

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

This chapter describes the experimental techniques and equipment used through the course of this work. ZnS_xSe_{1-x} thin films have been prepared by electron beam evaporation, the structure, optical and electrical properties of the samples have been investigated using energy dispersion analysis for x-ray (EDX), scanning electron microscope (SEM), x-ray diffraction (XRD), UV - VIS - spectroscopy and DC-electrical measurements at different ambient temperatures. Film thickness was estimated from the optical transmission spectrum at normal incidence and will be described in chapter 3.

2. 1 Electron beam apparatus

The electron beam apparatus (Edwards AUTO 306), which was used to prepare the samples of ZnS_xSe_{1-x} , has been provided by Edwards High Vacuum International. The apparatus consists of three main parts: vacuum pumping system, vacuum chamber, and electron beam power supply.

The vacuum system consists of a rotary vacuum pump (Edwards E2 M8 double stage) and a vapor diffusion pump (Edwards EO 4K). All switching sequences between roughing and backing process are achieved through electrically operated valves controlled by a microprocessor based control system.

The vacuum chamber contains a six-position electron beam source, manual source shutter assembly, substrate holder, electrical heater, thermocouple and two

cylindrical glass tubes. Figure 2.1 shows a plane view of component parts of the six-position electron beam source [73].

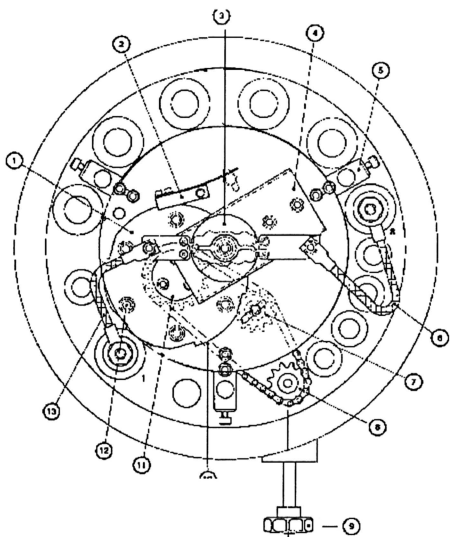
The Edwards, 400/800 electron beam power supply is used with AUTO 306. This power supply can provide high tension voltage HTV (maximum open circuit 4.5 kV \pm 10%), high tension current HTC (short circuit rating 100 mA \pm 10%), low tension voltage LTV (6 V) and low tension current LTC (20 A ac).

2.2 Sample preparation

Microscope glass slides were used as substrates to deposit the films of $\text{ZnS}_x\text{Se}_{1-x}$. The glass slides with thickness of 0.8-1.0 mm were cut to the sizes of approximately $(1.2 \times 1.2) \text{ cm}^2$. This size has been chosen to facilitate the fitting of the samples inside the different equipment used during the characterization processes. The substrates were ultrasonically agitated in acetone for a time of 15-20 minutes. This is to remove any grease or oil on the surface of the substrate. The substrates were then rinsed in distilled water and dried in an oven with the temperature of around 50 °C. Aluminum mask was designed with rectangular holes with dimension $(1.0 \times 1.0) \text{ cm}^2$ to be used as a holder for the glass substrates during the deposition of the samples. Another hole with dimensions of $(0.4 \times 0.4) \text{ cm}^2$ was made to hold the substrate suitable for EDX and SEM investigations.

Prior to each use of the preparation system, the components of the vacuum chamber were properly cleaned by acetone to avoid contamination during deposition. The glass substrates are fixed at the top of the aluminum mask that is fixed horizontally 15 cm above the tungsten filament of the electron beam source.

The typical procedure, which is followed in this work to prepare $\text{ZnS}_x\text{Se}_{1-x}$ samples by electron beam evaporation, will be presented now [73].



- | | |
|------------------------|--------------------------|
| 1. Turret | 8. Drive Sprocket |
| 2. Index Spring | 9. Drive Knob |
| 3. Electron Beam Gun | 10. Drive Chain |
| 4. Carrier | 11. Turret Sprocket |
| 5. Tripod Mounting Lug | 12. Turret Source Holder |
| 6. Live Braid | 13. Live Braid |
| 7. Tension Sprocket | |

Figure 2.1: Component parts of the six-position electron beam source (plane view) [73].

