Chapter 2

Growth of Nanocrystalline Tin Selenide (SnSe) Thin Films by Spin Coating Technique and its Chemical Composition Study
2.1 Importance of Deposition Technology in Modern Fabrication Processes

Deposition technology can well be regarded as the major key to the creation of devices such as computers, since microelectronic solid-state devices are all based on material structures created by thin-film deposition. Electronic engineers have continuously demanded films of improved quality and sophistication for solid-state devices, requiring a rapid evolution of deposition technology. Equipment manufacturers have made successful efforts to meet the requirements for improved and more economical deposition systems and for in situ process monitors and controls for measuring film parameters. Another important reason for the rapid growth of deposition technology is the improved understanding of the physics and chemistry of films, surfaces, interfaces, and microstructures that are made possible by the remarkable advances in analytical instrumentation during the past twenty years. A better fundamental understanding of materials leads to expanded applications and new designs of devices that incorporate these materials.

A good example of the crucial importance of deposition technology is the fabrication of semiconductor devices, an industry that is totally dependent on the formation of thin solid films of a variety of materials by deposition from the gas, vapor, liquid, or solid phase. The starting materials and epitaxial films of semiconductors are usually grown from the gas phase. Chemical vapor deposition of a single crystal silicon film on a single crystal silicon substrate of the same crystallographic orientation, a process known as homoepitaxy, is accomplished by hydrogen reduction of dichlorosilane vapor. If a single crystal film of silicon is deposited on a non silicon crystal substrate, the process is termed heteroepitaxy. Layers of single crystal compound semiconductors are created to a thickness of a few atom layers by molecular beam epitaxy. Subsequent steps in the fabrication process create electrical
structures that require the deposition of an insulating or dielectric layer, such as an oxide, glass, or nitride, by one of several types of chemical vapor deposition (CVD) processes e.g. by plasma-enhanced chemical vapor deposition (PECVD), or by any one of a number of sputtering deposition methods. The deposition of conductor films for contact formation and interconnections can be accomplished by vacuum evaporation or sputtering. CVD processes are especially suitable if polysilicon, polycides, or refractory metals are to be deposited. The deposition of subsequent levels of insulator is repeated to build multilevel structures. Deposition may be complemented by spin-on techniques of organic polymeric materials, such as a polyimide, or of organometallic based glass forming solutions. Spin on deposition is especially useful if planarization of the device topography is required, as in the case of most high-density, multilevel conductor, VLSI circuits etc. The sequence of alternate film deposition of metals and insulators may be repeated several more times, with repetitive spin on deposition of photopolymer masking solution for the delineation of contact openings, grid lines, and other pattern features by etching operations and lift off techniques. Film formation by methods other than deposition are used in a few steps of the fabrication sequence, these include thermal oxidation of the substrate, ion implantation, nitridation, silicide formation, electrolytic and electroless metal deposition, and spray deposition (e.g., of organometallic solutions for forming antireflection coatings). These examples attest to the fact that the vast majority of material formation processes in semiconductor device technology (and in other areas of electronic device fabrication) are crucially dependent on film deposition technology.
2.2 Overview of Various Thin-Film Deposition Technologies

There are many dozens of deposition technologies for material formation [1]. Since the concern here is with thin-film deposition methods for forming layers in the thickness range of a few Nanometers to about ten micrometers, the task of classifying the technologies is made simpler by limiting the number of technologies to be considered [2-4]. Basically, thin-film deposition technologies are either purely physical, such as evaporative methods, or purely chemical, such as gas- and liquid-phase chemical processes. A considerable number of processes that are based on glow discharges and reactive sputtering combine both physical and chemical reactions, these overlapping processes can be categorized as physical-chemical methods. A classification scheme is presented in Table 2.1 where thin-film deposition technologies are grouped according to evaporative, glow discharge, gas-phase chemical, and liquid-phase chemical processes.
**Table 2.1: Classification of Thin-Film Depositon Technologies**

### Evaporative Methods
- **Vacuum evaporation**
  - Convention vacuum evaporation
  - Electron-beam evaporation
  - Molecular-beam epitaxy
  - Reactive evaporation

### Glow- discharge processes
- **Sputtering**
  - Diode sputtering
  - Reactive sputtering
  - Bias sputtering (ion plating)
  - Magnetron sputtering
  - Ion beam deposition
  - Ion beam sputter deposition
  - Reactive ion plating

- **Plasma Processes**
  - Plasma-enhanced
  - Plasma oxidation
  - Plasma anodization
  - Plasma polymerization
  - Plasma reduction
  - Microwave ECR plasma
  - Cluster beam deposition

### GAS-PHASE CHEMICAL PROCESSES
- **Chemical Vapor Deposition (CVD)**
  - CVD epitaxy
  - Atmospheric-pressure CVD
  - Low-pressure CVD
  - Metalorganic CVD
  - Photo-enhanced CVD
  - Laser-induced CVD
  - Electron-enhanced CVD

- **Thermal Forming Processes**
  - Thermal oxidation
  - Thermal nitridation
  - Thermal polymerization

### LIQUID-PHASE CHEMICAL TECHNIQUES
- **Electro Processes**
  - Electroplating
  - Electroless plating
  - Electrolytic anodization
  - Chemical reduction plating
  - Chemical displacement plating
  - Electrophoretic deposition

- **Mechanical Techniques**
  - Spray pyrolysis
  - Spray-on techniques
  - Spin-on techniques
The following is a brief description of the principles, salient features, applications, and selected literature references of the more important technologies for thin-film deposition and formation categorized in Table 2.1.

2.2.1. Evaporative Methods

Although one of the oldest techniques used for depositing thin films, thermal evaporation or vacuum evaporation [1,3], is still widely used in the laboratory and in industry for depositing metal and metal alloys. The following sequential basic steps take place: (i) a vapor is generated by boiling or subliming a source material, (ii) the vapor is transported from the source to the substrate, and (iii) the vapor is condensed to a solid film on the substrate surface. Although deceptively simple in principle, the skilled practitioner must be well versed in vacuum physics, material science, mechanical and electrical engineering, as well as in elements of thermodynamics, kinetic theory of gases, surface mobility, and condensation phenomena. Evaporants cover an extraordinary range of varying chemical reactivity and vapor pressures. This variety leads to a large diversity of source components including resistance heated filaments, electron beams, crucibles heated by conduction, radiation, or rf-induction arcs, exploding wires, and lasers. Additional complications include source-container interactions, requirements for high vacuum, precise substrate motion (to ensure uniformity) and the need for process monitoring and control.

