CHAPTER-2

METHODS OF FILM DEPOSITION AND CHARACTERIZATION TECHNIQUES

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2.1 METHODS OF THIN FILM DEPOSITION

2.1.1 INTRODUCTION

Thin solid films can be prepared by various methods. The method to be employed depends on the application for which the films are prepared [1,2]. These films can be a single or multielement compound or multilayer coatings on substrate of different shapes and sizes [3-5]. The formation of a film on a substrate away from the source consists of three basic steps: (i) converting the condensed phase (generally a solid) into a gaseous or vapour phase, (ii) transporting the gaseous or vapour phase from the source to the substrate, and (iii) condensing the gaseous phase on the substrate, followed by the nucleation and growth of the film.

All the deposition methods can be distinguished by the way the three above mentioned basic steps are effected. One can in principle get films of desired properties by properly modifying these three steps.

Thin film deposition techniques have been broadly classified in two main categories, which can also be subdivided.

(I) Physical Vapour Deposition
(a) Thermal or Direct Evaporation
(b) Electron Beam Evaporation
(c) Molecular Beam Epitaxy (MBE)
(d) Activated Reactive Evaporation
(e) Ion Plating
(f) Sputtering

(II) Chemical Vapour Deposition
(a) Spray Pyrolysis
(b) Electrodeposition
(c) Anodization
One of the major advantages of the physical vapour deposition technique is that all three steps previously mentioned can be independently controlled. However, the deposition parameters should be carefully monitored in order to achieve reproducibility in the films. The pressure in the vacuum chamber and the design of the evaporation source play a vital role in physical vacuum deposition method. These factors affect the evaporation rate as well as structural and hence electrical, optical properties of the deposited films. Only the techniques which have been employed in the present investigation for the deposition of thin films are discussed here.

2.1.2 THERMAL OR DIRECT EVAPORATION

Thermal or direct evaporation is currently the most widely used method for the preparation of thin films. The method is comparatively simple and with proper arrangement provides films of extreme purity and to a certain extent of predetermined structure.

Vacuum is necessary since the presence of ambient gases during the film preparation could influence its properties. Also the liberated atoms coming from the evaporation source might collide with another particle in the vacuum chamber, resulting in poor adhesion of the film to the substrate. In the present work, films were prepared at pressure of 2.66x10^{-5} Pa. The thin film deposited in the present work were obtained in a conventional vacuum system unit(Fig. 2.1) from Hind High Vacuum System[Model15F6U].

2.1.3 ELECTRON BEAM EVAPORATION

Electron beam evaporation technique is the widely used vacuum evaporation technique for preparing highly pure films. Disadvantages of resistively heated
Figure 2.1 (a) Photograph of vacuum coating unit and electron gun power supply.

Figure 2.1 (b) Photograph of inner view of vacuum chamber.
evaporation sources include possible contamination by crucibles, heaters and support materials and limitation of relatively low input power levels. This makes it difficult to deposit pure films or evaporate high melting point materials such as Yttrium Oxide, Silicon Dioxide, etc. at appreciable rates in thermal evaporation technique. Electron beam evaporation technique eliminates these disadvantages. Principally this type of source enables evaporation of virtually all materials at any rate. As shown in Fig.2.2, the evaporant charge is placed in either a water cooled crucible or in the depression of a water cooled copper hearth. The purity of the evaporant is ensured because only a small amount of charge melts or sublimes so that the effective crucible is the unmelted skull material next to the cooled hearth. For this reason there is no contamination of the evaporant by copper. Multiple-source units are available for the sequential or parallel deposition of more than one material.

2.1.4 MASK ROTATING SYSTEM

The direct deposition of thin film patterns requires a suitably shaped aperture commonly referred to as a mask. The mask is placed in close proximity to the substrate, thereby allowing condensation of the evaporant vapour only in the exposed substrate area.

