

Thin Film Deposition and Characterization Techniques

1.1 Introduction

Herein, we will try to provide an outline of the method used in current work for the fabrication of ZnO thin films along with various characterization techniques applied. For the sake of simplicity this chapter will be divided into two sections. The first section will deal with the novel advanced spray pyrolysis technique for fabricating a highly sensitive chemical sensor based on nanocrystalline ZnO thin films. General aspects of the deposition technique, such as its inherent simplicity, the basic process and utensils utilized in advanced spray pyrolysis are described in general. The latter section will focus on various characterization techniques used.

Section (A): Thin film Deposition Technique

1.2. (A) 1. Introduction

Over the years, various materials have been synthesized in the form of thin films due to their prospective technological significance and scientific interest in their properties. They have very extensive range of applications and extend from nanostructures to coatings of several square meters on window glasses. Several techniques have been inspected in the search for the most reliable and inexpensive method of producing the thin films. Based on the nature of the deposition process, the techniques employed for thin film deposition can be classified into two groups, namely, physical and chemical deposition processes. The physical methods include physical vapor deposition (PVD), laser ablation, molecular beam epitaxy, and sputtering. While the chemical methods comprise gas phase deposition methods and solution techniques (Figure 1.1). The gas phase methods are chemical vapor deposition (CVD) [1, 2] and atomic layer epitaxy (ALE) [3], while spray pyrolysis [4], sol-gel [5], spin- [6] and dip-coating [7] methods use precursor solutions. The chemical techniques for the preparation of thin films have been studied extensively owing to their simplicity and inexpensiveness and such processes facilitate the designing of materials on a molecular level.

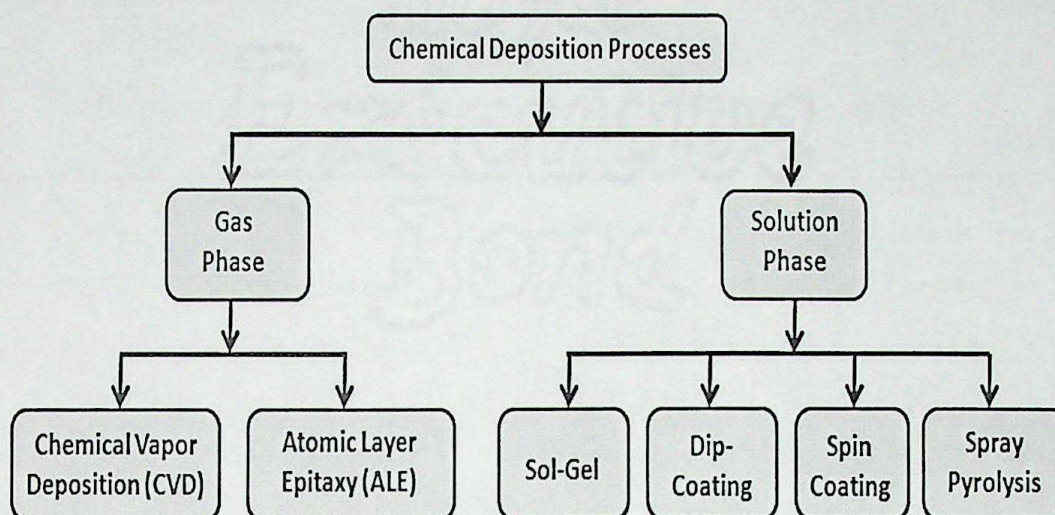


Figure 1.1: Chemical thin film deposition methods.

The chemical spray pyrolysis is one of the major chemical techniques applied to deposit variety of materials in the form of thin films, resulting in good productivity from an uncomplicated apparatus. Due to the simplicity of the apparatus and good productivity of spray pyrolysis (SP) technique on a large scale; it offered a most attractive way for the formation of thin films of noble metals, metal oxides, spinel oxides, chalcogenides and superconducting compounds. This technique is perhaps the most versatile mechanical coating technique of the deposition techniques noted, and it is particularly well-suited for high-speed automated mass production. Deposition of very thin films is possible by judicious selection and optimization of spray machine parameters for forming “atomized” droplets and the reagent and solvent systems used to formulate the spray solution.

Despite its simplicity, SP have a number of advantages.

- [1] It offers an extremely easy way to dope films with almost any element in any proportion by simply adding it in some form to the spray solution.
- [2] Unlike closed vapor deposition methods, SP does not require high quality targets and/or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
- [3] The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel which produces films of limited thickness.

- [4] Operating at moderate temperatures (373-773K) SP can produce films on less robust materials.
- [5] Unlike high-power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local overheating that can be detrimental for materials to be deposited. There are virtually no restrictions on substrate material, dimension or its surface profile.
- [6] By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.
- [7] It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well characterized film surfaces, provided the films are quiet compact, uniform and that no side effects from the substrate occur. SP offers such an opportunity.

The conventional spray pyrolysis deposition involves spraying an aerosol of a liquid precursor onto a hot surface, where it decomposes and converts into oxide. Herein, the optimization of preparative conditions viz. substrate temperature, spray rate, concentration of solution etc., is the most important requisite for obtaining good quality thin film. However, in recent years an emphasis has been given to a variety of atomization techniques such as ultrasonic nebulization, electrostatic spray pyrolysis, corona spray pyrolysis, improved spray hydrolysis, and microprocessor based spray pyrolysis. This is the most critical parameter as it enables control over the size of the droplets and their distribution over the preheated substrates. The enhancement in deposition efficiency and improvement in quality of the thin films can be achieved with these atomization techniques.

However, very few efforts have been made to modify the conventional spray system. In this work, the conventional spray pyrolysis system is modified by retaining all the advantages of the spray pyrolysis system [8]. However, the basic structure is completely changed. It is well known that the substrate temperature is the central parameter in spray pyrolysis that determines the physical and chemical properties of the deposits. Accordingly there can be three main routes of spray pyrolysis [9]:

1. If the temperature is low down enough, sprayed aerosols will directly arrive at substrate to form liquid films. Alternatively, in pyrosol-gel method gel films will grow by droplet solvent evaporation and hydrolysis.
2. If the degree of hotness is large enough, precipitation of droplets arise during solvent evaporation. Furthermore if these precipitates don't decay powder like deposits result. On the other hand, partial pyrolysis has an effect of high surface mobility on films. Although adequate high temperatures lead to homogeneous solid-gas phase reaction to deposit the powder.
3. The third approach is associated with the chemical vapor deposition (CVD) mechanism. In this, sufficient amount of heat is supplied to particles such that precursor becomes volatile through total solvent evaporation and gives rise to heterogeneous solid-vapor phase reaction which eventually results into thin solid film. The arbitrary rise in temperature introduces inhomogenities.

However, high substrate temperature required for the formation of the compounds in conventional spray route limits use of variety of substrates in device fabrication. In the present setup, it is planned to complete the reaction in the reaction chamber and the final product will be deposited on the substrates, which are kept at a low temperature. Indeed, we have employed Advanced Two Stage Spray Pyrolysis System (ATS-SPS) which is developed considering a notion of above third approach of CVD like process.

1.2. (A) 2. Advanced Spray Pyrolysis Set-up

The cross-sectional view of the newly fabricated system is shown in Figure 1.2. It is enclosed in an air-tight chamber provided with an exhaust to remove the gases and vapors produced during the spray pyrolysis process. It involves a reaction chamber, a substrate heater, temperature controllers and nozzle assembly. A glass nozzle is mounted on a fixed wooden block. The nozzle-substrate heater separation is adjustable. A cylindrical furnace is fixed on an MS stand, while the substrate heater is placed at the top of the cylindrical furnace. PID temperature controllers are used to control the reaction chamber temperature and substrate temperature with an accuracy of ± 5 K. The spray rate can be altered by varying the air pressure and solution height (not shown). When the solution is sprayed through the nozzle, the atomized droplets arrive at the core of the cylindrical furnace and undergo the expected chemical

reaction. The reaction products are now pushed upward and deposited on the preheated glass substrates.