MBE [5–13] is a sophisticated, finely controlled method for growing single-crystal epitaxial films in a high vacuum (10^{-11}torr). The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction,
epitaxy, and re-evaporation of excess reactants. The furnaces produce atomic or molecular beams of relatively small diameter, which are directed at the heated substrate, usually silicon or gallium arsenide. Fast shutters are interposed between the sources and the substrates. By controlling these shutters, one can grow super lattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thicknesses, and interfaces down to the level of atomic layers. The most widely studied materials are epitaxial layers of III-V semiconductor compounds, but silicon, metals, silicides, and insulators can also be deposited as single-crystal films by this versatile and uniquely precise method. Complex layer structures and superlattices for fabricating gallium arsenide heterojunction solid-state lasers, discrete microwave devices, optoelectronic devices, waveguides, monolithic integrated optic circuits, and totally new devices, have been created. An additional important advantage of MBE is the low temperature requirement for epitaxy, which for silicon is in the range of 673K to 1073K [12], and for gallium arsenide, 773K to 873K [6]. Several production systems with associated analytic equipment are now available [13]. The extremely limited product throughput, the complex operation, and the expensive equipment are, at present, the major limitations of this promising deposition technology for production applications.

2.2.2. Glow Discharge Technologies

The electrode and gas-phase phenomena in various kinds of glow discharges (especially rf discharges) represent a rich source of processes used to deposit and etch thin films. Creative exploitation of these phenomena has resulted in the development of many useful processes for film deposition (as well as etching), as listed in Table 1.
Sputtering

The most basic and well-known of these processes is sputtering [1-3], the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. From this definition, sputtering is clearly an etching process, and is, in fact, used as such for surface cleaning and for pattern delineation. Since sputtering produces a vapor of electrode material, it is also (and more frequently) used as a method of film deposition similar to evaporative deposition. Sputter deposition has become a generic name for a variety of processes.

Diode Sputtering

Diode sputtering uses a plate of the material to be deposited as the cathode (or rf-powered) electrode (target) in a glow discharge. Material can thus be transported from the target to a substrate to form a film. Films of pure metals or alloys can be deposited when using noble gas discharges (typically Ar) with metal targets.

Reactive Sputtering

Compounds can be synthesized by reactive sputtering, that is, sputtering elemental or alloy targets in reactive gases; alternatively, they can be deposited directly from compound targets.

Bias Sputtering

Bias sputtering or ion-plating [3] is a variant of diode sputtering in which the substrates are ion bombarded during deposition and prior to film deposition to clean them. Ion bombardment during film deposition can produce one or more desirable effects, such as resputtering of loosely-bonded film material, low-energy ion implantation, desorption of gases, conformal coverage of contoured surface, or modification of a large number of film properties. The source material need not originate from a sputtering target, but can be an evaporation source, a reactive gas with
condensable constituents, or a mixture of reactive gases with condensable constituents and other gases that react with the condensed constituents to form compounds. It should be noted that all glow discharge processes involve sputtering in one form or another, since it is impossible to sustain a glow discharge without an electrode at which these processes occur. In “electrodeless” discharges, rf power is capacitively coupled through the insulating wall of a tubular reactor. In this case, the inside wall of the tube is the main electrode of the discharge. However, sputtering can also lead to undesirable artifacts in this and other glow-discharge processes.

**Magnetron Sputtering**

Another variant in sputtering sources uses magnetic fields transverse to the electric fields at sputtering-target surfaces. This class of processes is known as magnetron sputtering [2]. Sputtering with a transverse magnetic field produces several important modifications of the basic processes. Target-generated secondary electrons do not bombard substrates because they are trapped in cycloidal trajectories near the target, and thus do not contribute to increased substrate temperature and radiation damage. This allows the use of substrates that are temperature-sensitive (for example, plastic materials) and surface sensitive (for example, metal-oxides-semiconductor devices) with minimal adverse effects. In addition, this class of sputtering sources produces higher deposition rates than conventional sources and lends itself to economic, large-area industrial application. There are cylindrical, conical, and planar magnetron sources, all with particular advantages and disadvantages for specific applications. As with other forms of sputtering, magnetron sources can be used in a reactive sputtering mode. Alternatively, one can forego the low-temperature and low radiation-damage features and utilize magnetron sources as high-rate sources by operating them in a bias-sputtering mode.
Ion Beam Sputtering

Ion beams, produced in and extracted from glow discharges in a differentially pumped system, are important to scientific investigations of sputtering, and are proving to be useful as practical film-deposition systems for special materials on relatively small substrate areas. There are several advantages of ion-beam sputtering deposition [2]. The target and substrate are situated in a high-vacuum environment rather than in a high-pressure glow discharge. Glow discharge artifacts are thereby avoided, and higher-purity films usually result. Reactive sputtering and bias sputtering with a separate ion gun can be used.

Plasma Processes

The fact that some chemical reactions are accelerated at a given temperature in the presence of energetic reactive-ion bombardment is the basis of processes for surface treatments such as plasma oxidation, plasma nitriding, and plasma carburizing [1,4,14]. A metal to be oxidized, nitrided or carburized is made the cathode of a glow discharge and is simultaneously heated by radiant or rf-induction means. The discharge gas is either O₂, N₂ plus H₂, or CH₄. Very thick (0.1–2 mm) protective coatings on a variety of metals can be produced in this way to render surfaces hard and/or corrosion resistant.

Anodization

Plasma anodization [1,4,2] is a technique for producing thin oxide films (less than 100 nm) on metals such as aluminum, tantalum, titanium, and zirconium, collectively referred as valve metals. In this case, a dc discharge is set up in an oxygen atmosphere and the substrates (shielded from the cathode to avoid sputter deposition) are biased positively with respect to the anode. This bias extracts negative oxygen ions from the discharge to the surface, which is also bombarded with electrons that assist the reaction. The process produces very dense,
defect-free, amorphous oxide films that are of interest as gate material in III-V compound semiconductor devices such as in microwave field-effect transistors etc.

