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CHAPTER – II

EXPERIMENTAL TECHNIQUES, PREPARATION OF PURE AND Cu DOPED CdTe THIN FILMS, AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

Thin film preparation technique is divided into two great categories namely, physical methods and chemical methods. Varieties of techniques are available under these two categories. Till now, different techniques have been adopted for the preparation of CdTe thin films. Few of them are: spray pyrolysis, sputtering, chemical bath deposition, arc vapor deposition, electroplating, electron beam evaporation. It is worth to mention here that the physical, chemical and electrical properties of thin films depend mainly on the deposition techniques and their underlying growth parameters. Therefore, it is important to select a suitable technique for the deposition of device quality thin film. Hence, in this present work, the electron beam evaporation technique was adopted for the preparation of pure and Cu doped CdTe thin films.

In this chapter, the details of few thin film preparation techniques have been briefly explained. In addition, the preparation of pure and Cu doped CdTe thin films by electron beam evaporation technique are clearly explained. Further, brief information about the characterization techniques which used to study the deposited films are discussed.

2.2 Spray pyrolysis

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. Spray pyrolysis involves many processes occurring either simultaneously or sequentially. The most important of these are aerosol generation and transport,
solvent evaporation, droplet impact with consecutive spreading, and precursor decomposition. Droplets impact on the substrate surface, spread into a disk shaped structure, and undergo thermal decomposition.

The spray pyrolysis setup mainly consists of spray nozzle, precursor solution, substrate heater, temperature controller and air compressor or gas propellant. Filtered carrier gas and solution are fed into a spray nozzle at a predetermined constant pressure and flow rate, respectively. Substrate is placed inside a tubular furnace, which is powered by an external heater supply. The thermocouple in the feedback network delivers proportional output to temperature monitor unit. The flow of precursor solution and air are measured by liquid and gas flow meters [1]. To achieve uniform deposition, the moving arrangements (either nozzle or substrates or both) have been used. The properties of the film depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also the cooling rate after deposition. Substrate temperature is the main parameter that determines the film morphology and properties. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure. The precursor solution is the second important process variable. Solvent, type of salt, concentration of salt, and additives influence the physical and chemical properties of the precursor solution. Therefore, structure and properties of a deposited film can be tailored by changing the composition of precursor solution. The film thickness depends upon the distance between the spray nozzle and substrate, substrate temperature, the concentration of the precursor solution and the quantity of the precursor solution sprayed. The film formation depends on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and momentum.
2.3 Chemical bath deposition

The chemical bath deposition (CBD) method uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. Chemical bath deposition has the advantage of being a simple, low temperature, and inexpensive large-area deposition technique [2]. CBD does not require sophisticated instrumentation like vacuum system and other expensive equipments. The starting chemicals are commonly available and inexpensive. Using CBD, a large number of substrates can be coated in a single run. Any insoluble surface to which the solution has a free access will be a suitable substrate for deposition, which makes CBD suitable for coating surfaces of any morphology and geometry. The low temperature deposition avoids oxidation and corrosion of metallic substrates.

In a typical experiment, substrates are immersed in an alkaline solution containing the source, i.e. the metal ion and added base. A chelating agent is also added to control the release of the metal ion. The process relies on the slow decomposition of metal ions in an alkaline solution. The free metal ion concentration is controlled by the formation of complex species. A large number of physico-chemical factors such as solubility product, supersaturation, type of precipitation, etc., control the growth of the deposit under a specified set of reaction conditions. Chemical bath deposition results in pin hole free, uniform and highly stoichiometric films since the basic building blocks are ions instead of atoms. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained.