1.2. (A) 3. Working of Advanced Spray Pyrolysis Technique

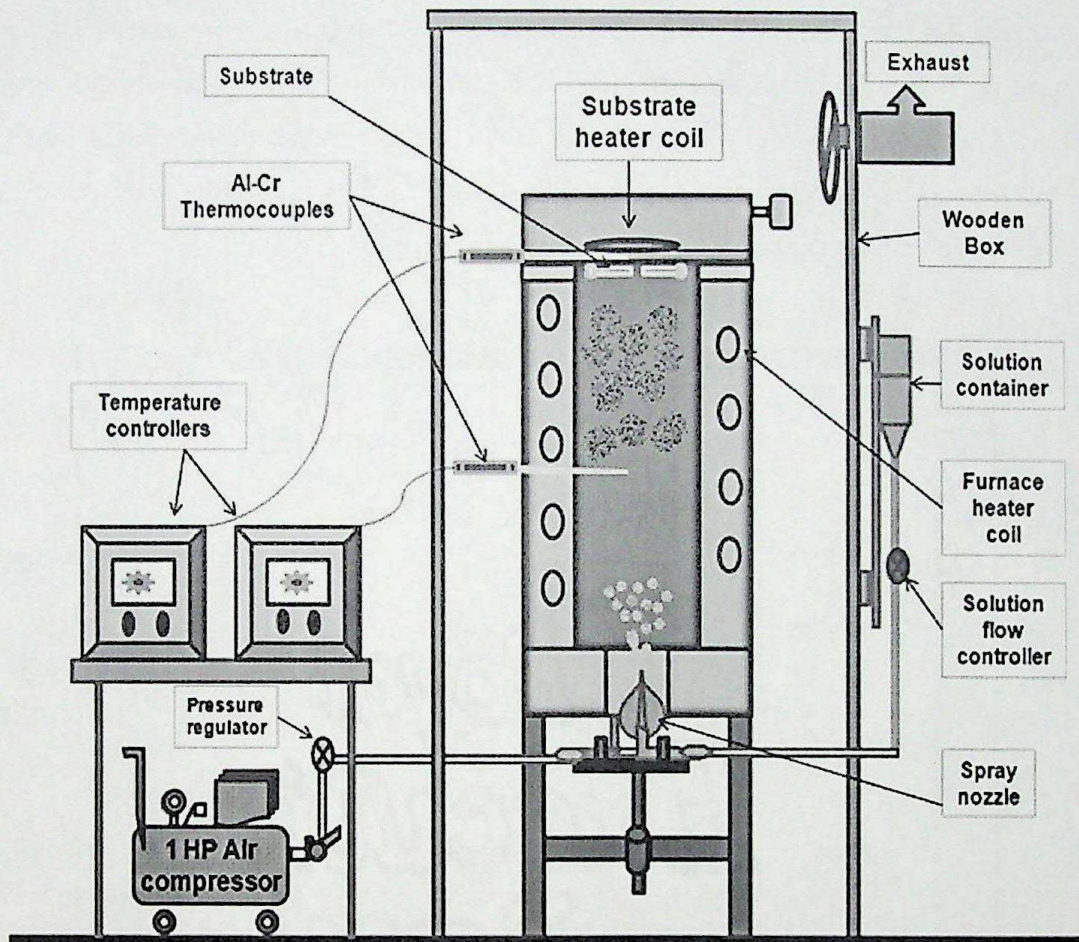


Figure 1.2: Schematic diagram of the modified spray pyrolysis unit.

To prepare the metal oxide films, the precursor solution is sprayed through the nozzle; when it enters the reaction chamber, it pyrolytically decomposes into metal oxide particles. These particles are pushed upward by the atomized air and reach the preheated substrates. The substrate heater offers the initial nucleation centers onto the preheated substrates for the growth of film and provides average kinetic energy for the even distribution of the deposits. After the initial nucleation process at the respective substrate temperature, the agglomeration of the grains may tend to form large clusters. This process is stopped or slowed down by increasing the heat energy which thereby increases the average kinetic energy of the grains and moves them to the thermally stable sites on the film to form an even distribution of the deposits.

Thus, deposition occurs in two steps, namely requisite chemical pyrolysis and nucleation/growth. The low substrate temperature and solid–vapor phase growth overcome probable film cracking and hazy ripples (as observed in some as-deposited sprayed films) and lead to a homogeneous coating. Hence, this novel method is the amalgamation of chemical vapor deposition and conventional spray pyrolysis technique. It was assumed that, at the suitable atomizing air pressure and nozzle–substrates spacing (about 30–38 cm), only critical-sized sprayed particles will reach the substrates and the residual particles will be drawn back by microgravity at the core of the reaction chamber, and result in large-area crack-free deposition.

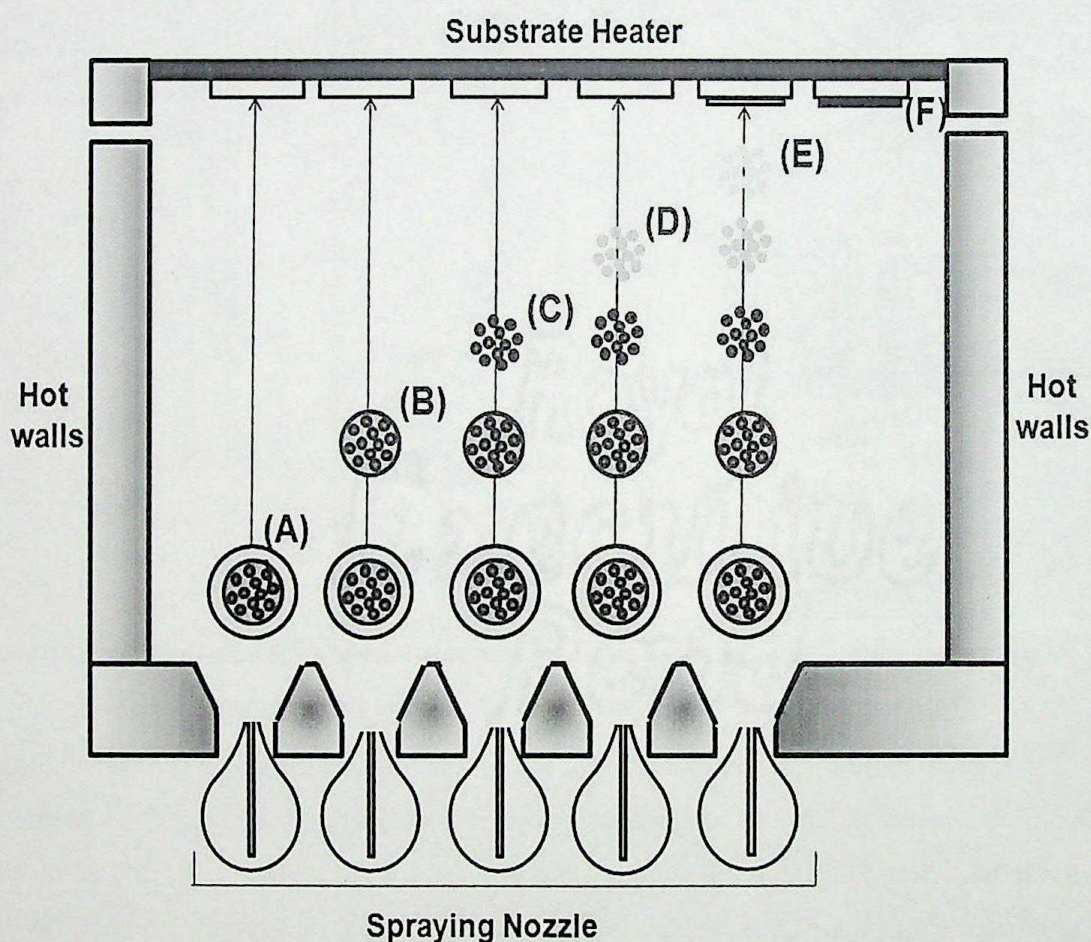


Figure 1.3: Supposed scheme of film formation by advanced spray pyrolysis

Various steps believed to involve during advanced spray pyrolysis of aerosols are summarized as follows and shown in Figure 1.3.