**Plasma polymerization**

Plasma deposition of inorganic films [2,3,14-20] and plasma polymerization of organic reactants to produce films of organic polymers [2] involve the introduction of a volatile reactant into a glow discharge which is usually generated by an rf field. The reactant gases or vapors are decomposed by the glow discharge mainly at surfaces (substrate, electrodes, walls), leaving the desired reaction product as a thin solid film. Plasma deposition is a combination of a glow-discharge process and low-pressure chemical vapor deposition, and can be classified in either category. Since the plasma assists or enhances the chemical vapor deposition reaction, the process is usually denoted as PACVD or PECVD. The possibilities for producing films of various materials and for tailoring their properties by judicious manipulation of reactant gases or vapors and glow-discharge parameters are very extensive. Plasma deposition processes are used widely to produce films at lower substrate temperatures and in more energy-efficient fashion than can be produced by other techniques. For example, they are widely used to form secondary passivation films of silicon nitride on semiconductor devices, and to deposit hydrogenated, amorphous silicon layers for thin-film solar cells.

**Microwave Electron Cyclotron Resonance Deposition**

ECR plasma deposition [21,22] employs an electron cyclotron resonance (ECR) ion source to create a high-density plasma. The plasma is generated by resonance of microwaves and electrons through a microwave discharge across a magnetic field. The main feature of this
recently introduced process is the high rate of deposition obtained at a 
low temperature of deposition.

Cluster Beam Deposition

Ionized cluster beam deposition (ICB) or cluster beam deposition [23-27] is one of the most recent emerging technologies for the deposition of thin films with growth-control capabilities not attainable by other processes. ICB deposition is one of several techniques classified as ion-assisted thin-film formation. The material to be deposited emerges and expands into a vacuum environment from a small nozzle of a heated confinement crucible, usually constructed of high-purity graphite. The vapor pressure within the crucible is several orders of magnitude higher than the pressure of the vacuum chamber so that the expanding vapor super cools. Homogeneous nucleation results in the generation of atomic aggregates or clusters of up to a few thousand atoms held together by weak interatomic forces. The clusters passing through the vacuum towards the substrate can, in part, be positively charged by impact ionization with electron beam irradiation. Closely controlled accelerating voltages add energy to the ionized clusters which then impinge on the substrate, diffuse or migrate along the plane of the surface, and finally form a thin film of exceptional purity. The complete and detailed process is extremely complex but offers unprecedented possibilities of film formation once the fundamentals and engineering technology are fully understood and exploited. Plasma deposition (and plasma etching) processes represent cases in which technology is leading science. The detailed interactions of plasma chemistry, plasma physics, and possible synergistic effects are still largely unexplained. In view of the technological importance of these processes, much more research and process modeling is required to obtain an adequate understanding of these deposition mechanisms.
2.2.3. Gas-Phase Chemical Processes

Methods of film formation by purely chemical processes in the gas or vapor phases include chemical vapor deposition and thermal oxidation. Chemical vapor deposition (CVD)\cite{1-4,16,28-32} is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. The deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of materials essential to advanced technology, particularly solid-state electronics where some of the most sophisticated purity and composition requirements must be met. The main feature of CVD is its versatility for synthesizing both simple and complex compounds with relative ease at generally low temperatures. Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition conditions. Fundamental principles of CVD encompass an interdisciplinary range of gas-phase reaction chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena, and reactor engineering. Chemical reaction types basic to CVD include pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation. A sequence of several reaction types may be involved in more complex situations to create a particular end product. Deposition variables such as temperature, pressure, input concentrations, gas flow rates and reactor geometry and operating principle determine the deposition rate and the properties of the film deposit. Most CVD processes are chosen to be heterogeneous reactions. That is, they take place at the substrate surface rather than in the gas phase. Undesirable homogeneous reactions in the gas phase nucleate particles that may form powdery deposits and lead to particle contamination instead of clean and uniform coatings. The reaction feasibility (other than reaction rate) of a CVD process under specified conditions can be predicted by thermodynamic
calculation provided reliable thermodynamic data (especially the free energy of formation) are available. Kinetics controls the rate of reactions and depends on temperature and factors such as substrate orientation. Considerations relating to heat, mass, and momentum transport phenomena are especially important in designing CVD reactors of maximum efficiency. Since important physical properties of a given film material are critically influenced by the structure (such as crystallinity), control of the factors governing the nucleation and structure of a growing film is necessary. Thin-film materials that can be prepared by CVD cover a tremendous range of elements and compounds. Inorganic, organometallic, and organic reactants are used as starting materials. Gases are preferred because they can be readily metered and distributed to the reactor. Liquid and solid reactants must be vaporized without decomposition at suitable temperatures and transported with a carrier gas through heated tubes to the reaction chamber, which complicates processing, especially in the case of reduced-pressure systems. Materials deposited at low temperatures (e.g., below 600°C for silicon) are generally amorphous. Higher temperatures tend to lead to polycrystalline phases. Very high temperatures (typically 1173K to 1373K in the case of silicon) are necessary for growing single crystal films. These films are oriented according to the structure of the substrate crystal, this phenomenon, known as epitaxy, is of crucial practical importance in solid-state device technology. CVD has become an important process technology in several industrial fields. As noted, applications in solid-state microelectronics are of prime importance. Thin CVD films of insulators, dielectrics (oxides, silicates, nitrides), elemental and compound semiconductors (silicon, gallium arsenide, etc.), and conductors (tungsten, molybdenum, aluminum, refractory metal silicides) are extensively utilized in the fabrication of solid-state devices. Hard and wear-resistant coatings of materials such as boron, diamond-like carbon, borides, carbides and nitrides have found important applications in tool technology. Corrosion
resistant coatings, especially oxides and nitrides, are used for metal protection in metallurgical applications. Numerous other types of materials, including vitreous graphite and refractory metals, have been deposited mainly in bulk form or as thick coatings. Many of these CVD reactions have long been used for coating of substrates at reduced pressure, often at high temperatures.

