CHAPTER
I

CHAPTER 1
INTRODUCTION

1.1 General

THIN FILMS of the noble metals have been used for decorative glasses and ceramics for over thousand years /1/. As early as seventh century, it was known how to paint a suspension of a silver salt on to a glass medicine vial and then heat it to convert the salt to metallic silver. Another very old method of forming thin films is the beating of gold to form "gold leaf". The thinnest films made this way are about four or five millionths of an inch thick. Too much stress applied to this gold leaf leads to rupture, thus imposing a limitation on its thinness. Thickness of the films is usually discussed in terms of angstrom units (A°) and is of the same order of magnitude as the dimension of a single atom /1/.

Now a days, these films have been used in the study of relationship between the structure of solids and their physical properties. Practical applications include electrical and electronic circuits, optical instruments and magnetic information storage devices. These ultramodern films are formed by depositing the materials onto the clean support termed the "substrate" to build up film thickness rather than by thinning down the bulk material. Thin films for electronic circuit applications range from a few hundred angstroms to tens of thousand angstroms in thickness. A typical film might be 1000 A° thick while the glass substrate supporting it would be 10000 times thick /1/. Films vary in structure from amorphous films such as anodic oxide dielectrics to single crystal films such as epitaxially grown silicon. Most of the films fall between these extremes and are polycrystalline, composed of many small crystals called "crystallites or grains", fitted together with more or less random orientation. For very thin films, size of the crystallites is

observed to be a function of thickness, however, for thicker films, it is usually independent of thickness /1/. Sizes range from 50 A^{0} to 2000 A^{0}. Crystallite size also depends on the deposition conditions such as substrate temperature, deposition rate and may be altered by annealing after deposition with the larger crystallites growing at the expense of the smaller ones /1/.

1.2 The Thin Film Technologies

The major role of thin film technology in the development of diverse and challenging frontiers as microelectronics, optical coatings and integrated optics, thin film superconductivity and quantum engineering, micromagnetism, metallurgical coatings and amorphous materials, surface engineering and solar energy conversion devices is all too well known and is now recognized as the frontier area of microscience and microtechonology /1,2/. New and even more exciting fields are also emerging. The origin of such new frontiers lies in the exciting phenomena of microscience associated with low dimensional micro and nanomaterials and the industrial applications of microscience and microtechonology in VLSI / GSI communication, informatics and solar energy conversion. With decreasing size of the active electronic devices, a higher packing density, higher speed performance and lower costs are obtained. Ultra thin films are 2-dimensional micromaterials which are obtained by one of the established techniques falling under the headings such as physical vapour deposition (PVD), chemical vapour deposition (CVD), electrochemical deposition (ECD) or a hybrid thereof. The films can be further cut into desired dimension and geometry by one or more microlithographic techniques. By tailored e-

beam resists, materials and devices of 0.1 to 0.2 μm or even less are easily obtained today.

The tailoring of materials properties arise basically from the numerous inherent characteristics of nucleation and growth of the thin films and the occurance of the new physical phenomena. The creation of the matter in a deposition process involves desorption and migration of adatoms and interaction of these adatoms to reach a critical nucleation stage, lateral and perpendicular growth of the nuclei, sintering and recrystallization. These processes take place under high supersaturation, rapid thermalisation and nonequilibrium thermodynamic conditions. By varying the deposition parameters one can manipulate one or more of these processes to obtain a whole range of structural disorder, microstructure, topographic and geometrical features, growth anisotropies and line defects and compositional profiles.

The enormous flexibility provided by the thin film growth processes allows the fabrication of desired geometrical, topographical, physical, crystallographic and metallurgical microstructures into two or lesser dimensions and to study their structure sensitive properties. Among the properties being studied today for significant application are; i) optical gap, ii) optical constants and thus reflectance, transmittance and emittance spectra, iii) spatial variation of the optical thickness, iv) anisotropy in the structure and properties, v) stoichiometric deviations, vi) polymorphic and metastable structures, vii) relaxed solubility, variable composition, multicomponent compounds and alloys, viii) spatial variation of an electrical gap and electron transport parameters, ix) surface activation and passivation behaviour and x) surface

mechanical and tribological properties. One can design micromaterials to give any desired reflectance / transmittance / emittance spectrum by using graded composition of two or more materials. The conversion of surface of a number of metals having high absorptance in the visible region of the solar spectrum and a high reflectivity in the infrared region represents one of the best examples of a tailored solar selective surface. A suitable columnar structure of a graded mixture (Cu, CuO, Cu_2O, thickness $\cong$ 1 μm) obtained during the chemical conversion process enhances the optical selectivity for a very efficient solar energy conversion /2/. By controlling stoichiometric deviation of oxygen (in the oxides of Cd, Zn, Sn etc and alloys) and with a suitable dopant impurity, an approximately 90 % transparent synthetic conductors are obtained that are used extensively in several thin film solar cells and in a number of optoelectronic devices /2/.

Due to the tetrahedral structure (geometrical constraints), rapid deposition of such materials (Ge, Si) results in the formation of defects such as voids and dangling bonds. The defects give rise to undesirable localised states in the band gap of the material. Incorporation of the impurity such as hydrogen helps to tie up the dangling bonds in amorphous silicon and thus effectively cleans up its dirty band gap which can be controlled to increase almost by a double value of the crystalline silicon /2/. It now becomes possible to dope such materials to yield n or p type conductivity. This hydrogenated amorphous silicon micromaterial has given birth to a whole new technology of junction device microelectronics including amorphous silicon solar cells.