2.4 Sputtering technique

Sputter deposition is the deposition of particles vaporized from a surface (“target”), by the physical sputtering process. Physical sputtering is a non-thermal vaporization process where surface atoms are physically ejected from a solid surface by momentum transfer from an atomic-
sized energetic bombarding particle which is usually a gaseous ion accelerated from plasma. Generally, the source-to-substrate distance is short compared to vacuum deposition. Sputter deposition can be performed by energetic ion bombardment of a solid surface (sputtering target) in a vacuum using an ion gun or low pressure plasma (< 5 mTorr) where the sputtered particles suffer few or no gas phase collision in the space between the target and the substrate. Sputtering can also be done in a higher plasma pressure (5-30 mTorr) where energetic particles sputtered or reflected from the sputtering target are “thermalized” by gas phase collisions before they reach the substrate surface. The plasma used in sputtering can be confined near the sputtering surface or may fill the region between the source and the substrate. The sputtering source can be an element, alloy, mixture or a compound and the material is vaporized with the bulk composition of the target. The sputtering target provides a long-lived vaporization source that can be mounted so as to vaporize in any direction. Compound materials are commonly reactively sputter deposited by using a reactive gas in the plasma. The presence of the plasma “activates” the reactive gas (“plasma activation”) making it more chemically reactive. Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, and reflective coatings on compact discs, magnetic films, dry film lubricants and decorative coatings [3, 4].

2.5 Arc vapor deposition

Arc vapor deposition uses a high current, low-voltage arc to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions (“film ions”) to the substrate surface [5-8]. The arc voltage has to be near the ionization potential of the gas or vapor (>25 volts). Ion bombardment at the cathode and electron
bombardment at the anode heat the electrodes. Most of the ejected material is thermally evaporated but some is ejected as molten droplets or solid particles from the cathode. A high percentage of the vaporized atoms are ionized in the arc vaporization process. The arc can be established between closely spaced electrodes in a good vacuum (vacuum arc) by vaporizing some of the electrode material, or between electrodes in a low-pressure or high-pressure gaseous environment (gaseous arc). High pressure gaseous arcs are not used in physical vapor deposition process but are used in processes such as plasma spraying, arc welding and electrospark plating [9].

2.6 Electroplating

In electroplating a metallic coating is electroplated on the cathode of an electrolytic cell consisting of a positive electrode (anode), a negative electrode (cathode), and an electrolyte solution (containing the metal ions) through which electric current flows. The quantitative aspects of the process are governed by Faraday’s laws. Important electroplating variables include current efficiency, current density, current distribution, pH, temperature, agitation and solution composition. Numerous metals and metal alloys have been successfully electroplated from aqueous solutions. However, technically most useful electroplated metals are chromium, copper, nickel, silver, gold, rhodium, zinc and a series of binary alloys including chromium/nickel composites. Electroplating is widely used in industry and can produce deposits that range from very thin films to very thick coating (electroforming).

2.7 Electron beam evaporation

Electron beam evaporation is one of the physical vapor deposition techniques, which is widely used for the deposition of high quality semiconductor thin films due to the reason of lower process risk and the flexibility in the control over various deposition parameters. Very thin
films with better surface finish can be deposited using electron beam evaporation technique. Compared with other vacuum evaporation techniques, electron beam heating avoid the possible contamination by crucibles, heaters, and support materials, which pave the way to get high pure films by the electron beam evaporation technique. In addition, multiple source units are available in electron beam evaporation for the sequential or parallel deposition of more than one material. It is a vacuum deposition technique, in which the vacuum system consists of an assortment of pumps, tubing, valves and gauges to establish and measure the reduced pressures [10]. Of these components, pumps and gauges are generally the most important. Vacuum pumps may be divided into two broad categories: gas transfer pumps and entrapment pumps. The gas-transfer pumps remove gas molecules from the pumped volume and convey them to the ambient in one or more stages of compression. Entrapment pumps condense or chemically bind molecules to surfaces situated within the chamber being pumped. In contrast to the gas transfer pumps, which remove gas permanently, some of the entrapment pumps are reversible and release trapped or condensed gas back into the system upon warm up. Gas transfer pumps may be further subdivided into positive displacement and kinetic vacuum pumps. Rotary mechanical and root pumps are important examples of the positive displacement variety. Diffusion and turbomolecular pumps are the outstanding examples of the so-called kinetic vacuum pumps.