**Reactors**

The reactor system (comprising the reaction chamber and all associated equipment) for carrying out CVD processes must provide several basic functions common to all types of systems. It must allow transport of the reactant and diluents gases to the reaction site, provide activation energy to the reactants (heat, radiation, plasma), maintain a specific system pressure and temperature, allow the chemical processes for film deposition to proceed optimally, and remove the by-product gases and vapors. These functions must be implemented with adequate control, maximal effectiveness, and complete safety. The most sophisticated CVD reactors are those used for the deposition of electronic materials. Low-temperature (below 873K) production reactors for normal- or atmospheric-pressure CVD (APCVD) include rotary vertical-flow reactors and continuous, in-line conveyorized reactors with various gas distribution features. They are used primarily for depositing oxides and binary and ternary silicate glass coatings for solid-state devices. Reactors for mid-temperature (873K to 1173K) and high-temperature (1173K to 1573K) operation are either hot-wall or cold-wall types constructed of fused quartz. Hot-wall reactors, usually tubular in shape, are used for exothermic processes where the high wall temperature avoids deposition on the reactor walls. They have been used for synthesizing complex layer structures of compound semiconductors for microelectronic devices. Cold-wall reactors, usually bell-jar shaped, are used for endothermic processes, such as the deposition of silicon from the halides or the
Hydrides. Heating is accomplished by rf induction or by high-intensity radiation lamps. Substrate susceptors of silicon carbide-coated graphite slabs are used for rf-heated systems. Reactors operating at low pressure (typically 0.1–10 torr) for low pressure CVD (LPCVD) in the low, mid, or high-temperature ranges are resistance-heated hot-wall reactors of tubular, bell-jar, or close-spaced design. In the horizontal tubular design, the substrate slices (silicon device wafers) stand up in a carrier sled and gas flow is horizontal. The reduced operating pressure increases the mean free path of the reactant molecules, which allows a closely spaced wafer stacking. The very high packing density achieved (typically 100 to 200 wafers per tube) allows a greatly increased throughput, hence substantially lower product cost. In the vertical bell-jar design, the gas is distributed over the stand-up wafers, hence there is much less gas depletion and generation of few particles, but the wafer load is smaller (50 to 100 wafers per chamber). Finally, the closespaced design developed most recently processes each wafer in its own separate, closed space chamber with the gas flowing across the wafer surface to achieve maximal uniformity. In LPCVD, no carrier gases are required, particle contamination is reduced and film uniformity and conformality are better than in conventional APCVD reactor systems. It is for these reasons that low-pressure CVD is widely used in the highly cost-competitive semiconductor industry for depositing films of insulators, amorphous and polycrystalline silicon, refractory metals, and silicides. Epitaxial growth of silicon at reduced pressure minimizes auto doping (contamination of the substrate by its dopant), a major problem in atmospheric-pressure epitaxy.

Vapor Phase Epitaxy

Vapor-phase epitaxy (VPE)[1,2,4,30-32] and metal-organic chemical vapor deposition (MOCVD)[1,2,4,30-32] are used for growing epitaxial films of compound semiconductors in the fabrication of
optoelectronic devices. Composite layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

- **Photo Enhanced Chemical Vapor Deposition (PHCVD)**

PHCVD [33-35] is based on activation of the reactants in the gas or vapor phase by electromagnetic radiation, usually short-wave ultraviolet radiation. Selective absorption of photonic energy by the reactant molecules or atoms initiate the process by forming reactive free-radical species that then interact to form a desired film product. Mercury vapor is usually added to the reactant gas mixture as a photosensitizer that can be activated with the radiation from a high-intensity quartz mercury resonance lamp (253.7 nm wavelength). The excited mercury atoms transfer their energy kinetically by collision with the reactants to generate free radicals. The advantages of this versatile and very promising CVD process is the low temperature (typically 523K) needed to form films such as SiO_2 and Si_3N_4, and the greatly minimized radiation damage (compared to PECVD). The limitations at present are the unavailability of effective production equipment and the need (in most cases) for photoactivation with mercury to achieve acceptable rates of film deposition.

- **Laser Induced Chemical Vapor Deposition (LCVD)**

LCVD [36-38] utilizes a laser beam for highly localized heating of the substrate that then induces film deposition by CVD surface reactions. Another mode of utilizing laser (or electron radiation) is to activate gaseous reactant atoms or molecules by their absorption of the specific wavelength of the photonic energy supplied. The resulting chemical gas phase reactions are very specific, leading to highly pure film deposits. On the other hand, the activation matching of the spectral properties with the reactant species limits the choice of reactions and
hence the film deposits that can be obtained. LCVD is still in its early development stages but promises many interesting and useful applications in the future.

† **Ion Implantation**

Recently, ion implantation[4,39-40] has been used to form silicon-on-insulator structures by implanting large doses of atomic or molecular oxygen ions in single-crystal silicon substrates to produce a buried oxide layer with sharp interfaces after annealing [39]. Simultaneous high-dose implantation of low energy oxygen and nitrogen ions into silicon yields very thin films of silicon oxynitride, whereas low-energy implantation of nitrogen or ammonia into silicon yields a low-density silicon nitride layer.[41]

† **Thermal Oxidation**

In the gas phase, thermal oxidation [4,14,42,43] is a chemical thin-film forming process in which the substrate itself provides the source for the metal or semiconductor constituent of the oxide. This technique is obviously much more limited than CVD, but has extremely important applications in silicon device technology where very high purity oxide films with a high quality Si/SiO₂ interface are required. Thermal oxidation of silicon surfaces produces glassy films of SiO₂ for protecting highly sensitive p-n junctions and for creating dielectric layers for MOS devices. Temperatures for this process lie in the range of about 973K to 1473K with either dry or moist oxygen or water vapor (steam) as the oxidant. Steam oxidation proceeds at a much faster rate than dry oxidation. The oxidation rate is a function of the oxidant partial pressure and is controlled essentially by the rate of oxidant diffusion through the growing SiO₂ layer to the SiO₂/Si interface, resulting in a decrease of the growth rate with increased oxide thickness. The process is frequently conducted in the presence of hydrochloric acid vapor or vapors of
chlorine-containing organic compounds. The HCl vapor formed acts as an effective impurity getter, improving the Si/SiO₂ interface properties and stability. Silicon oxidation under high pressure [1,42,43] is of technological interest where the temperature must be minimized, such as for VLSI devices. Since the oxidation rate of silicon is approximately proportional to pressure, higher product throughput and/or decreased temperatures can be attained. The oxidant in commercial systems is H₂O, which is generated pyrogenically from H₂ and O₂. Pressures up to 10 atm are usually used at temperatures ranging from 1123K to 1323K.

**Other Gas Phase Oxidations**

Gas-phase oxidation of other materials [1] is of limited technical importance. Examples include metallic tantalum films converted by thermal oxidation to tantalum pentoxide for use as antireflection coating in photovoltaic devices and as capacitor elements in microcircuits. Other metal oxides grown thermally have also been used as capacitor dielectrics in thin-film devices, to improve the bonding with glass in glass-to-metal seals and to improve corrosion resistance.