- (A) Precursor solution is converted into aerosols by spray nozzle.
- (B) Solvent evaporation takes places.

(C) & (D) Vaporization of the solvent leads to precipitate formation as the droplets/aerosols approaches the substrates and pyrolysis of the precipitate occurs in the core of the reactor furnace (kept at decomposition temperature of the precursor) consecutively before the precipitate reaches the substrates to form a solid-vapor phase.

(E) When the solid-vapor reaches the preheated substrate (kept at comparatively low temperature) nucleation and growth of thin films on the substrate surface takes place.

(F) Finally, growth of the nuclei leads to the formation of continuous thin layer of films.

1.2. (A) 4. Important parameters

The properties of the advanced spray deposited films are determined essentially by the growth conditions during their deposition. There are many factors, which can influence the growth processes and modify the structure of the films. In general some stages are essential in the thin film deposition processes: decomposition, nucleation and coalescence, followed by different growth processes as special cases of crystal growth (columnar, polycrystalline, epitaxial). Accordingly following are the factors affecting the above processes:

1. Core temperature

The core temperature i. e. the reactor temperature should be optimum so that the sprayed solution aerosols could undergo decomposition process. If the core temperature is lesser than optimum value (for optimum air pressure —or optimum nozzle–substrate distance), devoid of proper decomposition the sprayed aerosols will directly arrive at substrate which are essentially kept at lower temperature. In such as case, no reaction will be observed and rather than solid-vapor phase merely semi-solid deposits will arrive at the substrates and due to lack of thermal energy at the substrate surface, non-adherent film will form. On the other hand, if the core temperature is higher than its optimum value (for optimum air pressure or optimum nozzle–substrate distance), the oxidation reaction occurs totally in the gas phase and inhomogeneous oxide particles or clusters are deposited on substrates without adherence. Thus the core temperature is recommended to set at the decomposition temperature of the relevant precursor salt.

2. Atomizing air pressure

If air pressure atomizing the spraying solution is higher than optimum value (at the optimum core temperature); the atomized aerosols will be of very minute sized. In this case, thermal energy experienced by aerosols will be much larger in order that much earlier decomposition will result into (very thin) powdered film on the substrates. Whereas if the air pressure is smaller than its optimum value, aerosol size will be much larger so that the solvent can vaporized, but the precursor is not completely decomposed in their way. This will result into the powder deposits.

3. Nozzle to substrate distance

This parameter has the similar effects resembling the atomizing air pressure. In fact both these parameters are mutually dependent. The decreasing nozzle-substrate distance will introduce the nozzle tip to the increasingly hot ambient which can result into the blockage of the nozzle. Conversely increasing nozzle-substrate distance will increase the aerosol traverse path. This will cause the aerosols to experience thermal energy further and either powdered films or no deposition will result. Therefore, it is suggested that the nozzle-substrate distance and atomizing air pressure should be optimized mutually.

4. Substrate temperature

Similar to the conventional route, the substrate temperature in the advanced spray pyrolysis is the foremost parameters which have the profound influence on the film properties. As the intent behind the development of advanced spray technique is to prepare the films at lower temperature than that required in conventional spray pyrolysis method, there are deliberately enforced limitations over the substrate temperature. Therefore, the role of substrate temperature in the present case is not to undertake decomposition reaction but merely limited to the nucleation and coalescence, followed by different growth processes. As a result, this important parameter will certainly affect structural, morphological, opto-electronic properties. Furthermore, insufficient substrate temperature results into the amorphous films; while the increasing substrate temperature will increase the film crystallinity. In case of the insufficient substrate temperatures, low average kinetic energy will adversely affect the

distribution of the deposits and consequently the agglomeration of the grains may tend to form large clusters.

1.2. (A) 5. Shortcomings

1. The additional parameter, that is, the core temperature has been incorporated to bring the pyrolytic reactions ahead of the nucleation and growth processes at preheated substrate. However, controlling this critical parameter is tricky job as the temperature measurements are done with the thermocouple which senses the temperature of the hot ambience. The use of exothermic solvents such as alcohols may enhance the core temperature further than the set value. Individual expertise is needed to minimize this difficulty.
2. As the pyrolytic reaction occurs in the ambience rather than onto the substrate surface, chemical wastage could be the troublesome case. Especially in case of expensive chemicals, for example, palladium acetylacetonate this spray route is not affordable. Indeed, this is the most disquieting problem with the advanced spray pyrolysis.

However, such shortcomings immensely motivate one for further research and to go deeper into understanding the thermodynamics of advanced spray pyrolysis, and especially to better understand the entire processes of film formation.

Section (B): Thin film Characterization Techniques

1.3. (B) 1. Introduction

The growth mechanism and properties of the films can be well understood by their characterizations using a variety of investigative techniques. The optimization is the most important aspect to control material processing and regularize sensor performance. Before using the films in applications, one has to characterize the films to achieve optimum performance of the films prepared. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. In the present work, the structural, morphological, electrical and optical analysis was carried out by X-ray diffraction, field emission scanning electron microscope (FESEM), Atomic force microscope (AFM), electrical

resistivity, optical spectroscopy, etc. Further, gas sensing performance of the as-characterized undoped and doped ZnO films was tested using a homemade gas sensor assembly.

The intent of this section is to facilitate the comprehension of the work by an inexperienced reader in characterization and, in some way, to include a general description of a group of essential characterization techniques in a clear way. For that, different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation and working.

1.3. (B) 2. Differential Thermal Analysis and Thermo Gravimetric Analysis

Thermal analysis includes a group of techniques in which physical and chemical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program in different gas environments. Modern thermal analysis instrument measures phase transition temperature, weight losses in materials, energies of transitions, dimensional changes, modulus and viscoelastic properties. Current applications include environmental measurements, product reliability, compositional analysis, stability, chemical reactions and dynamic properties.

(a) Differential Thermal Analysis (DTA)

In DTA, the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature). Any phase transition that the sample undergoes will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. This differential temperature (ΔT) versus the programmed temperature (T) at which the whole system is being changed yields the temperature of transitions and the nature of the transition such as exothermic or endothermic [10].