The source, which is to be evaporated, is placed in a carbon hearth mounted on one of the turrets which can be raised by turning the turret rotation knob in a clockwise direction until the source is positioned just below the filament. The chamber is made of a cylindrical glass tube that is surrounded by another cylindrical Perspex tube used as an implosion guard. The base pressure inside the vacuum chamber is normally pumped down by the vacuum system to approximately 2×10^{-5} torr. A stainless steel manual shutter, which can be operated from outside the vacuum chamber, is positioned between the filament and the substrates to prevent heat radiation and volatile constituents reaching the substrates during source degassing periods. During operation the low - tension (LT) control knob is increased to the position where the filament and the source will degas (approximately 60% power). The degassing operation is accompanied by a rise in the chamber pressure and the (LT) power is adjusted to control the chamber pressure below 9×10^{-5} torr. The degassing process continues until the system pressure reaches a steady level for a desired period of time where the (LT) is switched off to end the degassing process. The pressure then reduces again to approximately 2×10^{-5} torr where the high tension (HT) is switched on and the applied voltage is increased up to 4 kV. Then the (LT) is switched on again and increased slowly until the emission current between 50 and 100 mA is achieved. The (HT), (LT) and the hearth height are adjusted until the source material starts to evaporate. The manual shutter is moved to allow the vapor to deposit onto the substrates for the required deposition time, which is between 3 to 6 minutes varying from one sample to another. The substrate temperature is monitored through the control panel which is connected to a thermocouple that is fixed very close to the substrates at about 60°C for all $\text{ZnS}_x\text{Se}_{1-x}$ samples studied in this work. When the

deposition is completed, the shutter is moved to block the space between the filament and the substrates, and the controllers are then returned to their zero positions and (HT) and (LT) switches are switched off. The vacuum system is switched off and the chamber is vented. Then the samples are stored in a box inside a desiccator prior to characterization.

During the earlier attempts to prepare ZnS samples, an amount of ZnS powder -325 mesh, typically 99.99% pure, provided by (CERAC/ Pure Advanced Specialty Inorganics, U. S. A.) was used as an evaporation source. The powder was packed into the carbon hearth. When the evaporation process began the powder splattered and the vapor of ZnS could not be obtained. This led to the use of pellets of pressed powder as the evaporation source. The pellets were 8 mm in diameter and 5 mm thick formed by pressing the powder by air and electric powered hydraulic pumps (ENERPAC) as a binder at a pressure of 30000 kPa. Zinc selenide granules (1-3 mm pcs, typically 99.9999% pure, provided by (CERAC Coating Materials, U. S. A.) were used as an evaporation source to prepare ZnSe samples. To form pellets of ZnS-ZnSe, the zinc selenide granules were ground in a ceramic crucible to obtain a very fine powder. Different amounts of zinc sulfide powder were mixed properly in the crucible with certain amounts of zinc selenide powder to form well-mixed mixtures. These mixtures were pressed to produce the pellets. The proportion between the amounts of ZnS and ZnSe powders has been chosen arbitrarily and changed from one pellet to another to get samples with different compositional variations of sulfur and selenium when these pellets were used as evaporation sources.

2.3 EDX and SEM

Different physicochemical techniques have been reported in the literature for the compositional analysis of semiconducting thin films [59, 74-76]. The choice of a suitable analytical technique for the quantitative determination of the elements, from which the film is prepared, is dependent on individual factors such as the amount of film available, the form of the sample and the type of treatment to which the film can be subjected, the nature of the element (whether an impurity or a major constituent) to be detected, the availability of equipment and of course the cost of the analysis as well as the time requirement.

In this work energy dispersive analysis of x-ray (EDX) technique was used to determine the composition in ZnS_xSe_{1-x} thin films. In this technique an electron beam generated by electron gun impinges upon the area of interest on the sample surface and excites electrons to emit primary x-rays characteristic of the elements present. Spectrometers and detectors are built into the instrument to select and measure the characteristic radiation. This technique enables the detection of the elements with atomic numbers of 11 or greater and also elements with minimum concentrations varying from 0.001% to 0.1% can be detected. Identification of the elements and semi-quantitative analysis are easily obtained.