**2.2.4. Liquid-Phase Chemical Formation**

The growth of inorganic thin films from liquid phases by chemical reactions is accomplished primarily by electrochemical processes (which include anodization and electroplating), and by chemical deposition processes (which include reduction plating, electroless plating, conversion coating, and displacement deposition). A number of extensive reviews [1-3] of these film formation processes discuss theory and practice. Another class of film forming methods from the liquid phase is based on chemically reacting films that have been deposited by mechanical techniques [1,3]. Finally, liquid phase epitaxy [4] is still being used for growing a number of single-crystal semiconductors.
Electrolytic Anodization

In anodization, as in thermal oxidation, an oxide film is formed from the substrate. The anode reacts with negative ions from the electrolyte in solution and becomes oxidized, forming an oxide or a hydrated oxide coating on semiconductors and on a few specific metals, while hydrogen gas is evolved at the cathode. Nonporous and welladhering oxides can be formed on aluminum, tantalum, niobium, titanium, zirconium, and silicon. The most important applications are corrosionprotective films and decorative coatings with dyes on aluminum and its alloys, and layers for electrical insulation for electrolyte capacitors on aluminum and tantalum.

Electroplating

In electroplating a metallic coating is electrodeposited 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, the 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 coatings (electroforming).

Chemical Reduction Plating

Chemical reduction plating is based on reduction of a metal ion in solution by a reducing agent added just before use. Reaction is
homogeneous, meaning that deposition takes place everywhere in the solution, rather than on the substrate only. Silver, copper, nickel, gold, and some sulfide films are readily plated. The oldest application of the process is the silvering of glass and plastics for producing mirrors using silver nitrate solutions and one of various reducing agents, such as hydrazine.

Electroless Plating

Autocatalytic or electroless plating is a selective deposition plating process in which metal ions are reduced to a metallic coating by a reducing agent in solution. Plating takes place only on suitable catalytic surfaces, which include substrates of the same metal being plated, hence the definition autocatalysis. Electroless (or electrodeless) plating offers a number of advantages over electroplating, such as selective (patterned) deposition, but is limited to a few metals and some alloys. Nickel, nickel alloys, and copper are most widely used commercially on conductive and on sensitized insulating substrates, including plastic polymeric materials.

Electrophoretic Deposition

Electrophoretic coating is based on deposition of a film from a dispersion of colloidal particles onto a conductive substrate. The dispersion in a conductive liquid dissociates into negatively charged colloidal particles and positive ions (cations), or the reverse. On application of an electric field between the positive substrate electrode (anode), the colloidal particles migrate to the substrate, become discharged, and form a film. Chemical or electrochemical treatments of a metal surface can produce a thin and adherent layer on that metal. Examples of such conversion coatings are black oxides on steel, copper, and aluminum. Widely used chromate conversion coatings on zinc, cadmium, silver, copper, brass, aluminum, and magnesium are formed.
by reaction of hexavalent chromium ions with the metal, forming protective and decorative films that consist of oxides, chromates, and the substrate metal. Phosphate conversion coatings result from treatments, especially of iron and steel, with phosphoric acid-containing salts of iron, zinc, or manganese.

**Immersion Plating**

Deposition of a metal film from a dissolved salt of the coating metal on a substrate by chemical displacement without external electrodes is known as displacement deposition or immersion plating. Generally, a less noble (more electronegative) metal displaces from solution any metal that is more noble, according to the electromotive force series. Actually, different localized regions on the metal surface become anodic and cathodic, resulting in thicker films in the cathodic areas. The industrial uses of this process are limited to a few applications, mainly thin coatings on copper and its alloys.

**Mechanical Methods**

Mechanical techniques for depositing coatings from liquid media that are subsequently reacted chemically to form the inorganic thin film product are spraying, spinning, dipping and draining, flow coating, roller coating, pressure-curtain coating, brushing, and offset printing of reagent solutions. Chemical reaction of the coating residue, often by thermal oxidation, hydrolysis, or pyrolysis (in the case of metal organics) produces the desired solid film. Spin-on deposition of film-forming solutions is widely used in solid-state technology. Liquid spray coating is probably 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 liquid. An example of the capability of this refined method is the mass production spray-on deposition of organometallic alkoxy compounds, such as titanium(IV) isopropoxide, in an optimally formulated spray solution. Controlled pyrolysis of the deposit can form TiO$_2$ films of 70 nm thickness which serves as a highly effective and low-cost antireflection coating for silicon solar cells. It should be noted that spray deposition encompasses several other types of spraying processes that are based on either liquid sources, such as harmonic electrical spraying, or on dry source reactants that include flame spraying, arc plasma spraying, electric arc spraying, and detonation coating.

### 2.3 Choice Of Deposition Technique

Thin solid films can be prepared by a variety of techniques as discussed in section 2.2. Several of these techniques permit automatic monitoring and control of the deposition and hence of the thickness. Since the properties of thin films depends on various parameters and technique used, the choice of the technique also assumes significance.

The deposition technique can be chosen depending upon the type of material and its intended use for various applications (which is actually decided by various parameters characterizing the material). The important material parameters e.g. density, melting point, boiling point, vapor pressure etc. are generally used to select the appropriate deposition technique. Besides, the nature of the material (whether metallic or semiconducting or insulating) can also focus some light on the steps involved in the complete deposition process. Generally, it has been seen that the spin coating deposition technique is the simplest and economical convenient technique for deposition of semiconducting thin films.
Various thin film deposition techniques, especially for the deposition of Nanocrystalline Tin Selenide (SnSe), used by several research workers. It has been reported that Nanocrystalline SnSe thin film can be prepared by various techniques i.e. chemical bath deposition, electro deposition, ALD synthesis, chemical route synthesis etc. [44 – 54].

However, from the literature survey it appears that there are only few reports the preparation of Nanocrystalline SnSe thin films by spin coating technique. It is well known that the structural and optical parameters of the deposited thin films are very much dependent on method for deposition. Various deposition parameters are easier to maintain and control in case of spin coating technique in comparison with other techniques. This simplicity makes this technique more common and attractive for thin film deposition as well as device preparation. Hence, in present investigations, efforts have been made to deposit Nanocrystalline SnSe compound semiconductor thin film using spin coating techniques. Complete description for preparation of Nanocrystalline SnSe thin film by sing spin coating technique is describe in next section.