In the present work, the pure and Cu doped CdTe thin films were prepared by electron beam evaporation technique using 12” HIND-HIVAC vacuum coating unit (Model: 12A4D) with electron beam solid state power supply (EBG-PS-3K). The photograph of coating unit and electron beam power supply is shown in Fig. 2.1. The coating unit consists of collar with bell jar (coating chamber) pumped by a conventional oil diffusion pump backed by an oil rotary pump.
Fig. 2.1: Photograph of coating unit and electron beam power supply.
2.7.1 Rotary pump

The rotary piston and rotary vane pumps are the two most common devices used to attain reduced pressure. In the rotary piston pump, gas is drawn as the keyed shaft rotates the eccentric and piston. There the gas is isolated from the inlet after one revolution, then compressed and exhausted during the next cycle. The schematic diagram of rotary vane pump is shown in Fig. 2.2. The rotary vane pump contains an eccentrically mounted rotor with spring loaded vanes. During rotation the vanes slide in and out within the cylindrical interior of the pump, enabling a quantity of gas to be confined, compressed and discharged through an exhaust valve to the atmosphere. Compression ratio up to $10^6$ can be achieved in this way. Oil is employed as a sealant as well as lubricant between components moving within tight clearances of both types of rotary pumps. Rotary pumps are frequently used to produce the minimum vacuum ($\sim 10^{-3}$ m bar) required to operate both oil diffusion and turbo molecular pumps, which can then attain far low pressures.

2.7.2 Diffusion pump

In contrast to the mechanical rotary pump, diffusion pump has no moving parts and its schematic sketch is shown in Fig. 2.3. They are designed to operate in the molecular flow regime and can function over pressures ranging from well below $10^{-10}$ torr to about $5\times10^{-2}$ torr. Because they cannot discharge directly into the atmosphere, a mechanical forepump is required to maintain the latter outlet pressure. Diffusion pumps have been designed with pumping speeds ranging from a few liters per second to over 20,000 liters per second. Pumping is achieved through the action of a fluid medium (usually silicone oil), which is boiled and vaporized in a multistage jet assembly. As the oil vapor stream emerges from the top nozzles, it collides with and imparts momentum to residual gas molecules that happen to bound into the pump throat. These molecules are thus driven toward the bottom of the pump and compressed to the side
Fig. 2.2: Schematic sketch of rotary pump.
Fig. 2.3: Schematic sketch of diffusion pump.
where they are exhausted. A region of reduced gas pressure in the vicinity of the jet is produced and more molecules from the high-vacuum side move into this zone, where the process is repeated. The complete vacuum system combines the rotary pump, diffusion pump, and the deposition chamber as shown schematically in Fig. 2.4. The pirani and penning gauges are used to measure the pressure inside the vacuum chamber.

2.7.3 Electron gun

Apart from the above accessories, electron gun plays a major role for the deposition of films. In electron beam evaporation, the beam of electrons is emitted from the electron gun, such that it will heat and vaporize the material to be deposited. Once the material changes its state of being a liquid to a vapor, it is able to condense itself on the substrate. The working principle of electron beam evaporation is explained as follows and its schematic diagram is shown in Fig. 2.5. Firstly, heating process of the hot filament (made of tungsten) will take place. This hot filament will produce a beam of electrons that is excited due to heating. This can be done by applying thermionic emission. Thermionic emission is a process of discharging of electrons from a heated material, i.e. the hot filament. In order to excite the electrons, the hot filament needs to supply enough energy for the electrons to overcome the attractive force that holds them together. Once the electrons are excited and released, the electrons can move randomly. Since the electrons are required to heat the material, the beam of electrons must have a certain path in order to use effectively. The excited electrons are able to move randomly in the high vacuum area without any force of attraction to it. Hence, the magnets are used to move towards the material to be evaporated. In this case, two magnets are required. The first magnet is a focusing magnet, which is used to attract the electrons towards it immediately after the electrons are excited. Then, in order to deflect the route of the beam of electrons towards the material to be evaporated, a deflecting magnet will be used. After the whole process of attracting and deflecting
Fig. 2.4: Schematic sketch of vacuum system.
Fig. 2.5: Schematic sketch of electron beam gun.
of magnets, now the path towards the material is set and the material can be heated. The material will be heated up to a boiling point, of which is governed by the principle of evaporation. Once the boiling point is reached, the molecules in the liquid will collide and transfer energy to each other and thus the liquid would turn into vapor. Now the material evaporant is able to move freely in the high vacuum area. The vapor is now able to move towards the substrate inside the vacuum chamber, and thus the material evaporant which is now in the form of vapor can be condensed on the surface of the substrate as thin film.