(b) Thermo Gravimetric Analysis (TGA)

It provides a quantitative measurement of any weight change associated with a transition. Thermogravimetry can directly record the loss or gain in weight with time or temperature due to oxide phase formation, dehydration or decomposition. Thermogravimetric curves are characteristic for a given

compound or systems because of the unique sequence of physiochemical reactions, which occur over definite temperature ranges and at rates that are function of the molecular structures. Changes in weight are due to rupture or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical reactions, reaction mechanism and the intermediate and final reaction products. The usual temperature range is from ambient to 1200 °C with inert or reactive atmospheres. All weight-change processes absorb or release energy and are thus measurable by DTA or DSC, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a clear distinction to be made between physical and chemical changes when the samples are subjected to both DTA and TGA tests. In general, each substance will give a DSC or DTA curve whose shape, number and position of the various endothermic and exothermic features serve as a means of qualitative and quantitative identification of the substance. When an endothermic change occurs the sample temperature lags behind the reference temperature because of the heat in the sample. The initiation point for a phase change or chemical reaction is the point at which the curve first deviates from the base line. When the transition is complete thermal diffusion brings the sample back to equilibrium quickly. The peak (or minimum) temperature indicates the temperature at which the reaction is completed. Endotherms generally represent physical rather than chemical changes. Sharp endotherms are indicative of crystalline rearrangements, fusion, or solid-state transition for relatively pure materials. Broader endotherms cover behavior ranging from dehydration, temperature-dependent phase behaviors to melting of polymers. Exothermic behavior (without decomposition) is associated with the decrease in enthalpy of a phase or chemical system. Narrow exotherms usually indicate crystallization (ordering) of a metastable system, whether it is supercooled organic, inorganic, amorphous polymer or liquid, or annealing of stored energy resulting from mechanical stress. Broad exotherms denote chemical reactions, polymerization or curing of thermosetting resins. Exotherms with decomposition can be either narrow or broad depending on kinetics of the behavior. The area of

exotherms or endotherms can be used to calculate the heat of the reaction or the heat of a phase formation [11].

Specifications

It is SDT-2960 from TA Instruments, USA. It is capable of performing both DSC and TGA at the same time. DTA can also be carried out using SDT 2960. It measures the heat flow and weight changes associated with transitions and reactions in material over the temperature range from RT to 1500 °C. These experiments can be carried out in either of the optional environment like N₂, O₂, Ar or air at pre decided flow-rate (ml/min) and heating rate (°C/min). The gas-switching accessory is used to turn on and off or to switch between two different purge gases during SDT experiment. Heat-flow accuracy is equal to 1% where as DTA sensitivity is 0.001°C and that of weight is 0.1 µ gm. This SDT- 2960 controller is connected to PC and the special software makes the thermal analysis. It stores the data as well as runs the analysis programs.

Applications

Melting point, crystallization behavior, glass transition temperature, thermal stability, dehydration, oxidation, phase-transition, specific heat, reaction kinetics etc can be determined.

1.3. (B) 3. Thickness Measurement

The thickness of the film is the most significant parameter that affects the properties of the thin film. It may be measured either by in situ monitoring of the rate of the deposition or after the film is taken out from deposition chamber. Technique of the first type often referred to as monitor methods generally allow both monitoring and controlling of deposition rate film thickness. Any known physical quantity related to film thickness can be used to measure the thickness. The method chosen should be convenient, reliable and simple.

One of the most convenient and advanced methods for determining film thickness is surface profilometer method. Basically, profilometer is a measuring instrument used to measure a surface's profile, in order to quantify its roughness. Vertical resolution is usually in the nanometer level, though lateral resolution is usually poorer.

Contact Profilometers

A diamond stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance and specified contact force. A profilometer can measure small surface variations in vertical stylus displacement as a function of position. A typical profilometer can measure small vertical features ranging in height from 10 nm to 1 mm. The height position of the diamond stylus generates an analog signal which is converted into a digital signal stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nm to 25 μm , and the horizontal resolution is controlled by the scan speed and data signal sampling rate. The stylus tracking force can range from less than 1 to 50 milligrams [12].

Non-contact Profilometers

An optical profilometer is a non-contact method for providing much of the same information as a stylus based profilometer. There are many different techniques which are currently being employed, such as laser triangulation (triangulation sensor), confocal microscopy (used for profiling of very small objects) and digital holography.

In the present work, a contact profiler was used to measure the thickness of ZnO thin films. In order to measure the film thickness, a 'step' has to be made on the film (either by doctor blade or by dipping the film in acidic medium). While measurement the stylus is scanned over this step at various (step) positions and the average step height will prove the film thickness.

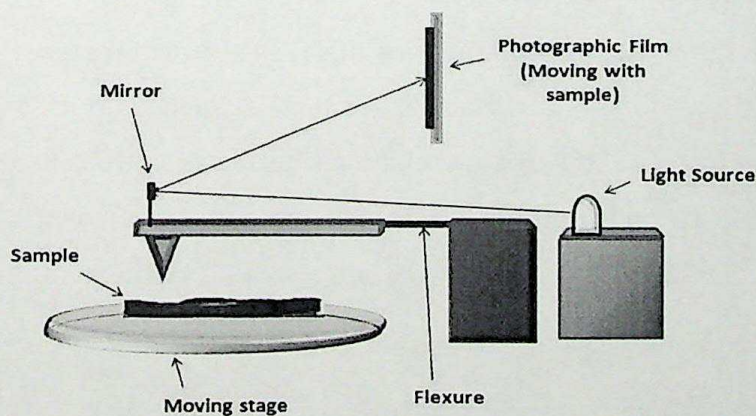


Figure 1.4: Surface Profilometer

Roughness is a measure of the texture of a surface. It is quantified by the vertical deviations of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth. Roughness is typically considered to be the high frequency, short wavelength component of a measured surface.

1.3. (B) 4. X-Ray Diffraction

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the *crystalline* phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayers, and atomic arrangements in amorphous materials (including polymers) and at interfaces. XRD offers unparalleled accuracy in the measurement of atomic spacing and is the technique of choice for determining strain states in thin films. XRD is noncontact and nondestructive, which makes it ideal for in situ studies. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces (e.g., in multilayers). Materials composed of any element can be successfully studied with XRD, but XRD is most sensitive to high-Z elements, since the diffracted intensity from these is much larger than from low-Z elements. As a consequence, the sensitivity of XRD depends on the material of interest. The basic principles of X-ray diffraction are found in textbooks e.g. by Buerger [13], Klug and Alexander [14], Cullity [15], Tayler [16], Guinier [17], Barrett and Massalski [18].

Figure 1.5 shows the schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg's law and is given as,

$$2d \sin\theta = n\lambda \quad \text{-----} \quad (1.1)$$

where, d = interplaner spacing, θ = diffraction angle, λ = wavelength of x-ray, n = order of diffraction.

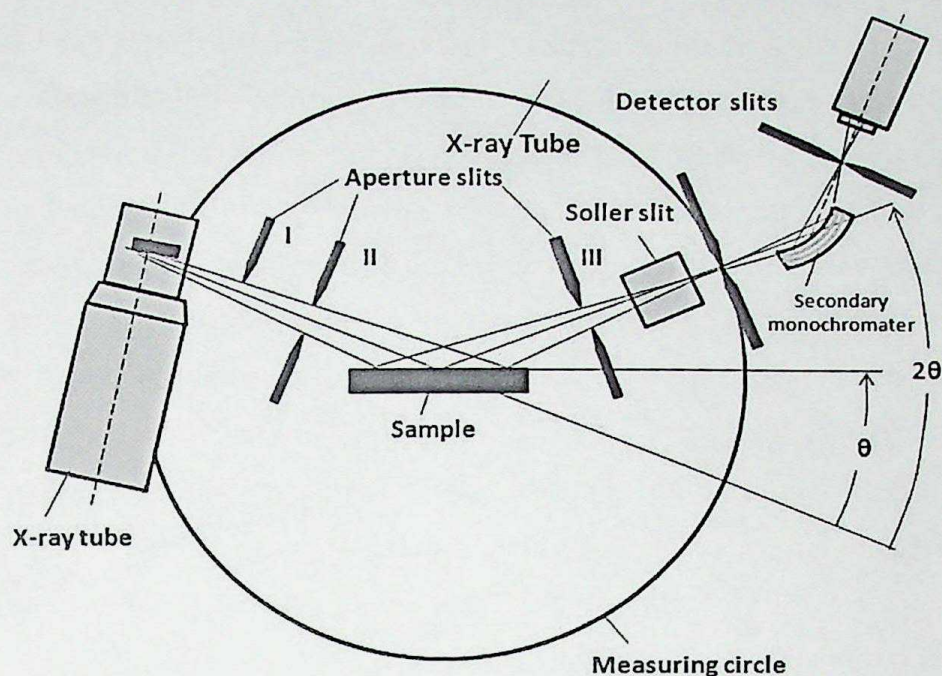


Figure 1.5: Schematics of X-ray diffractometer.