2.3.1 Spin Coating

Spin coating is a process for applying uniform coatings to wide variety of substrates. The formation of a thin, uniform layer of semi liquid on flat rotating substrates by centrifugal force is widely known as the spin coating technique. This technique is widely used in the electronic industry to produce thin coating of polymeric photoresists for photolithography, sol-gel films for dielectric applications, planar structures for different optical applications etc. Figure 2.1 shows the spin coating process and fluid flow during spin coating. Here basic spin coating process is discussed below and physics of spin coating method is also discussed.
The equipment used here consists of a Headway spin coater that was placed in the glass jar envelop. The substrate can be placed on a horizontal chuck with grooves. This ensures the substrate to stay in a stable position during the process. The equipment allows setting the final spin speed and time as well as the spin acceleration. However, no programming is possible to include additional steps in the procedure. The applied coating procedure can then eventually be divided in four major steps: deposition of the solution, a spin-up stage to fully spread the fluid over the surface followed by the actual film formation during the spin-off phase and the complete evaporation of the solvent. The deposition of the coating solution onto the substrate is the first stage. Basically a substantial excess of material compared to what remains in the final film is required. At this moment, the substrate is not yet rotating and the solution is dispensed to spread all over the surface. This prevents incomplete coverage of the coating area by solution rolling over the substrate without wetting it. As mentioned before, the dispensing itself has no substantial influence on the final film thickness or quality. Nevertheless, one has to take into account that during this stage the evaporation of the solvent already starts. Skin formation in the early stage may keep this effect limited to a small boundary layer not influencing the bulk of the liquid. However, care has to be taken to spend not too much time on this process step.

The second stage (spin-up) is when the rotation of the substrate starts and accelerates up to its intended constant rotational speed. It has been shown that this spin acceleration also has very little effect on the final film formation. Therefore, it was concluded to take acceleration speeds always high enough to restrict this phase to less than 1 s. During this cycle, while the spinning speed is still low, the solution spreads at first further over the substrate. However, due to the growing centrifugal force, excess solution flings off the substrate.
Then the third and probably most influential stage is reached: spin-off. The substrate rotates at constant speed and a gradual thinning occurs because the fluid flows uniformly outward and off the substrate. It has to be remarked that maybe even over 90% of the initially suspended solution flings off the substrate during the spin-up and spin-off phases of the coating process. As mentioned before, no programming of the equipment is possible. This means that no deceleration of the spin speed is foreseen during or after this phase and the rotation remains constant from now on. Typically rotation speeds are in the order of 150 to 2500 rotations per minute (rpm). Edge effects may be seen due to droplet formation at the edges before the fluid is being flung off. Here, a balance between centrifugal and viscous forces controls the fluid thinning behavior.

The fourth and final stage starts when the solvent evaporation begins to dominate the coating thinning behavior. The radial outflow ceases because of increased solution viscosity and the film densities by further evaporation of the solvent. No clear distinction between the third and fourth phase can be made, since the rotation remains at constant speed during both stages. Another way to make distinction between the two phases would be to influence the evaporation rate. Placing a cover over the substrate during spinning can slow the evaporation down due to saturation of the surrounding atmosphere with the solvent gas such that flow behavior remains dominant (third stage). Removing the cover and even applying additional fume exhaust would then favour fluid thinning due to increased solvent evaporation (fourth stage).
The final film thickness depends on viscosity, drying rate, percentage of solids, surface tension and other factors. Emslie, Bonner and Peck [55] developed an analytical model for the formation of a uniform layer for a Newtonian fluid. They showed that the final thickness is independent of the liquid profile at the beginning of rotation. The thickness decreases continuously with time as material is spun away. The evaporation rate of the solvent plays an important role in uniformity of the final coating. Emslie, Bonner and Peck [55] in their paper illustrated the hydrodynamics of the spin coating process. The hydrodynamics are governed by the following two equations:

(i) Conservation of mass:
\[
\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial (r \nu)}{\partial r} \tag{2.1}
\]

(ii) Momentum equation (force balance i.e. during the spinning process the viscous force is balanced by the centrifugal force):
\[
-\eta \frac{\partial^2 \nu}{\partial z^2} = \rho \omega r^2 \tag{2.2}
\]

where, \( \eta \) is the viscosity, \( \nu \) is the radial velocity component, \( z \) is axial coordinate, \( q \) is the flow rate , \( h \) is the fluid height, \( \rho \) is the density, \( \omega \) is the angular speed and \( r \) is the radius.

The following assumptions were made to derive the momentum equation:

- The rotating plane is infinite in extent.
The plane is horizontal, so that there is no radial gravitational component.

The liquid layer is radially symmetric and so thin that differences in gravitational potential normal to the surface of the disk have negligible effect in distributing the liquid compared with the effect of centrifugal forces.

The viscosity is independent of the rate of shear, i.e, the liquid is Newtonian.

The liquid layer is everywhere so thin that shear resistance is appreciable only in horizontal plane.

The radial velocity is everywhere so small that Coriolis forces may be neglected.

By integrating Equation (2.2) with two boundary conditions, first, the no slip condition of the fluid at the substrate i.e, $v = 0$ at $z = 0$; second is the shearing force is zero at the free surface i.e, $\partial v / \partial z = 0$ at $z = h$.

Emslie, Bonner and Peck [55] also determined the total fluid thinning rate and derived a function for the fluid depth with time. The average thinning rate was found to be

$$\frac{dh}{dt} = -2 \frac{\rho \omega^2}{3 \eta} h^3$$  \hspace{1cm} 2.3

Meyerhofer [56] investigated the effect of solvent evaporation on the film thickness. He modified the thinning rate equation by adding another term for thinning due to evaporation with the existing shear thinning term. This modified equation is stated below with evaporation rate $e$.

$$\frac{dh}{dt} = -2 \frac{\rho \omega^2}{3 \eta} h^3 - e$$  \hspace{1cm} 2.4

Meyerhofer [56] assumed that the early stages of spin coating were entirely flow dominated, and later stages would be entirely evaporation dominated. This leads to the transition point at the condition where the
evaporation rate and the viscous flow rate became equal. He also noted that the modified thinning rate equation leads to a cross over from viscous flow controlled thinning at early stages of the process to evaporative controlled thinning near the end. He showed that the evaporation rate depends on vapor diffusion through the aerodynamic boundary layer above the substrate surface. In his model, the film thickness was evaluated for certain value of solvent evaporation rate and a specific relation between concentration and viscosity was considered. He expressed the film thickness as a function of spin speed, initial viscosity and evaporation rate. The two factors governing the modified thinning rate equation are the flow constant $K$ and the evaporation rate $e$. The flow constant, $K$ represents the combined effect of viscosity and spin speed. $K$ is defined as

$$k = \frac{\rho \omega^2}{3\eta}$$

where, $\rho$ is the fluid density, $\omega$ is the angular speed and $\eta$ is the viscosity.