The thin film active devices such as solar cells, transistors, gas sensors, etc. have multilayer structures. Usually they are fabricated by deposition of thin film layer at suitable growth conditions with appropriate mask step by step. In this procedure it is required to change the mask for deposition of each layer. This can be possible by two ways, in the first case mask can be changed by breaking the vacuum and replace with another mask for the next deposition. This method is simple but has more drawbacks such as (1) possibility of formation of a oxide layer on a surface of a deposited film. (2) possibility of formation of surface states which may affect the preformation of the device (3) require long time for fabrication of
Figure 2.2 Photograph of a multihearth electron beam evaporation unit.
devices and (4) consumes more electricity too. All such drawbacks can be avoided if the mask can be changed in the vacuum chamber for deposition of different layers without breaking vacuum. This requires a special type of a mask rotating system which can be operated electromechanically. Such mask rotating system was fabricated in our laboratory and installed in our vacuum coating unit (Fig. 2.3).

The multilayers active thin film devices such as solar cells, transistors and gas sensors are successfully fabricated with the mask rotating system.

2.1.5 PREPARATION OF THIN FILMS IN THE PRESENT STUDIES

Above described techniques are used for preparation of semiconductor thin films. However, the selection of a method depends on the material to be deposited, the nature of work intended to be done and facilities available. The direct evaporation method is most suitable for II-VI compounds, which have high heat of formation and have nearly identical vapour pressures at their evaporation and condensation temperatures. Thus, in the present studies, direct thermal evaporation technique and built in electron beam gun facility are used for the deposition of thin film devices. The thin film deposited in the present work were prepared in a conventional vacuum evaporation unit (Fig.2.1) from Hind High Vacuum System [model-15F6U] with useful facilities like electron beam evaporation, quartz crystal digital crystal monitor, digital temperature controller, digital pirani and ionization gauge for measurements of pressure in the bell-jar and digital panel meter for the measurements of current for HT-LT power supply. Ultimate residual air pressure in the bell-jar was maintained at about 2.66x10^{-5}Pa. during the evaporation of the charge. The mask rotating system was used for the fabrication of p-ZnTe/n-CdSe thin film solar cells, CdSe thin film transistor and CdSe gas sensor.
Figure 2.3 Photograph of a mask rotating system.
2.2 CHARACTERIZATION TECHNIQUES

2.2.1 INTRODUCTION

In order to understand fully the behaviour of thin films, it is essential to characterize them physically, chemically and structurally. The methods of examination of the films can be divided into two categories i.e. macroscopic and microscopic. The macroscopic examination methods include the X-ray diffraction and other methods used in the measurement of physical properties of the film such as structural, electrical, optical, etc.. The microscopic examination includes getting information about the structure of the films and thus involves an extensive use of transmission electron microscopy and transmission electron diffraction techniques. The combination of the above two techniques is very useful in investigating the orientation of the particular regions of interest of the film and also in the evaluation of the orientation of the initial deposits and individual nuclei. The films in the present work were examined by transmission electron microscope (TEM) [Philips EM 400] attached with Energy Dispersive Analysis of X-rays (EDAX) [PV 9100/60].

2.2.2 TRANSMISSION ELECTRON MICROSCOPE (Philips EM 400)

EM 400 is an advanced transmission electron microscope based on ultra clean and high vacuum technology. It incorporates a computer memory controlled seven lenses optical system and accelerating voltage can be selected between 20 to 120kV. The cross section of column is shown in Fig.2.4. The lens system of the microscope incorporates a total seven lenses of which two are condenser lenses, one objective, the diffraction lens, one in termediate lens and two projecting lenses. The objective lens give exceptionally low aberration constants. The five imaging lenses ensure that a wide range of high fidelity, full field images are produced on the screen. The magnification on the screen can be varied from 55X to 2,60,000X in 35 steps, while the camera length can varied from 400mm to
Figure 2.4 Photograph of a cross section of electron microscope optical unit.
10,000mm in 12 steps. The EM 400 has ±60° eccentric high tilt capability of the goniometer stage with analytical pole-pieces. The thermal, mechanical and electrical insulation make line attainable, line and point resolution of 0.34, 0.45 and 0.7nm respectively. The column is pumped to an operational pressure of 10⁻⁵Pa. by an ion getter pump. A 35mm roll film and plate films (size 4"X3.25") are used to record the images.