The electron beam evaporation process offers many desirable characteristics such as relatively high deposition rates (up to 150 µm/minute with an evaporation rate of approximately 10-15 kg/hour), dense coatings, controlled composition, low contamination, and uniform microstructure. The microstructure and composition of the coating can be easily altered by manipulating the process parameters and ingot compositions. Thus, multilayered ceramic/metallic coatings can also be deposited at relatively low temperatures.

2.8 Preparation of pure and Cu doped CdTe films

2.8.1 Choice of substrates

The role of the substrate is to provide the base or support onto which the film has to be deposited. The stability of thin films depends upon the nature of the substrate that it should not react with the film material which could change the properties of the film. Therefore, the substrate must have certain requirements such as mechanical strength, chemically inert and there must be adequate adhesion of the film, not only at normal temperature, but also at relatively higher temperature. Also the surface of the substrate should be smooth and flat in order to get defined and reproducible properties. Further, the films should not peel off from the substrates.
under normal conditions of stress and strain, mechanical or thermal to which the deposits are exposed during their uses.

Problems like poor adhesion and the film peel off can be caused due to,

(i) the presence of a physical barrier between the deposit and the substrate at the interface due to oil, grease, dirt, undesired surface layers such as oxidic, sulphide, halide, etc. over the substrate surface

(ii) the intrinsic stress in the deposit film caused by the presence of point defects, lattice misfits, and grain boundary misfits

(iii) different thermal expansion of the deposit and the substrate

(iv) differential surface tension at the vacuo/deposit and deposit/substrate interface

While the factor (i) causes poor adhesion to the substrate, the other factors (ii) to (iv) generate stresses, tensile or compressive, in the deposits tending them to come out of the substrate and hence are related to the growth process. The effects of these can often be reduced or completely eliminated by appropriate annealing at a suitable temperature or sometimes by varying the deposition conditions.

The substrates can be selected by considering the properties and the end use of the films. In the present work, the 7059 corning microscopic glass substrates and fluorine doped tin oxide coated (FTO or SnO$_2$:F) ($R_{sh} \sim 15\Omega$/sq) glass substrates were chosen for the deposition of pure and Cu doped CdTe thin films.

2.8.2 Cleaning of substrates

The glass substrates were degreased by the following cleaning procedures to remove the unwanted impurities normally present on the surface of the glass plates when exposed to the atmosphere:
(1) The glass substrates are washed in soap solution by scrubbing the surfaces with the cotton swab dipped in liquid soap to remove oil, grease etc. 

(2) The substrates are then rinsed thoroughly in deionized water to remove any traces of the soap solution left on the surface. 

(3) Later on, the glass slides are soaked in chromic acid and heated to about one hour to dissolve the fine silica layer formed on the surface and to make a new surface for the deposition of film. 

(4) The substrates are then rinsed thoroughly in deionized water. Finally, the substrates were ultrasonically cleaned with 2-propanol, acetone, and deionized water for 15 minutes each. Now the glass substrates are ready for the deposition of the films. 

The surface of the fluorine doped tin oxide coated glass substrates were cleaned gently with acetone. 

2.8.3 Film preparation

Thin films of CdTe were deposited on 7059 corning glass substrates (75 mm length × 25 mm width × 1 mm thickness) by electron beam evaporation technique (HIND-HIVAC vacuum coating unit model 12A4D with electron beam power supply model EBG-PS-3K) under a chamber pressure of $2 \times 10^{-5}$ mbar. Cadmium telluride powder (Sigma-Aldrich; 99.99% purity) was made into pellet of 10 mm diameter with 4 mm thickness and annealed at 400°C for 2 hrs. The pelletized CdTe ingots were placed in graphite crucible (12 mm outer diameter × 10 mm inner diameter × 6 mm depth) and kept on water-cooled copper hearth of the electron gun, inside the vacuum chamber. The distance between the substrate and the target material was kept fixed at 12 cm. The chamber was evacuated to a high vacuum of the order of $2 \times 10^{-5}$ mbar using rotary and diffusion pumps and the chamber pressure was measured by pirani and penning
gauges. In the electron gun, the electrons extracted from a dc-heated cathode of tungsten filament, by the application of electric field, pass through an anode, and deflected through an angle of about 180° by the magnetic field and reach the target material. The surface of CdTe pellet on the graphite crucible was scanned by the resultant and deflected electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW/cm². The ablated material was evaporated and the vapor phase condensed and deposited as thin film on the substrate. The homogeneous distribution of evaporated CdTe particles on the substrate was attained by continuously rotating the substrate during deposition. The deposition time was 10 min and the deposition rate was 0.1 μm/min. The thickness of deposited film was in the range of ~1 (±0.03) μm, measured by surface profilometer (Mitutoyo, SJ-301). Similarly, the Cu doped CdTe films were prepared with different Cu content (2 wt.%, 3 wt.%, and 4 wt.%). The films were deposited at different substrate temperatures (T_{sub}) viz. room temperature (RT), 100°C, 150°C, and 200°C. Later on, the as-deposited films were annealed in air (post deposition heat treatment) (T_{anneal}) at 300 and 400°C for 10 min.