Table 1.1: X-ray diffraction methods.

Method	λ	θ
Laue Method	Variable	Fixed
Rotating crystal Method	Fixed	Variable (in part)
Powder Method	Fixed	Variable

In crystalline solids the atoms are ordered in particular repeated pattern referred as unit cell with its interatomic spacing comparable to wave length of x-rays (0.5 to 2.5Å). Hence crystals are the best gratings for the diffraction of x-rays. The directions of diffracted x-rays give information about the atomic arrangements and hence the crystal structure and phase formation can be confirmed by x-ray diffraction studies.

The way of satisfying Bragg's condition is devised and this can be done by continuously varying either λ or θ during the experiment. The way, in which these quantities are varied, distinguish the three main diffraction methods and tabulated in Table 1.1.

In powder method the crystal to be examined is reduced to a fine powder and placed in a beam of a monochromatic x-rays. Each particle of the powder is the tiny crystal, or assemblage of smaller crystals, oriented at random with respect to incident beam. Some of the crystals will be correctly oriented so that their (100) planes, for example, can reflect the incident beam. Other crystals will be correctly oriented for (110) reflections and so on. The result is that every set of lattice planes will be capable of reflection. This is the principle of a powder diffractometer.

Ideally, according to Bragg's law, for the particular d value, the constructive interference of x-rays should occur only at particular θ value i. e Bragg's angle and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum there.

Identification of Phases

One of the most important uses of thin-film XRD is phase identification. Although other techniques (e.g., RBS, XPS, and XRF) yield film stoichiometries, XRD provides positive phase identification. This identification is done by comparing the measured d -spacing in the diffraction pattern and, to a lesser extent, their integrated intensities with known standards in the JCPDS Powder Diffraction File (Joint Committee on Powder Diffraction Standards, Swathmore, Pennsylvania, 1986) and the reflections can be indexed with Miller indices.

However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at $\theta \pm \delta\theta$, which broadens the peak corresponding to diffracted beam in proportion to the size of the tiny crystal. This can be used to calculate the particle size. The relation for the same is given by Debye Scherrer and formulated [20] as,

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \text{-----} (1.2)$$

Where, D =particle size, θ_B =diffraction angle, λ =wavelength of X-rays and β line broadening at Full Width at Half Maxima (FWHM).

Further, the powder diffractometer can also be used for X-ray diffraction from thin films. Epitaxial or polycrystalline (may or may not be oriented) thin films can be considered as single crystal or powder (crystals or assembly of

crystals spread on substrate) respectively. Hence, a typical epitaxial or oriented film may not show all corresponding reflections and show only few reflections for example say, a c-axis oriented film will show only (hkl) for which h and k indices are zero and l is non zero. However, these hidden peaks can be detected by small angle X-ray diffraction technique.

1.3. (B) 5. Scanning Electron Microscopy (SEM)

Interaction of electrons with elements is well understood and has been extensively used for characterizing of the materials. As the electrons can be focused to micron or sub-micron size, it is well suited for analyzing sub-micron sized areas or features. When an electron strikes the atom, variety of interaction products are evolved. Figure 1.6 shows the regions from which different signals are detected [19].

Scattering of electron from the electrons of the atom results into production of backscattered electrons and secondary electrons. Electron 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. Scanning electron microscope is an instrument that uses electrons instead of light waves which are used in conventional microscopes, to observe the morphology of a sample at higher magnification, higher resolution and depth of focus. Of these, backscattered electrons, secondary electrons and transmitted electrons give information about the microstructure of the sample. Auger electron, ejected electrons and X-rays are energies specific to the element from which they are coming. These characteristic signals give information about the chemical identification and composition of the sample.

The SEM work principles are as follows:

1. Using an electron gun a beam of electrons produces. Electrons may be emitted from a conducting cathode material either by heating it to the point where outer orbital electrons gain sufficient energy to overcome the work function barrier of the conductor (thermionic sources) or by applying an electric field sufficiently strong that electrons "tunnel" through the barrier (field

emission sources). Tungsten filament is used as cathode in electron guns. The energy required for a material to give up electrons is related to its work function. For Tungsten this energy is around 4.5 eV.

2. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and electromagnetic lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample.

3. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.

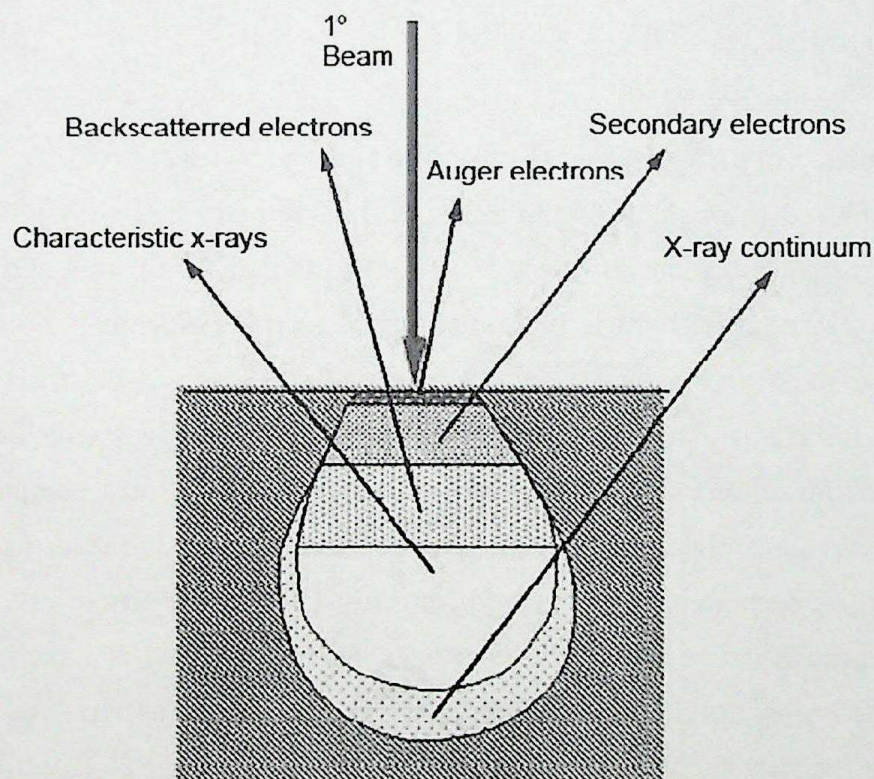


Figure 1.6: Illustration of several signals generated by the electron beam–specimen interaction in the SEM and the regions from which the signals can be detected.

In scanning electron microscopy, (SEM) an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. The three signals which provide

the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays.

Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology. A high resolution image can be obtained because of the small diameter of the primary electron beam.

