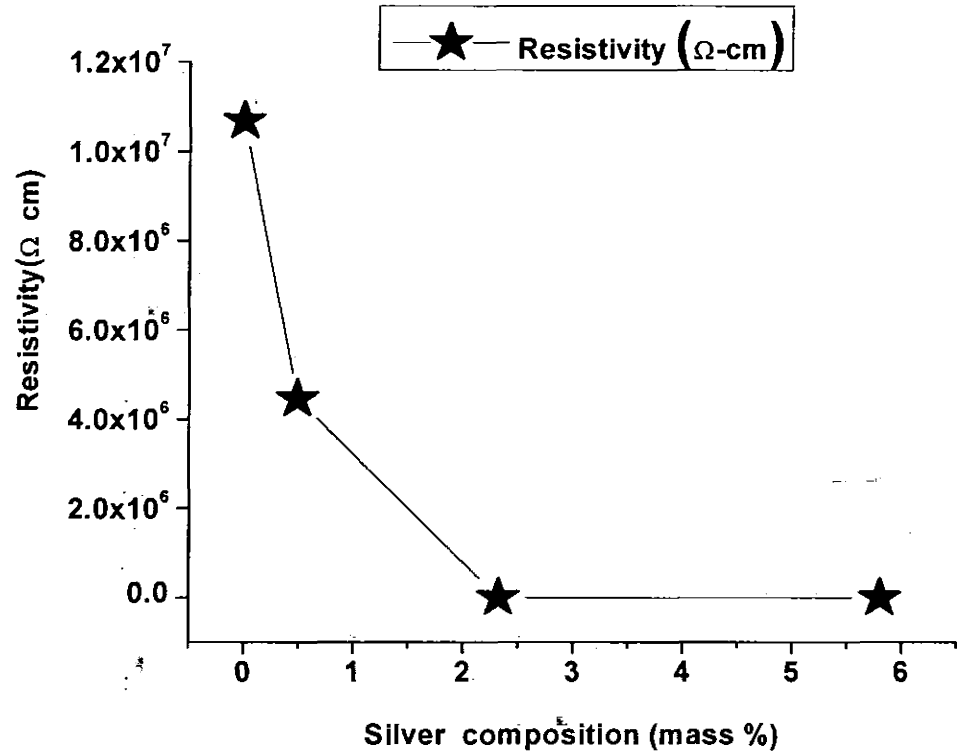

Fig. 5.15: Variation in resistivity with the increase in silver composition

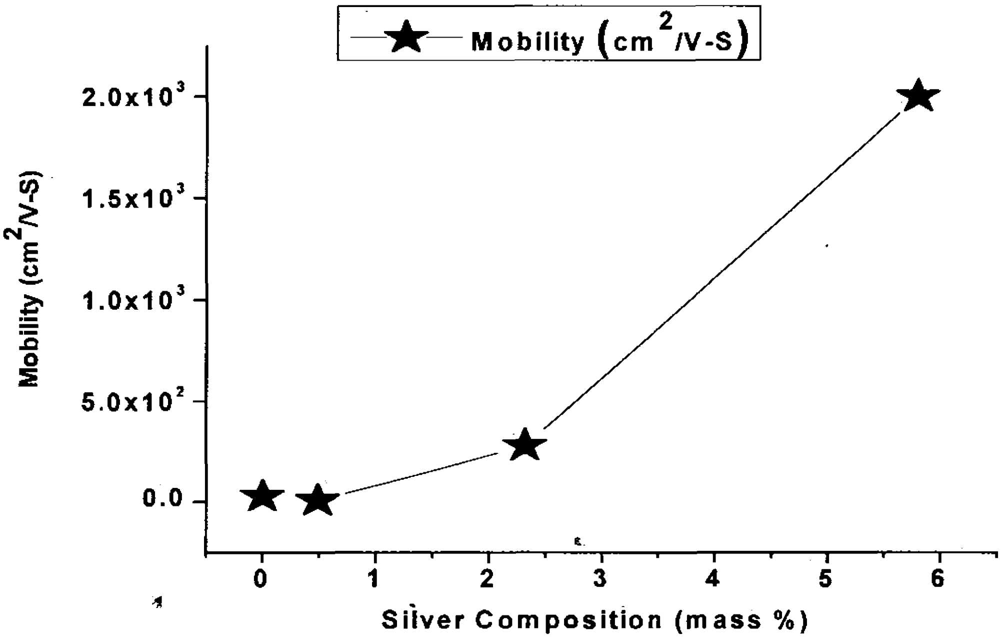

Fig. 5.16: Variation in mobility with the increase in silver composition

The mobility increases with the increase in the silver concentration as shown in the figure 5.16.