All the deposited films are uniform, pinhole free and well adherent to the substrates. The preparation of pure and Cu doped CdTe films by electron beam evaporation technique was reported by the author [11, 12].

2.9 Characterization techniques

The electron beam evaporated CdTe and CdTe:Cu thin films have been subjected to various characterization studies to identify their various properties. The thickness of films was measured by stylus profilometer. X-ray diffraction (XRD) study was used to analyze the structural property. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the surface morphology of deposited films. The elemental
The composition of the films was studied using energy dispersive x-ray analysis (EDAX). The optical properties of CdTe and CdTe:Cu films were studied using UV-Vis-NIR spectrophotometer and photoluminescence (PL) spectrophotometer. Vibrational property of deposited films was analyzed using micro-Raman spectrometer. The electrical properties of deposited films were studied by Van der Pauw technique. The details of characterization techniques used in the present work are explained in the following sections.

2.9.1 Stylus profilometer

Thickness is the most important film parameter, which controls the film properties. Hence, precise knowledge of the film thickness is necessary for the intensive study of the properties of thin films. It is a non-destructive technique and the coatings may be used for further studies without any damage. The Mitutoyo surftest (SJ-301) is a stylus type surface roughness and thickness measuring instrument to measure the thickness of the thin film coatings on any uniform surface. The schematic diagram is shown in Fig. 2.6. It consists of a diamond stylus probe placed over the uncoated surface and made to move towards the coating. The electrical signals corresponding to the mechanical movements of the stylus are amplified to produce DC signals and digital data recording methods are developed in modern stylus instruments. The vertical displacement when it steps over the coating surface gives the thickness of the thin film. The thickness of the prepared thin film samples was found by using surface profilometer (Mitutoyo; SJ-301).

2.9.2 X-ray diffraction

X-ray diffraction (XRD) is a powerful method for the structural study. X-ray diffraction is a primary tool for probing structure, since its wavelength is on the atomic scale and it offers unparalleled accuracy in the measurement of atomic spacing and is the technique of choice for
Fig. 2.6: Schematic diagram of stylus profilometer.
determining strain states in thin films. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces. XRD is a non-contact and non-destructive technique which makes it ideal for in-situ studies. X-ray diffractograms provide a wealth of information – from phase composition to crystallite size, from lattice strain to crystallographic orientation.

A typical powder X-ray diffractometer consists of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector. The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the center of the circle. Bragg’s law is the basis of XRD analysis. With this law, it is possible to make accurate quantifications of experimental results in the determination of crystal structures. The angle between the plane of the specimen and the X-ray source is \( \theta \), known as Bragg’s angle and the angle between the projection of X-ray and the detector is \( 2\theta \). When a beam of X-ray is incident on the sample (consist of randomly oriented crystallites), X-rays are scattered by each atom in the sample. If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as ‘reflecting planes’. The schematic illustration of X-ray diffractometer and the diffraction of X-ray from a crystal plane are shown in Figs. 2.7 (a) and (b), respectively.