2.2.3 ENERGY DISPERSIVE ANALYSIS OF X-RAY(EDAX)[PV 9100/60]

Philips EM 400 has an attachment of EDAX system for the purpose of chemical analysis. When a beam of electrons strikes a specimen, a fraction of the incident electron excites the atoms of the specimen which then emit X-rays when they return to their ground state. The energy of these X-rays is strictly related to the atomic number of the elements excited, while the intensity of X-rays is related to the concentration of element. The detection of X-rays form the basic of elemental analysis in the electron microscope. The EDAX is the non-destructive technique and it gives simultaneous analysis of all the elements having a atomic no. ≥11 and the resolution of the energy peak (at Mn Ka) is 154eV, while sensitivity is down to 10⁻¹⁷ gram of Na. The EDAX gives fully qualitative calculations (Weight% or atomic% of elements or oxides) for bulk samples, particles and thin specimens, including ZAF correction, with and without standards; with composition for irregular specimen geometries.

The EDAX gives information about the chemical elements present in the specimen, irrespective of their state of chemical combination of the phases in which they exist, unlike the X-ray diffraction which discloses various compounds and phases present in the specimen.

2.2.4 X-RAY DIFFRACTION ANALYSIS

X-ray diffraction techniques are useful tools for the microstructural investigations of thin films. The X-ray diffraction obtained by using monochromatic
radiation are generally more important because the d-spacing can be calculated from the observed diffraction angles. For thin film work the powder method in conjunction with diffractometer is most commonly used. In a diffractometer the diffracted radiation is detected by reflections. The intensities are recorded on synchronously advanced strip charts. An important feature of the diffractometers is their ability to focus into a sharp diffraction line, the radiation which is Bragg-reflected from an extended specimen area. This improves the sensitivity as well as the signal to noise ratio. The profile of the diffraction maxima for epitaxial films is a qualitative measure of the perfection and alignment of crystallites[6].

The Bragg-Brento X-ray diffractometer is widely used in thin film work. Here the specimen is mounted in the center of the diffractometer and rotated by an angle θ around an axis in the film plane. The counter is attached to an arm rotating around the axis by angles twice as large as those of the specimen rotation. Only (hkl) planes parallel to film planes contribute to the diffracted intensity. The effective thickness of a film of thickness(t) is given by (t/sinθ) which decreases with increases with increasing diffraction angle. Therefore the effective thickness of a film in the 100nm thickness range is sufficient to excite measurable diffracted radiation at small angles but the intensity falls off rapidly for higher index reflections.

2.2.5 SPECTROPHOTOMETER ANALYSIS

In the present work, SYSTRONICS spectrophotometer-105 was used for the determination of the optical energy gap of cadmium selenide thin films. This particular spectrophotometer is a single beam grating spectrophotometer with a wavelength range of 340nm to 960nm. It has constant spectral bandwidth of 10nm over the entire wavelength range. Maximum 1cm wide film specimen can be accommodated in it. The light source is a filament tungsten iodide lamp. The light energy is condensed in the entrance slit, which is placed at the focal plane of
collimating lens. Thus, plane parallel beam strikes the grating surface. The dispersed spectrum is refocused on the exit slit by another decollimating lens. Thus, the exit slit is an image of entrance slit in different colours (wavelengths).

The grating is coupled to a cam through a layer and the rotating of the cam gives the spectral scan in the exit plane. The radiation that passes through the exit slit is calibrated against standard emission lines of Cd, Hg, He sources. The wavelength is displayed on a dial fixed to a cam which is calibrated from 340nm to 960nm at intervals of 5nm numbered at every 20nm. The optics for the instrument is set for the first order dispersion of the grating, as the second order dispersion of the spectrum of grating would invariably overlap with cut off filter in the light path. The radiation finally passes through the sample and falls on the photocell. To protect the photocell from exposure to light radiation, a mechanical shutter is provided in the light path. Since it is operated by a press focused button on the cabinet the light reaches the photocell only when the button is pressed.

2.2.6 MASS FLOW CONTROLLER (MFC)

Flowmeters measures the volume of a gas passing through a system. Volumetric flow measurements depend on the process conditions. Since the density of gas varies with changing temperature and pressure, volumetric flow measurement provide less accurate results. Mass flow controller gives superior performance as linear flow is independent of pressure and temperature changes.

Portable carbon dioxide analysers are easy to operate and ideal for location where accurate CO\textsubscript{2} measurements are critical. The non dispersive infrared detector measures the concentration of CO\textsubscript{2} in only 10 seconds with an accuracy of 5% of upto the concentration of 5000ppm.
REFERENCES