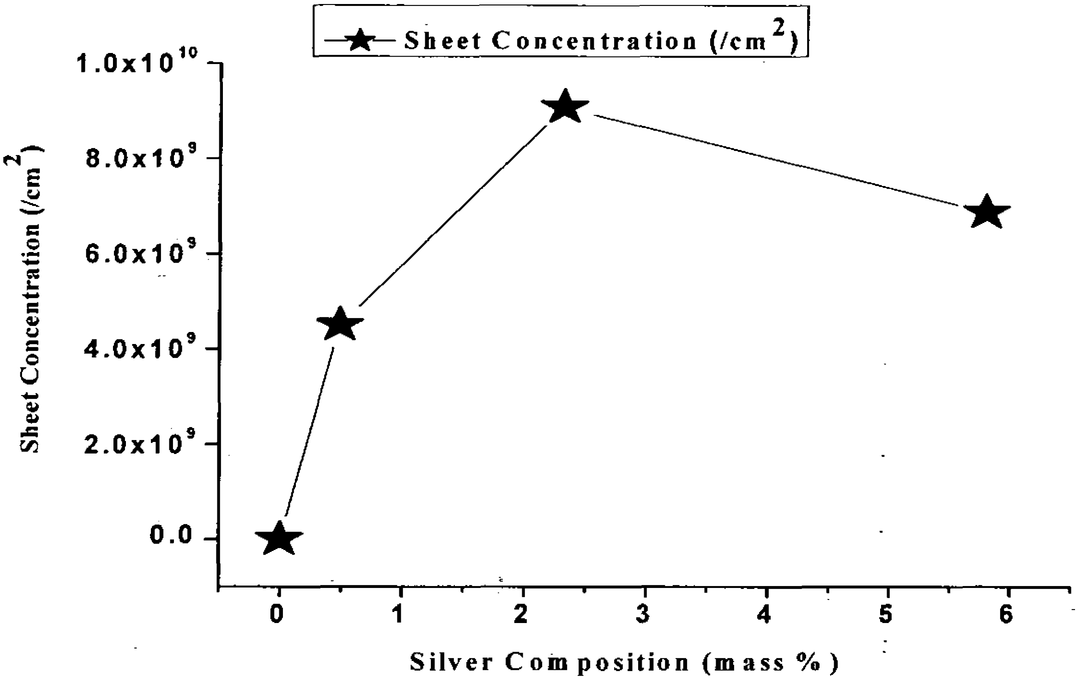

Fig. 5.17: Variation in sheet concentration with the increase in silver composition

The sheet concentration increases with the increase in the silver composition up to some extent and then reduces sharply as shown in figure 5.17.

If silver doping improves there is also increase in the number of charge carries and increase of silver composition effects on the changes of mobility, resistivity, sheet concentration and all this was observed. Due to dipping of ZnSe films in $AgNO_3$ solution many possibilities due to ions exchange process could occur such as, diffusion of Ag ions into ZnSe films or replacing of Zn or for forming of Ag_2Se, but due to small quantity of Ag in the films it was not possible to confirm the exact process, however the optical result shows the change in resistivity is due to Ag diffusion in the films, which reduces the optical transmission of the films and does not affect the position of optical band gap (i.e. there is no new compound formed to cause drastic shift in the band gap).

Conclusions

ZnSe thin films are deposited by close spaced sublimation technique onto cleaned glass substrates. The films are uniform and have good adherence with the substrate surface. XRD analysis confirms the cubic structure of the substance with predominant [111] orientation. On increasing the film thickness the intensity and width of the peak [111] gradually increases, which indicates the improvement of crystallinity with film thickness. With the increase of film thickness the average grain size of the films is found to increase. However, the internal strain and dislocation density decreased. The films which were treated by $AgNO_3$ solution and post heated were less oriented in [111] direction, the loss in the texture of the ZnSe thin film is exhibited by the treatment of silver nitrate solution followed by heat treatment in vacuum at 400 °C for one hour.

SEM analysis of ZnSe samples before and after immersion into the silver nitrate solution shows that, before doping average grain size was approximately 0.25 μm and after immersion into the silver nitrate solution, the average grain size has increased up to (0.35-0.4) μm due to silver doping. EDX results of Ag-doped ZnSe thin films illustrate that the concentration of selenide decreases after Ag-doping showing replacement of Se-atoms by Ag-atoms and Selenide goes into the solution. The number of grains decreases, due to the diffusion of silver impurity in the ZnSe films. The AFM images confirm that the change occurred after silver doping in ZnSe samples.

The optical studies which have been done by using spectrophotometer technique showed a decrease of transmission and optical gap energy with the increase of film thickness. The XRD have not shown a drastic change in the film structure, while the optical results show a decrease in the transmission and slight shift in the optical band gap. This shrinkage of energy gap is due to the larger number of overlapping energy levels which were created due to the Silver diffusion. The lowest resistivity ~1.395Ω-cm can be achieved by silver doping which was found before doping 1.069×10^8Ω-cm. If silver doping improves there is also increase in the number of charge carries and increase of silver composition effects on the changes of mobility, resistivity, sheet concentration and all this was observed. On the basis of the XRD, SEM, AFM and Hall measurements, it is concluded that the Ag doping strongly affects the morphology as well as electrical properties.

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Recommendations for Future Studies

The CSS system could be modified to enable it to be used to get films of materials having high Sublimation temperatures. Heating assembly of the system which is halogens lamps in the present situation can be replaced by resistive heating unit to get higher temperature range. An Electro-mechanical shutter can be installed between source and substrate to stop at once at a particular time. Further, ZnSe thin films could be obtained from different techniques like sputtering, chemical bath and the properties of ZnSe thin films obtained by CSS, could be compared with those obtained using sputtering and chemical bath.