In X-ray diffractometers, the diffraction angle \( 2\theta \) is the angle between the incident and diffracted X-rays. A typical diffraction pattern consists of a plot of reflected intensities versus the diffracted angle \( 2\theta \). The \( 2\theta \) values of the peak depend on the wavelength of the anode material of the X-ray tube. By choosing the right anode and energy of accelerated electrons, a known wavelength and therefore a known energy of X-rays will be generated. Copper X-ray tubes are most commonly used. For practical applications of X-ray diffraction, we typically want to use X-
Fig. 2.7: (a) Schematic diagram of X-ray diffractometer, (b) Diffraction of X-rays from crystal plane.
rays of a single wavelength, i.e. monochromatic radiation to improve the experimental results. In general, $K\alpha$ radiation is used for analytical work while all other radiations are removed by means of a nickel (Ni) filter. The lattice planes in the sample crystal are separated by a distance $d$. The Bragg’s law related the wavelength ($\lambda$) of the reflected X-ray, spacing between the atomic planes ($d$) and the angle of diffraction ($\theta$) as follows:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (2.1)

The angle between the transmitted and diffracted beams will always be equal to $2\theta$. This angle can be obtained readily in experimental situations and the results of X-ray diffraction are therefore given in terms of $2\theta$. It is however very important to remember that the angle that is used in the Bragg’s equation must correspond to the angle between the incident radiation and the diffracting plane, i.e. $\theta$ [13].

For the first order diffraction, $n = 1$, and knowing $\theta$ and $\lambda$, one can calculate the interplanar spacing $d$-value for a particular plane. The first step of X-ray diffraction pattern involves the indexing of XRD peaks. There are three main methods for indexing a diffraction pattern,

- Comparing the measured XRD pattern with the standard data base (JCPDS-cards)
- Analytical methods
- Graphical methods

The intensity of the diffraction signal is usually plotted against the diffraction angle $2\theta$ (°), but $d$ (nm) or $1/d$ (nm$^{-1}$) may also be used. The most common wavelength used in XRD is 1.5418 Å ($Cu-K\alpha$). In the present investigation, the structural property of pure and Cu doped CdTe thin films deposited at various growth conditions were studied by X-ray diffraction (X’pert Pro PANalytical) with $Cu-K\alpha$ radiation source.
2.9.3 Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX)

Scanning electron microscope (SEM) is an instrument that is used to observe the morphology of the solid sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope [14]. When an electron strikes the atom, variety of interaction products are evolved. These products, when analyzed are useful to obtain the various kinds of information about the sample. Scattering of electron from the electrons of the atom results into the production of backscattered electrons and secondary electrons. Electrons may get transmitted through the sample if it is thin. Primary electrons with sufficient energy may knock out the electron from the inner shells of atom and the excited atom may relax with the liberation of Auger electrons or X-ray photons. All these interactions carry information about the sample. The schematic diagram of scanning electron microscope and the interaction of electrons with the material atom are shown in Figs. 2.8 (a) and (b), respectively. SEM instrument consists of an electron gun and a series of electromagnetic lenses and apertures. A well-focused mono-energetic (~ 25 keV) beam is incident on a solid surface giving various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM application, their intensity being dependent on the atomic number of the host atoms. Both the backscattered and secondary electrons are collected, amplified and utilized to form an image in the SEM.

In EDAX technique, a sample is made the target in an X-ray tube and is bombarded with electrons of suitable energy, it emits characteristic X-rays. The emitted X-rays are analyzed in an X-ray spectrometer and the elements present in the sample are quantitatively identified by their characteristic wavelengths. For compositions greater than or about 1% and elements separated by few atomic numbers, energy dispersion analysis is very useful because the intensities are
Fig. 2.8: (a) Schematic diagram of SEM instrument, (b) interactions between electrons and material atoms.
increased about 100-Fold [15]. The surface morphology and compositional properties of CdTe and CdTe:Cu films were identified by scanning electron microscope equipped with EDAX (Tescan Vega 3).