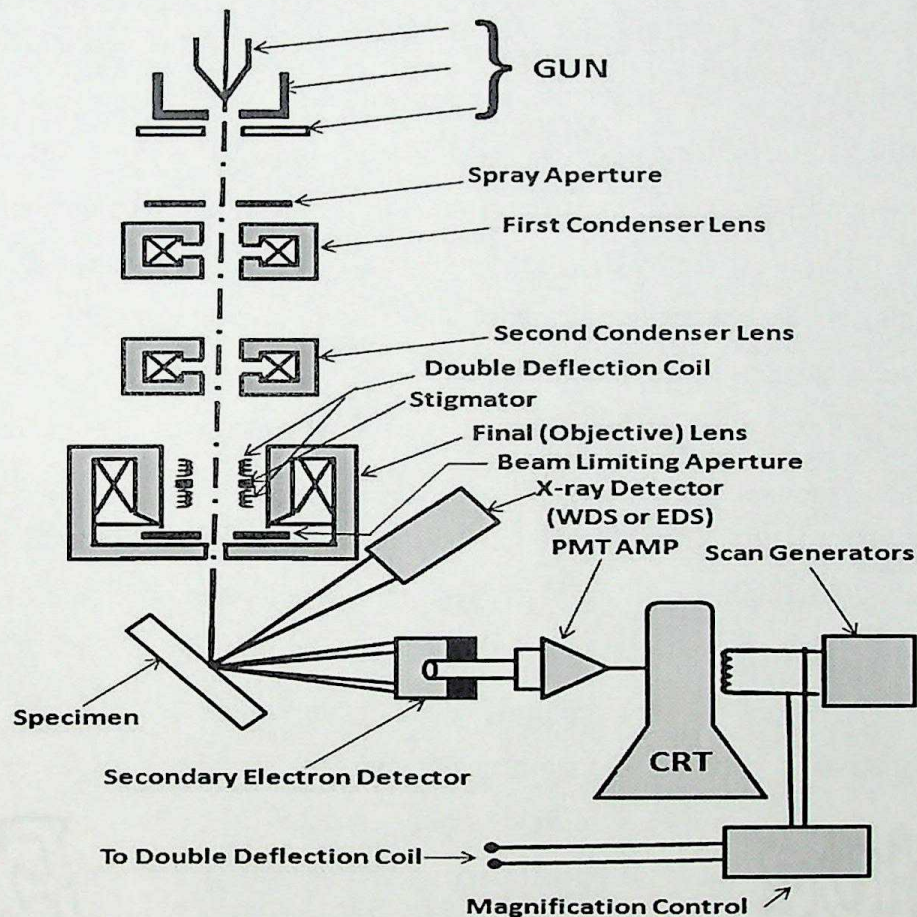


Figure 1.7: Schematic diagram of Scanning Electron Diagram (SEM)

Backscattered electrons are primary beam electrons which are 'reflected' from atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are emitted from a depth in the sample, the resolution in the image is not as good as for secondary electrons.

Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The emitted X-ray has an

energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis (Energy Dispersive X-ray Spectroscopy or EDS). EDS can provide rapid qualitative, or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1-2 microns. X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface.

Why Conductive Samples?

Specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Non-conductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultra-thin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials currently used for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation.

Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z). The improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

Field emission Scanning Electron Microscopy (FESEM)

Field emission Scanning Electron Microscopy or FESEM uses field emission gun instead of typical electron gun sources. A field emission gun is a type of electron gun in which a sharply-pointed Muller-type emitter is held at several kilovolts negative potential relative to a nearby electrode, so that there is sufficient potential gradient at the emitter surface to cause field electron emission. Emitters are either of cold-cathode type, usually made of single crystal tungsten sharpened to a tip radius of about 100 nm, or of the Schottky type, in

which thermionic emission is enhanced by barrier lowering in the presence of a high electric field. Schottky emitters are made by coating a tungsten tip with a layer of zirconium oxide, which has the unusual property of increasing in electrical conductivity at high temperature.

Table 1.2: Comparison of thermionic and field emission guns

Type of Gun	Brightness (A /mm sr)	Source diameter (μm)
Tungsten hairpin	10^2 - 10^3	50
Tungsten point, thermionic LaB6 } Tungsten point, Field emission	10^3 - 10^4 10^6	1 - 10 0.01-0.1

In electron microscopes, a field emission gun is used to produce an electron beam that is smaller in diameter, more coherent and with up to three orders of magnitude greater current density or brightness than can be achieved with conventional thermionic emitters such as tungsten or lanthanum hexaboride (LaB6)-tipped filaments. The result in both scanning and transmission electron microscopy is significantly improved signal-to-noise ratio and spatial resolution, and greatly increased emitter life and reliability compared with thermionic devices.

1.3. (B) 6. Atomic Force Microscopy (AFM)

The principal behind the operation of an AFM in the contact mode is shown in Figure 1.8.

The AFM tip is first brought (manually) close to the sample surface, and then the scanner makes an ultimate adjustment in tip-sample distance based on a set point determined by the user. The tip, now in contact with the sample surface through any adsorbed gas layer, is then scanned across the sample under the action of a piezoelectric actuator, either by moving the sample or the tip relative to the other. A laser beam aimed at the back of the cantilever-tip assembly reflects off the cantilever surface to a split photodiode, which detects the small cantilever deflections. A feedback loop, shown schematically in Figure. 1.8 maintains constant tip-sample separation by moving the scanner in the z direction to maintain the set point deflection. Without this feedback loop, the tip

would “crash” into a sample with even small topographic features (although this phenomenon can happen even with careful AFM operation).

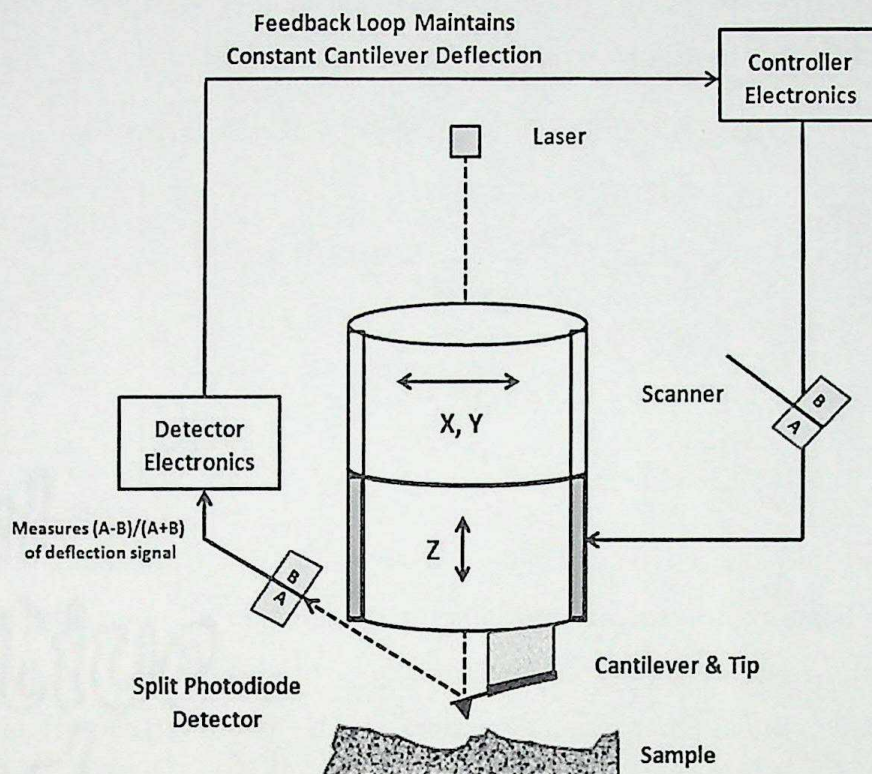


Figure 1.8: Schematic diagrams showing the operating principles of the AFM in contact mode

By maintaining a constant tip-sample separation and using Hooke’s Law ($F = -kx$ where F is force, k is the spring constant, and x is the cantilever deflection), the force between the tip and the sample is calculated. Finally, the distance the scanner moves in the z direction is stored in the computer relative to spatial variation in the x - y plane to generate the topographic image of the sample surface.