An energy dispersion x-ray analyzer (EDAX) (Philips model PV 9800) attached to a scanning electron microscope (SEM) (Philips model 515) was used for compositional analysis of ZnS_xSe_{1-x} thin films samples, while the SEM was used to obtain micro graphs of selected areas of the film surface. Samples for EDX/SEM studies were mounted on aluminum stubs with a conductive carbon cement (Agar Aids). Since ZnS_xSe_{1-x} non-conductive materials, the films were coated with carbon

using a Bio Rad (model E5100 series 11) evaporator. The coating of the films with carbon is necessary to avoid excessive specimen charging. EDX setup was calibrated to detect the expected elements in the samples. The detection was carried out with 0.01 KeV and 0.04 KeV energy range. The channel resolution was 10 eV/ch. Super quantitative analysis was used to obtain net x-ray intensities for each element in the film, i.e. intensities corrected for background and peak overlaps. These intensities were converted to concentrations for each element. ZAF (Z= atomic number correction, A absorption correction, F= fluorescence correction) is an iterative calculation method for applying matrix correction. ZAF factors and k-ratios (the normalized ratio of the net intensities to pure element intensity factor calculations) were obtained. The compositional results for the samples were reported in atomic percentages (AT%) and weight percentages (WT%).

SEM photographs were obtained by using acceleration voltage in the range of 2-5 kV and a magnification of 10^2 - 10^4 . Figure 2.2 shows a schematic diagram of a scanning electron microscope according to Wells [77]. An electron beam is produced by an electron gun and accelerated with a high negative voltage, the diameter of the beam is reduced to the order of 100 Å by electron lenses. The scanning coils deflect this beam and sweep it over the specimen surface. A cathode-ray display tube is scanned synchronously with the electron beam. The brightness of the display tube is modulated by the signal arises from the interaction of the beam with the probed surface element. The strength of this signal is thus translated into image contrast. Secondary electrons, which the beam probe liberates from the specimen surface, are collected and used as the contrast signal. The yield of the collected electrons depends on the nature of the specimen surface and on its inclination with respect to the probing beam.

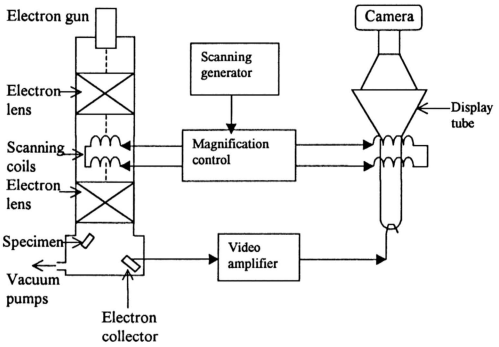


Figure 2.2: Schematic diagram of a scanning electron microscope [77].

Consequently pictures with highly perspective appearances can be obtained by using the camera that is fixed to the system.

2.4 X-ray diffraction

A Philips PW 1840 compact X - ray diffractometer system, with CuK_α radiation ($\lambda_{\alpha 1} = 1.54060 \text{ \AA}$ and $\lambda_{\alpha 2} = 1.54438 \text{ \AA}$), and Siemens X-ray diffractometer system, with CuK_α radiation ($\lambda_\alpha = 1.5406 \text{ \AA}$), were used to perform XRD scanning. The samples were scanned in the 2θ range of $15\text{--}45^\circ$. Current of 20 mA was used to heat the filament of the electron gun while 20 kV was used to accelerate the electrons. The diffractometer consists of a goniometer complete with an automatic divergence slit and a solid-state detector, stepper motor to drive the goniometer, a high-voltage generator and x-ray tube, and electronic unit to control the system and a strip chart recorder. The diffractometer is equipped with a dust – cover as a part of the safety enclosure. Figure 2.3 illustrates the goniometer X-ray path [78]. The Philips PC-PAD (PW 1877) powder diffraction analysis software package, which can be run by a personal computer connected to the x-ray system, was used to operate the system and analyze the data while Siemens software was used to operate the Siemens system. These computer soft-wares are capable to analyze the x-ray spectrum in order to determine the intensity ration, the position and the full width at half maximum (FWHM) of the diffraction peaks and the inter-planar spacing of the lattice planes. These data are useful to determine the crystallographic structure and to estimate the structure parameters such as the lattice constants and the grain size of the material under investigation.