2.9.4 Atomic force microscope

The surface morphology of thin film samples can also be analyzed using atomic force microscope. The atomic force microscopy (AFM) probes the surface of a sample with a sharp tip, a couple of microns long often less than 100 Å in diameter. The tip is located at the free end of a cantilever, which is 100 to 200 μm long. The forces between the tip and sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as tip is scanned over the sample or the sample is scanned under the tip. The measured cantilever deflection allows computer to generate a map or surface topography. Several forces typically contribute to the deflection of an AFM cantilever. AFM operates by measuring the attractive or repulsive forces between a tip and the sample. The forces most commonly associated with atomic force microscopy are interatomic force called Van der Waals force. The schematic diagram of AFM is shown in Fig. 2.9 (a). The dependence of the Van der Waals force upon the distance between the tip and the sample is shown in Fig. 2.9 (b). In the contact regime, the cantilever is held at a distance less than few angstroms from the sample surface, and the inter-atomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held at a distance of the order of tens to hundred of angstroms from the sample surface, and the inter-atomic force between the cantilever and the sample is attractive [16, 17]. AFM incorporates a number of refinements that enable it to achieve atomic scale resolution. The atomic force microscopic study on the solid sample offers the information related to the surface homogeneity, uniformity, nature of grains, and also the roughness of sample surface. The surface
Fig. 2.9: (a) Schematic illustration of cantilever scanning, (b) Van der Waals force curve.
morphological nature of pure and Cu doped CdTe films was studied by atomic force microscope (Nanoscope-E).

2.9.5 UV-Visible-NIR spectrophotometer

Study on the optical property of semiconducting thin films is important for solar cell applications. The measurement of absorbance and/or transmittance of a sample provides a satisfactory way to identify its optical properties. Spectrophotometer is an instrument that measures the amount of the intensity of light absorbed after it passes through the sample. When light of sufficient energy incident onto a material, it induces transition of electrons from occupied states below the Fermi energy to unoccupied states above the Fermi energy. A quantitative study of these transitions must provide some understanding of the initial and final states for the transitions and thus infers the knowledge of the band structure [18]. When sample molecules are exposed to light, some of the light energy will be absorbed. An optical spectrophotometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength. The intensity of light after it passes through the sample can be related to transmittance (T). Transmittance is the fraction of light that passes through the sample.

The block diagram of UV-Vis-NIR spectrophotometer is shown in Fig. 2.10 (a). The basic structure of spectrophotometer consists of a light source, a collimator, a monochromator, a wavelength selector, sample holder, a photoelectric detector (photomultiplier tube) and a digital display. Generally, a spectrophotometer may works with either single beam or double beam. In the case of single beam, all the light passes through the sample and the intensity of incident light can be measured by removing the sample. Whereas in a double beam method, the light is split into two beams before it reaches the sample. Here, one beam is passed through the sample and
Fig. 2.10: (a) Schematic diagram of UV-Vis-NIR spectrophotometer, (b) electron transition between direct and indirect band gap.
the other is through the reference. The reference beam intensity is considered as zero absorbance (or 100% transmittance) and the resultant data is the ratio of the intensities of two beams. Spectrophotometer produces a desired range of wavelength of light, which is passed through a prism or diffraction grating to produce a monochromatic light. Then the monochromatic light is splited into two beams of equal intensity by a beam splitter, one of which passes through sample and the other through reference. The intensities of these light beams are measured by detectors. The detector is typically a photomultiplier tube, a photodiode array or a charge-coupled device (CCD).

Two typical transitions are being considered while the measurement of optical absorption. The first of these is called an intraband transition, corresponds to the optical excitation of an electron from below the Fermi energy to another state above the Fermi energy but within the same band. The second transition is interband transition. It is the optical excitation of an electron from one band to another band which often exists between valence band maximum (VBM) and the conduction band minimum (CBM). The interband transitions are of four types, direct allowed, indirect allowed, direct forbidden and indirect forbidden. Fig. 2.10 (b) represents the allowed direct and indirect transition of electrons. The direct transition involves the electron whose energy and wave vector $k$ are same whereas in indirect transition, the wave vector $k$ is changed. This involves the non radiative phonon assisted transition. The existence of minimum threshold energy that requires for the electron to jump from VBM to CBM is often referred to as absorption edge. The optical transmittance of CdTe and CdTe:Cu thin films were studied by UV-Vis-NIR spectrophotometer (JASCO UV-Vis-NIR, V-670) in the wavelength range of 300 to 2500 nm.
2.9.6 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a very efficient, contactless, nondestructive, widely used technique for the analysis of the optoelectronic properties of semiconductors, which requires very little sample manipulation. Photoluminescence is defined as the spontaneous emission of light from a material under optical excitation and can be therefore used to provide detailed information on discrete electronic states involving both intrinsic optical processes and about the wide variety of defect which are endemic in practical semiconductor materials and extrinsic optical processes (internal transitions involving defects and their energy levels) by applying an external light energy \( h\nu \geq E_g \), where \( E_g \) denotes the energy band gap, and observing the re-emitted photons \([19, 20]\). The schematic diagram of photoluminescence spectrometer is shown in Fig. 2.11. The photoluminescence spectroscopy consists of light source, sample holder, and detector. Xenon lamp is used as a source of exciting light. The excitation and emission wavelengths are selected in the monochromator. Then the light beam falls on the sample with photon energy greater than the band gap energy of the sample and excites electron-hole pairs within the sample. The optical emission from the resultant recombination of these excitons with shallow defect centers is scanned with a monochromator and detected by a photomultiplier. The photoluminescence study is used to identify the optical quality of semiconducting thin films. In the present work, the optical property of CdTe and CdTe:Cu films was also studied by photoluminescence spectrometer (Varian Cary Eclipse).