The evaporation rate $e$ depends on rotation rate according to the following relation,

$$e = C \omega^{1/2}$$

where, $C$ is the proportionality constant and depends on the specific experimental conditions.

Birnie III and Manley [57] showed the contribution of fluid flow and fluid evaporation to the total rate of thinning during spinning of a fluid on a silicon wafer. They applied laser interferometry to measure the shear flow and evaporation rate of fluid on the spinning substrate. They found that the flow behavior is consistent with the hydrodynamic equations given by Emslie, Bonner and Peck. They also show that Meyerhofer’s modification to the Emslie, Bonner and Peck equation is required to account for evaporating fluids. One key aspect of spin coating
is the shear forces that are experienced by the fluid before solvent evaporation takes over and freezes in a final particle arrangement. Grasher and BirnieIII [58] found that a small fraction of fluid that starts near the center of the wafer delivers the bulk of the final coating while the majority of the fluid is flung off. They developed a set of equations for calculating shear rate with respect to the radial and axial directions. They expressed the flow rate and the velocity component with respect to $r$ and $z$ as:

$$q = \int_0^z v_r \cdot dz = k \left( -0.5rz^3 + 1.5rz^2 h \right)$$  \hspace{1cm} (2.7)

$$v_r = \frac{\partial r}{\partial t} = 3krz (h - 0.5z)$$  \hspace{1cm} (2.8)

$$v_z = \frac{\partial z}{\partial t} = kze^2 (z - 3h)$$  \hspace{1cm} (2.9)

where $q$ is flow rate, $z$ is the height within fluid as it flows, $r$ is the radial position of a particle.

Film thickness $h$ as stated in Equation (2.7) through (2.9) can be expressed as the following equation:

$$h = \frac{h_0}{\sqrt{1 + 4kh_0^2 t}}$$  \hspace{1cm} (2.10)

where, $h_0$ is film thickness at time zero and shows variation of fluid height with time. Equations (2.8) and (2.9) give the radial and axial velocities of a volume element respectively, that can be determined from the position, height of the fluid and process constant. Alignment of the particles in the final coating can be advantageous for various optical, electrical and magnetic applications.
**Preparation of Nanocrystalline Tin selenide (p-SnSe) Thin Film**

Semiconducting Nanocrystalline thin films of tin selenide were deposited onto glass substrates with dimensions of a standard microscope glass. In order to improve the adhesion i.e. to ensure the highest possible quality of the deposited films which is of essential importance for further investigation of their properties, the substrates were subjected to pre deposition treatment. It consisted of cleaning of glass substrates by detergents to remove contaminants and after that the substrates were ultrasonically cleaned in acetone. Finally cleaned substrates were placed in oven at 573K for 2h.

In our present research work we deposited thin films of SnSe from the solutions prepared with the help of various chemical routes by spin coating method as discussed below.

(1) **In Aqueous Ethylenediamine:** A total of 1.4gm of SnCl₂.2H₂O and 0.24gm of selenium were added to 50mL of aqueous ethylenediamine solution. As a result precipitation of SnSe formed in solution. these Obtained precipitations were filtered and further they have been used to deposite SnSe thin films on to glass slide by spin coating technique at 500 rpm. [59]

(2) **In Hydrazine Hydrate:** Addition of 0.7gm of SnCl₂.2H₂O to 50mL of hydrazine formed a light yellow precipitate. Then 0.24gm of selenium was added. A heat treatment was applied. After heat treatment, the obtained products were filtered and then used to deposite SnSe thin films on to glass slide by spin coating technique at 500 rpm. [59]

(3) **In Tartaric Acid:** The selenium alkaline aqueous solution was prepared as follows: 0.56 mol of NaOH and 2gm of elemental Se were added to 50 ml of distilled water. The mixture reached about 700K in a few minutes because the dissolution of NaOH in water is an exothermic
process and the produced heat enhance the dissolution of elemental Se. 0.0026 mol of SnCl₂·2H₂O was added to 5ml of distilled water with 3gm of tartaric acid and then the mixture was combined with the selenium alkaline aqueous solution through rapid stirring. A black precipitate occurred and then further used to deposite SnSe thin films by spin coating at 500rpm [60].

The SnSe thin films prepared by all above mentioned methods yielded in to poor quality of deposit having less adhesive to the substrate. Various parameters of film preparation such as rpm, pre and post heat treatment were also resulted in to the films which were bucked or with numerous cracks etc. It is found by R & D efforts that SnSe thin films prepared by a method described below resulted in to a good adhesion with the substrate and hence later on the same has been used for further study.

Tin salt (SnCl₂·2H₂O), gray selenium powder (Se), ammonia buffer (pH=11), and sodium sulfite (Na₂S₉O₃) were used in our experiments. All chemicals were purchased from ALFA AESAR Company having 99.99% purity. Our thin films deposition process divided in to four steps as discussed below.

1. In the first step SnCl₂·2H₂O was dissolved in double distil water and ammonia buffer is added drop wise to obtain an alkaline media of pH 11.
2. Sodium selenosulfate, which was used as a source of selenide ions for the purpose of this study, is commercially unavailable substance because it is relative instable, especially upon exposure to light and it has to be freshly prepared prior to the thin film deposition process. Hence in second step we prepared the solution of sodium selenosulfate by adding gray selenium to a hot solution of sodium sulfite. The resulting
heterogeneous solution was stirred for 10h at 373K by magnetic stirrer and afterwards the excess of gray selenium was filtered. The preparation of sodium selenosulfate solution is based on the following redox process.

\[ \text{Se}_\text{(S)} + \text{Na}_2\text{SeO}_3(aq) \rightarrow \text{Na}_2\text{SeS}_\text{(aq)} \]

3. In the third step prepared solution of Sodium selenosulfate and solution of SnCl₂·2H₂O were mixed as results precipitation of Nanocrystalline SnSe formed in mixed solution based on following reaction.