2.5 UV – VIS – Spectrophotometer

The transmission spectrum of ZnS_xSe_{1-x} films were measured in the range of 200-3200 nm of the electromagnetic spectrum using a Shimadzu UV-3101-PC spectrophotometer associated with UV-3101 PC software operates under the Microsoft windows environment. The monochromator is a double monochromator of grating-to-grating type which is composed of the first monochromator (pre-monochromator) having 3 gratings and the second monochromator (main monochromator) having 3 gratings. Ample optical energy is available for various measurements over a wide wavelength range of 190 nm (ultraviolet) to 3200 nm (near infrared). Figure 2.4 shows the schematic diagram of UV-3101 PC optical system [79]. The sources of the light beam are a 50 W halogen lamp (long life type 2000 H) and a Deuterium lamp (socket type). The light sources are switched on/off automatically corresponding to the wavelength scanning. The light beam passing into the detector is detected by the photomultiplier PM (in the visible/ultraviolet region) or by PbS cell (in the near-infrared region). The scanning procedure starts by placing two glass substrates into the sample and reference holders and performing base line correction. The base line operation is to perform background correction over a certain selected wavelength range. The reference glass is then replaced by the sample and the transmission scanning is obtained over the selected range of the wavelength.

2.6 Electrical measurements

For DC-electrical measurements aluminum was used to form planar electrodes by thermal evaporation on the surfaces of the samples investigated in this work. The pumping system is basically similar to the one used in the electron beam apparatus with a diffusion pump backed by a rotary pump. The aluminum source was fixed inside

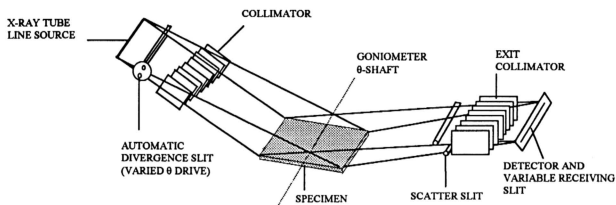


Figure 2.3: Schematic diagram for the goniometer x-ray path [78].

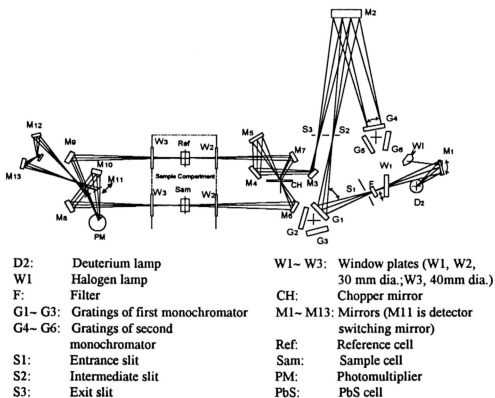
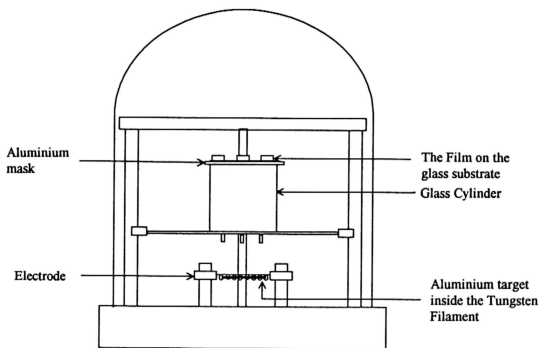


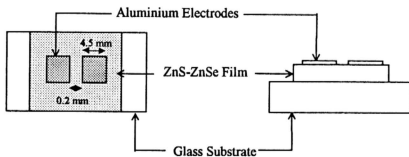
Figure 2.4: The schematic diagram of the UV-3101 PC optical system [79].

a helical tungsten filament with the ends connected to the anode and cathode. The current across these two electrodes is controlled by a variac. The $\text{ZnS}_x\text{Se}_{1-x}$ samples were fixed on an aluminum mask which rest on the top of a cylindrical shaped glass. The electrodes were prepared under a pressure lower than 10^{-4} torr. The dimension of the electrodes was approximately (4.5×4.5) mm² with almost 0.2 mm separation. Figure 2.5 shows the arrangement of the chamber along with a plane and a cross-section views of the electrodes deposited onto the film. Electrical leads of copper (0.1 mm in diameter) were attached to the electrodes using a silver paint.