Modes of operation

Contact Mode

In the so-called contact-AFM mode, the tip makes soft “physical contact” with the surface of the sample. The deflection of the cantilever is proportional to the force acting on the tip, via Hook’s law. In contact-mode the tip either scans at a constant small height above the surface or under the conditions of a constant force. In the constant height mode the height of the tip is fixed, whereas in the constant-force mode the deflection of the cantilever is fixed and the motion of

the scanner in z direction is recorded. By using contact-mode AFM, even “atomic resolution” images are obtained.

Non Contact Mode

In this mode, the probe operates in the attractive force region and the tip-sample interaction is minimized. The use of non-contact mode allowed scanning without influencing the shape of the sample by the tip (sample forces. In most cases, the cantilever of choice for this mode is the one having high spring constant of 100 N/m so that it does not stick to the sample surface at small amplitudes. The tips mainly used for this mode are silicon probes.

Table 1.3: Properties of the different operation modes in AFM.

Operation Mode	Contact mode	Non-contact Mode	Tapping mode
Tip loading force	low → high	Low	Low
Contact with sample Surface	Yes	No	Periodical
Manipulation of sample	Yes	No	Yes
Contamination of AFM tip	Yes	No	Yes

Tapping Mode (intermittent contact Mode)

In tapping mode-AFM the cantilever is oscillating close to its resonance frequency an electronic feedback loop ensures that the oscillation amplitude remains constant, such that a constant tip-sample interaction is maintained during scanning.

1.3. (B) 7. Optical Absorption Studies

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is altogether considered to be due to 1) inner shell electrons 2) valence band electrons 3) free carriers including holes as well as electrons and 4) electrons bound to localized impurity centers or defects of some type. In study of the fundamental properties of some semiconductors, the

absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons so that electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer the electrons from valence band to conduction band. The optical absorption spectra of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from valence to conduction band (may also involve acceptor or donor impurity levels, traps etc.). The conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap in the conduction band. However, indirect transition also involves simultaneous interaction with lattice vibration. Thus the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. The direct interband optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Figure 1.9 (a). Hence a wave vector k for electron remains unchanged in E-k space.

The optical transition is denoted by a vertical upward arrow. Absorption coefficient α for simple parabolic bands and for direct transition is given by the relation [20].

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \text{-----} (1.3)$$

where, E_g is the separation between bottom of the conduction and top of the valence band, $h\nu$ is the photon energy, n is constant and is equal to $1/2$ or $3/2$ depending on whether transition is allowed or forbidden and α_0 is a constant depending upon the transition probability for direct transition. For allowed direct transitions $n = 1/2$ and for allowed indirect transition $n = 2$. Thus if the plot of $(\alpha h\nu)^2$ against $h\nu$ is linear then the transition is direct allowed. The band gap

energy E_g is determined by extrapolating the linear portion of the curve to the energy axis at $\alpha = 0$.

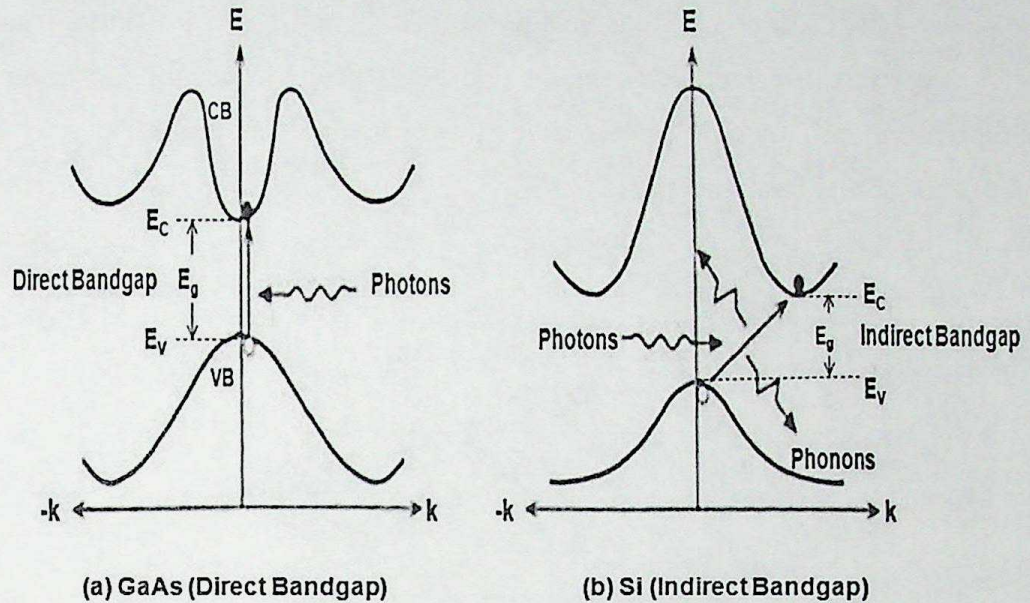


Figure 1.9: (a) Direct and (b) Indirect interband band transition

Let's visualize a situation in Figure 1.9 (b), where interband transition takes place between different k -states. Since these must satisfy the momentum conservation laws; the only way such a transition can take place is through the emission or absorption of a phonon with wave vector q as;

$$K' \pm q = k + K \text{ ----- (1.4)}$$

The transition defined by equation (5) is termed indirect transition. For indirect transition equation (3.3) prevails,

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^2}{h\nu} \text{ ----- (1.5)}$$

Where, $E_g = E_g' \pm E_g$, E_g is indirect band gap energy and E_g is the phonon energy. For allowed transition $n = 2$ and for forbidden transition $n = 3$. The band gap energy is determined by extrapolating the linear portion of the plot $(h\nu)^n$ versus $h\nu$ to the energy axis at $\alpha = 0$.

1.3. (B) 8. Electrical Resistivity Measurement

The extensive study of conductivity, temperature dependent stability etc has led by use of thin film as resisters, contacts and interconnections. Investigation of critical resistivity as a highly structure sensitive properties make it possible to be an insight in to the structural and electrical properties of the

metal films which is important from both the theoretical and practical point of view.

The contact methods are most widely used for the measurement of resistivity; these methods include two-point probe, four point probe and the spreading resistance. The two-point probe method is simple, easy to use and useful for high resistive thin films.