The chemical deposition of tin selenide films described in this thesis was based on two important properties of selenosulphate. One is its complexing ability, much like the well known complexing ability of thiosulphate. Tin selenosulphate complexes are formed in excess of selenosulphate. The other one is the ability of selenosulphate to gradually release selenide ions upon hydrolytic decomposition, in alkaline media, as follows.

\[ \text{SeSO}_\text{3}^- + \text{OH}^- \rightarrow \text{HSe^-} + \text{SO}_\text{4}^2^- \]

\[ \text{HSe^-} + \text{OH}^- \rightarrow \text{Se}^2^- + \text{H}_2\text{O} \]

The released selenide ions then combine with the tin ions released from the tin selenosulphate complexes, upon hydrolysis, precipitating of Nano crystalline SnSe.

\[ \text{Sn}^{+2} + \text{Se}^{-2} \rightarrow \text{SnSe} \]

4. In the fourth step these obtain precipitation were filtered and deposited on to glass substrates by spin coating unit as discussed in section 2.3.1 at 500 rpm to get SnSe thin films.
The deposited films were tested for adhesion by subjecting it to a steady stream of distilled water.

In this investigation Nanocrystalline p-SnSe thin films have been grown with different thickness and different annealing temperature. Prepared thin films are listed below

1. Nano crystalline p-SnSe thin film having 1µm thickness,
2. 2µm thickness,
3. 3µm thickness,
4. 4µm thickness.
5. We perform annealing of the above thin film having 1µm thickness at 373K for 1h in open atmosphere (AA 373K) and labeled as AA 373K in entire thesis.
6. We perform annealing of the above thin film having 1µm thickness at 523K for 1h in open atmosphere (AA 423K) and labeled as AA 423K in entire thesis.

In this thesis the effect of above variation on to the Structural, optical and electrical properties of prepared thin films have been discussed. In addition to this we prepared p-SnSe/n-MoSe₂ Hetrojunction diode and study the effect of above variation on to the diode parameter.

2.4 Energy Dispersive Analysis of X-Rays (EDAX)

As growth of Nanocrystalline p-SnSe thin films depends on various growth conditions, it is essential to know about the chemical content of the grown thin films. For device applications of these thin films their chemical content is an important parameter to look for its influence on electrical properties such as resistivity, carrier concentration etc. on the deposited thin films. Energy Dispersive Analysis of X-ray (EDAX), a most suitable technique for this purpose is
employed in the present work and hence it is discussed in brief along with the analysis and conclusions of investigations made for the material in thin form used in the present thesis.

Energy Dispersive Analysis of X-ray spectroscopy (EDAX) is a chemical analysis technique used in conjunction with scanning electron microscopy (SEM). The EDAX technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. This technique generates a spectrum in which the peaks correspond to specific X-ray lines and the elements can be easily identified. Quantitative data can also be obtained by comparing peak heights or areas in the unknown with a standard material. Data collection and analysis with EDAX is a relatively quick and simple process because the complete spectrum of energies is acquired simultaneously.

The essential feature of analysis is the localized excitation of a small area at the sample surface by a finely focused electron beam, or probe giving a resolution of about 1 µm. The energy of the beam is typically in the range 10-20 keV. This causes X-ray to be emitted from the point of the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region of about 2 microns in depth. By moving the electron beam across the material an image of each element in the sample can be acquired. In principle, the concentration of an element could be determined by comparison of the intensity of a particular characteristic line from the sample to that of a known standard, usually the pure element, under identical experimental conditions. Analysis at a point could be carried out, or the specimen could be moved continuously in one direction while the X-ray output is recorded to give the distribution of the element.
Figure 2.2 shows an experimental arrangement of EDAX attached to a SEM (Model: JSM-5610LV Make: JEOL, Japan) used in experiment study. Table 2.1 shows some feature of EDAX. An EDAX system comprises four basic components that must be designed to work together to achieve optimum results: the beam source, the X-ray detector, the pulse processor and the analyzer. X-ray detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium-drifted silicon, a solid state surface barrier device. When an incident X-ray strikes the detector, it creates a charge pulse that is proportional to the energy of X-ray. The charge pulse is converted to a voltage pulse (which remains proportional to the X-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The energy, as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.

Elements of low atomic number are difficult to detect by EDAX. The Si(Li) detector is often protected by a Beryllium window. The absorption of the soft X-rays by the Be preclude the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced [61, 62].
Figure 2.2: Experimental set up of Energy Dispersive analysis of X-rays (EDAX).

Table 2.2: Some features of EDAX used in our experiment.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>3.0 nm in HV., 4.5 nm in LV.</td>
</tr>
<tr>
<td>Magnification</td>
<td>18 X to 3 X 105 X</td>
</tr>
<tr>
<td>Modes of Image</td>
<td>(a) Secondary electron Image</td>
</tr>
<tr>
<td></td>
<td>(b) Back Scattered electron Image, TOPO, COMPO and SHADOW</td>
</tr>
</tbody>
</table>

2.4.1 Results and Discussion

Figure 2.3 shows EDAX spectra of the deposited Nanocrystalline p-SnSe thin films. The weight percentage of the constituent elements obtained from the EDAX of grown thin films is shown in Table 2.3.
Figure 2.3: EDAX spectra of p-SnSe thin films grown by spin coating method.
Table 2.3: Chemical composition (wt. %) of p-SnSe thin films grown by spin coating method.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wt % of elements obtain from EDAX</th>
<th>Wt % of elements Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1µm  2µm  3µm  4µm  1µm AA 373K 1µm AA 423K</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>59.45  59.47  59.44  59.40  59.42  59.41  60.05</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>40.55  40.53  40.56  40.60  40.58  40.59  39.95</td>
<td></td>
</tr>
</tbody>
</table>

From the above figure it is observed that our deposited thin films contain only Sn and Se without any major impurities. From the above table it is also seen that all deposited thin films are nearly stoichiometry in nature.

2.5 Conclusion

From the above discussion on thin film deposition technique and EDAX analysis following conclusion carried out.

- ✔ With the help of Spin Coating technique we successfully deposited Nano crystalline p-SnSe thin film.
- ✔ From the EDAX analysis it is concluded that we successfully deposited impurity free thin films.
- ✔ It is also conclude from EDAX analysis that we obtain good stoichiometry thin films.
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