A closed cycle refrigerator system (Janis model CCS-100) with high purity (99.999%) helium gas as the working fluid was used to operate at a temperature between 20 K and 475 K. Figure 2.6 illustrates the closed cycle refrigerator cryostat [80]. In this system the cold head is separated from the compressor by a couple of flexible high pressure tubes which carry the compressed helium into and out of the cold head. The refrigerator second stage cold finger includes a 1.5 inches diameter sample mount, a 25 ohm heater, and a silicon diode thermometer used when controlling the refrigerator temperature. The control heater was connected to an autotuning temperature controller (manufactured by Lake shore cryotronic, Inc., model 330) which can be used to display and control the sample temperature. The model CCS-100 is equipped with a bellows sealed evacuation valve, which allows evacuation and sealing of the insulating vacuum jacket. An Edwards rotary pump was connected to the valve to evacuate the system to a pressure less than 5×10^{-2} torr prior to the cooling down procedure. Re-evacuation was required whenever a new sample was installed or when the pressure increased beyond 10^{-2} torr according to out-gassing and O-ring permeation.



(a)



(b)

Figure 2.5: (a) A cross sectional view of the chamber used in the deposition of the electrodes and (b) a plane and a cross - section views of the deposited electrodes on the film.

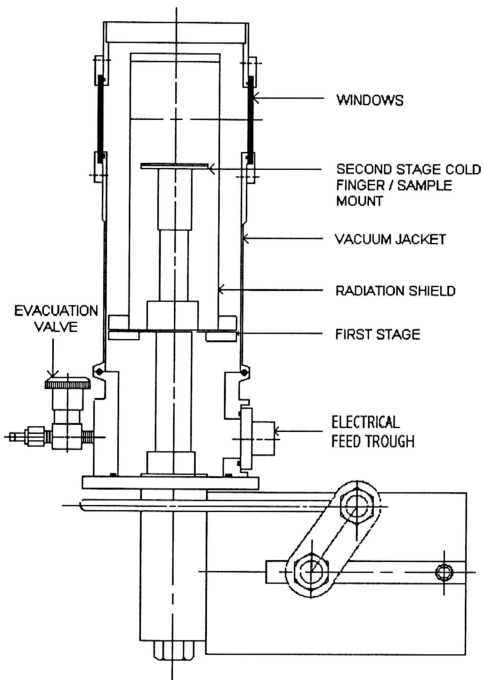


Figure 2.6: Schematic diagram for closed cycle refrigerator cryostat [80].

$\text{ZnS}_x\text{Se}_{1-x}$ sample was mounted inside the cryostat and the free ends of the copper leads were connected to electrical feed trough. Source measure unit (SMU, Keithely 238) was used as a DC power source and a current measuring unit. SMU was connected to a PC in which a Metrics software operating under the Microsoft windows environment was installed. The Metrics software was programmed to change the applied voltage across the sample and to record both of the applied voltage and the current passing through the sample. Two types of DC-measurements were made on the $\text{ZnS}_x\text{Se}_{1-x}$ samples investigated in this work. These two types are current-voltage measurements at constant temperature and current-temperature measurements at constant voltage. In the first type of measurements the sample was cooled down to about 20 K, then the applied voltage was changed from 0-50 V in a step of 0.25 V and for each step the current across the sample was recorded against the applied voltage at fixed temperature. The (I-V) measurements were taken at different fixed temperatures in the range of 20 K to 475 K at an interval of 50 K.

In the second type of measurements the applied voltage was fixed at 10 V and the current across the sample was recorded against the sample temperature in the range of 20 K to 475 K at an interval of 5 K.