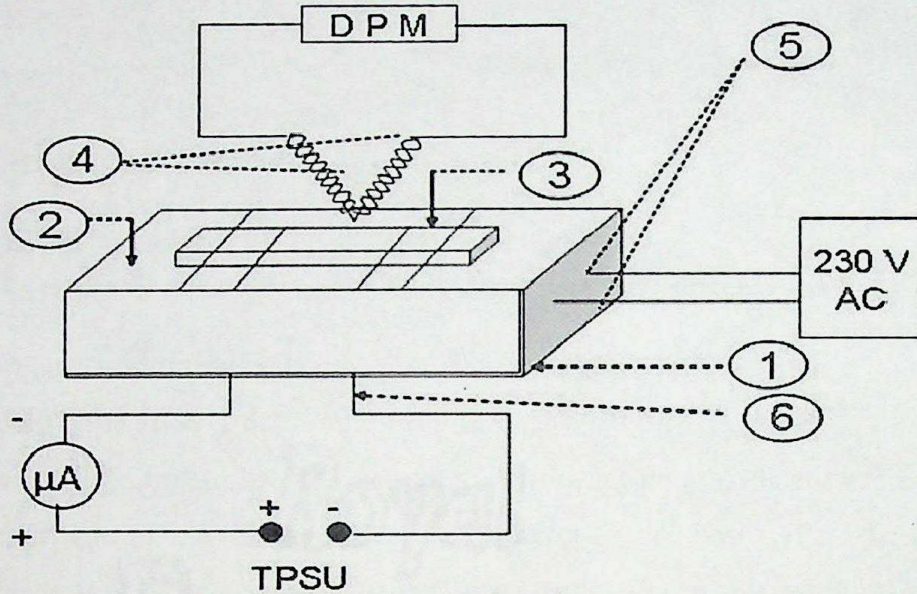


Figure 1.10: Schematic circuit diagram for the measurement of the two probe electrical resistivity of the thin film sample. Herein, 1: Sample holder, 2: Mica Sheet, 3: Sample (thin film), 4: Thermocouple, 5: Heater and 6: Copper wire.

In this method, constant voltage 'V' is applied between two-fixed positions probes separation 'd' and current passing thorough a sample of known dimensions (cross section area A) is measured with an appropriate current meter. For uniform sample the resistivity is given by,

$$\rho = \frac{A}{I} \times \frac{V}{d} \text{-----} (1.6)$$

In case of semiconducting thin films, resistivity decreases with increase in temperature. The thermal activation energy 'E_a' are calculated by using resistivity [21].

$$\rho = \rho_0 \exp \left[-\frac{E_a}{k \cdot T} \right] \text{-----} (1.7)$$

Where symbols have their usual meanings. The slope of log vs. (1000/T) leads to the estimation of activation energy. The electrical resistivity

measurement gives room temperature resistivity, activation energy and type of material (NTC or PTC). However, there is disadvantage of metal contact, which forms a low resistance ohmic or non-ohmic junction with material. The metal contacts form heating effect of current, especially when sample resistivity is high.

1.3. (B) 9. Gas Sensing Measurement Assembly

Before giving a description of the assemblies that we have utilized to carry out gas sensitivity measurements on our films, we briefly give below the methodology used to achieve the desired gas concentrations for sensing studies.

The desired gas concentration in parts per million (ppm) was attained by taking a measured quantity of the gas from a canister, containing pressurized gas ($\sim 20 \text{ kg/cm}^2$) at 1000 ppm concentration, by means of a syringe, and introducing it into an airtight SS housing having a volume of 250 cc. The gas was injected through a septum in the housing. The "unit" ppm being a volume ratio, 1 ppm of a given gas therefore occupies a volume of $2.5 \times 10^{-4} \text{ cc}$ in 250 cc housing. Therefore, the volume of gas required to be taken in a syringe from a canister containing the gas at 1000 ppm such that it gives rise to 1 ppm of gas concentration in a 250 cc housing is $(2.5 \times 10^{-4} \times 10^6 \text{ cc}) / (1000) = 0.25 \text{ cc}$. Other gas concentrations employed in our gas sensing studies were thus obtained proportionally.

We now describe the set-up, shown in figure 1.11, which was exploited to establish the optimum operating temperature of a deposited film. It consists of an SS heater block that is contained in an airtight SS enclosure having a volume of 250 cc with a provision for gas inlet through a septum with a rubber gasket. It also contains a pair of spring-enabled pressure contacts made of nichrome rods, the upper ends of which are brazed to copper wires that go to the connector within the enclosure. A "Rigol DM3062 model" digital multimeter/ data acquisition system connected to the external leads from the connector was used for resistance measurements. The heater temperature was monitored and controlled using an ON/OFF digital temperature controller unit.

For the purpose of verifying the optimum operating temperature, films were deposited over the entire substrate area of $\sim 8 \times 5 \text{ mm}^2$. Electrical contacts onto the film surfaces were then made by means of Au paste. Such a film was then placed on the heater block and its resistance was monitored after placing

the pressure contacts onto the Au colloidal pads on the film surface. Sensitivity of the films at a given gas concentration was measured at different temperatures in the range 298-673K depending on their nature and response. Once the optimum operating temperature was determined, the undoped and doped ZnO films were applied for the sensing characteristics measurements at their respective optimum temperatures on the above set-up.

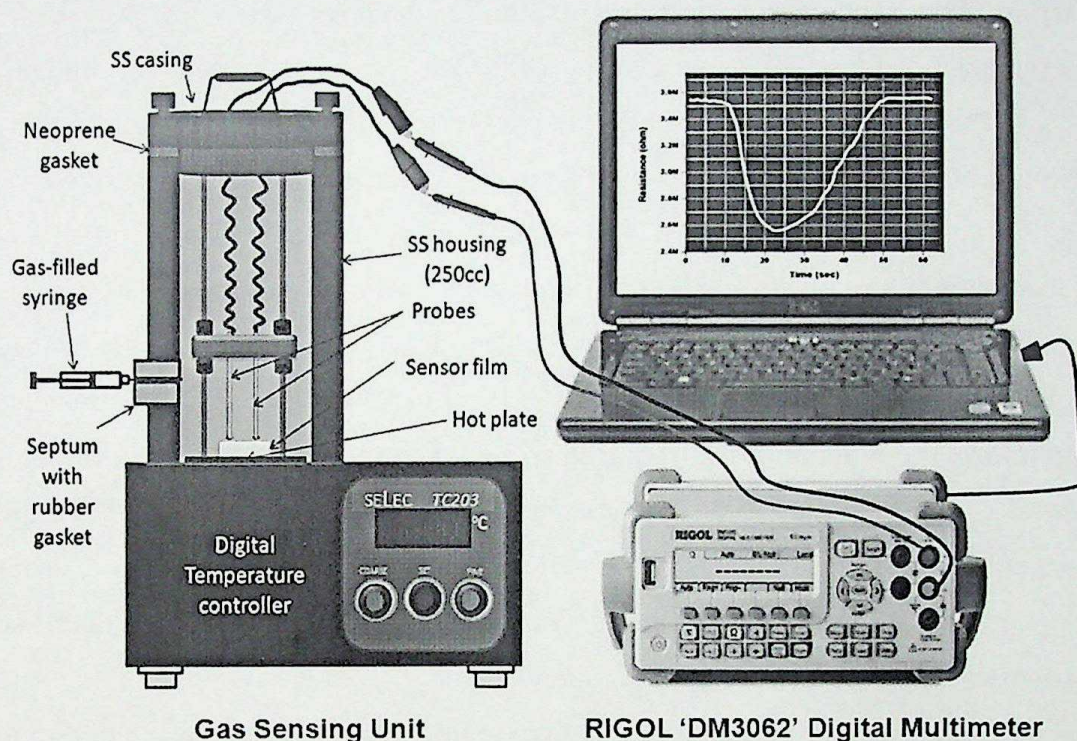


Figure 1.11: Schematic diagram of the sensor evaluation system consisting of an airtight SS chamber with the assembly housing the sensor film connected to a temperature controller circuit.

Response and recovery measurements

For response and recovery measurements, film response to a particular gas is studied by introducing the gas of known concentration into the housing and recording the resistance using “Rigol” digital multimeter as a function of time till its steady state value is reached. The housing is then opened to the atmosphere and the subsequent film recovery on gas removal is recorded that is characterized by the resistance reaching its base value. The response and recovery characteristics of films exposed to different gas concentrations are thus studied by plotting their resistance as a function of time.

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