2.9.7 Raman spectroscopy

Raman spectroscopy is used to observe vibrational, rotational and other low-frequency modes in a system \([21]\). It relies on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared or near ultraviolet range. The laser light interacts with
Fig. 2.11: Schematic diagram of photoluminescence spectrometer.
molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. The schematic diagram of Raman spectrometer is shown in Fig. 2.12. The major components of Raman spectrometer are laser source, monochromator and detector. When a sample is illuminated with a laser beam, electromagnetic radiations from the illuminated spot is collected with a lens and sent through a monochromator. Elastically scattered radiation at the wavelength corresponding to the laser line (Rayleigh scattering) is filtered out, while the rest of the light is dispersed onto a detector by either a notch filter or a band pass filter. Finally a complete spectral profile of the Raman phonon peak can be obtained.

The micro-Raman measurement on electron beam evaporated CdTe and CdTe:Cu thin films was carried out by Raman spectroscopy (LABRAM HR-800) at room temperature using backscattering geometry. The spectra were recorded using the 488 nm line of \textit{Ar}^+\textit{-ion} laser with a 5 mW power.

2.9.8 Electrical measurement

The most general technique used for the measurement of resistivity is the four point probe method. This method is a non-destructive; however the probe points may damage certain semiconductor material when excessive probe pressure is applied. Frequently, when the sample does not have a geometry that is favorable for four point probe measurement, leads to an unknown current distribution. Also, it is often difficult to determine accurately the geometry of the sample, limiting the accuracy of the calculated resistivity. In such a case, one often uses the technique of Van der Pauw to determine the resistivity of the sample \cite{22, 23}. A common geometry for such a measurement has four electrical contacts at the four corners of a roughly square sample. However, the Van der Pauw technique is applicable for any arbitrary shaped
Fig. 2.12: Block diagram of Raman spectrometer.
sample as long as the thickness of the sample is known and is uniform, the contact areas are small, and the contacts are all on the perimeter of the sample. Current is passed through the outer two probes and the potential develop across the inner two probes is measured [24]. The sheet resistivity of the top emitter layer is easy to measure experimentally using a “four point probe” method or “Van der Pauw” technique. The current is passed through the outer probes and induces a voltage in the inner voltage probes. The resistivity of thin film samples can be measured using the formula,

$$\rho = \frac{\pi}{\ln(2)} \left(\frac{V}{I}\right) = 4.523 \left(\frac{V}{I}\right)$$

(2.2)

where ‘t’ is the thickness of the film. The above formula is used for the film in which the thickness is less than half of the probe spacing, i.e. t < s/2 (Schroder). For thicker samples, the formula becomes:

$$\rho = \frac{V}{I} \left(\frac{\pi}{\ln\left(\frac{t}{s}\right)} - \frac{\pi}{\ln\left(\frac{t}{2s}\right)}\right)$$

(2.3)

Using this technique the semiconducting parameters of the deposited films have been extracted. In addition, the conducting nature of films was identified by hot probe method.

2.10 Conclusions

The details of various thin film preparation techniques have been discussed in this chapter. In addition, the details of electron beam evaporation are summarized clearly. The preparation details of CdTe and CdTe:Cu thin films by electron beam evaporation technique are also discussed in this chapter. Further, the details of characterization techniques which were used to study the deposited films have been discussed.
References