A combination of Ge with S or Se chalcogen, structurally tailored, obliquely deposited amorphous Ge-Se (S) alloy film behaves as an

inorganic polymer. On irradiation with energetic particles collapsing of voids occur and material exhibits radiation induced giant contraction effect. The physical densification is accompanied by large changes in the refractive index, shift of an absorption edge and a variety of chemical and electrochemical changes. These changes allow for the generation of high resolution optical memories, reprographic images and lithographic patterns in submicron range /2/.

Thin film deposition techniques have been broadly classified as: 1) Physical Vapour Deposition (PVD) and 2) Chemical Deposition Techniques.

1.2.1 Physical vapour deposition (PVD)

The physical vapour deposition techniques are those in which the material to be deposited is made available in an atomic, molecular or particulate form before being put for deposition. The PVD's can further be subdivided into: i) Thermal Evaporation (TE), ii) Electron Beam Evaporation (EBE), iii) Molecular Beam Epitaxy (MBE), iv) Activated Reactive Evaporation (ARE) and v) Ion Plating.

The first three techniques are different in the way the vapour beam is created (step-I). In ARE, step-II is modified in that the vapour beam is transported through a reactive plasma. In ion plating, conditions at the substrate (step-III) are modified by an ion beam. The major advantage of using PVD techniques is that all the above three deposition steps can be independently controlled. However, this spells out a warning that the deposition parameters would be carefully monitored and controlled in order to achieve reproducible deposits. The details of all the PVD techniques is beyond the aim of this dissertation.

1.2.2 Chemical deposition techniques

Chemical deposition techniques are the most powerful tools for growth of the thin films owing to their versatility in depositing a very large number of elements and compounds at relatively low temperatures /2/. These films can be deposited with required stoichiometry in both vitreous and crystalline layers with a high degree of perfection and purity. Large or small and even or uneven surfaces of all types can be coated with relative ease. The processes are very economical and have been industrially exploited on large scale. The various chemical deposition processes are: a) Chemical vapour deposition (CVD), b) Spray pyrolysis, c) Electrodeposition d) Anodization e) Screen printing, f) Solution growth or Chemical bath deposition (CBD) etc.

A detailed history of each of the above techniques is not possible to mention here however, a short account is given for the sake of understanding.

a) Chemical Vapour deposition (CVD)

A simple definition of CVD is the condensation of compound (s) from the gas phase onto a substrate where reaction occurs to produce a solid deposit. A liquid or solid compound to be deposited is made gaseous by volatilization and is caused to flow either by a pressure difference or by a carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface to produce the desired deposit on the substrate. In some processes, the chemical reaction may be activated through an external agency such as heat, R.F. field, light, x-rays, electric field or glow discharge, electron bombardment etc. The morphology, microstructure and the adhesion of the deposit is

dependent on the nature of the reactions involved. These are thermal decomposition, hydrogen reduction, nitridation, carbidization or oxidation, disproportionation, chemical transport and combined reactions. The deposition may be either homogeneous or heterogeneous. The homogeneous depositions produce powdery or flaky deposits.

The feasibility of a CVD process can be predicted by studying the thermodynamics of the reactions. The reaction kinetics and mechanism of film growth are so different in the individual processes that a generalised account is not possible. However, some of the features common to all these methods are:

1) CVD set-ups are simple and fast recycle times are possible.

2) High deposition rates are achieved.

3) Deposition of the compounds and multicomponent alloys and control of their stoichiometry is possible.

4) Epitaxial layers of high perfection and low impurity content can be grown.

5) Objects of complex shapes and geometries can be coated and

6) In-situ chemical vapour etching of the substrates prior to the deposition is possible.

The factors, which are uncommon and affect the deposition, uniformity, composition and properties of the films, are:

1) The thermodynamics and reaction kinetics are very complex and poorly understood.

2) The working temperatures are higher compared to PVD processes.

c) Electrodeposition

It is the process of depositing a substance on an electrode by electrolysis; the chemical changes being brought about by the passage of a current through an electrolyte solution. Upon immersion of an electrode in a solution containing ions of the electrode itself, a dynamic equilibrium of the kind $E = E^+ + Xe$ (E^+ - electrode atom) is achieved. The electrode gains a certain charge on it which attracts oppositely charged ions and molecules holding them at the electrode / electrolyte interface. A double layer consisting of an inner layer of water molecules and outer layer of the charge opposite to that on the electrode is formed. During deposition, ions reach the electrode surface, stabilise on it, release their ligands and charge and undergo electrochemical reaction. The depletion of the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk of the electrolyte. The transport of ions to the depletion region occurs due to the diffusion owing to the concentration gradient and migration owing to the applied electric field and convection currents. The factors that influence the electrodeposition process are: 1) pH of the electrolyte, 2) current density, 3) temperature, 4) bath composition, 5) electrode shape and 6) agitation.

d) Anodization

It is an electrolytic process wherein metal is made the anode in a suitable electrolyte. When an electric current is passed, the surface of the metal is converted into its oxide having decorative, protective or other properties. The cathode is a metal or graphite where H_2 evolves. The pH of the electrolyte plays an important role in obtaining the coherent films. Thickness of the oxide layer depends on the voltage

applied to the electrode, temperature of the bath, and time of the deposition.

e) Screen printing

Screen printing is essentially a thick film process in which pastes containing the desired materials are screen printed by a conventional method onto a suitable substrate to define conductor, resistor or a device pattern. Subsequently, the substrate is kept under appropriate conditions of the time and temperature to yield the rugged components bonded to the substrate. For the substrates which have smooth surface, capability of withstanding for higher temperature, enough mechanical strength, high thermal conductivity and good electrical properties and are compatible with film material, normally pastes are used (alumina, beryllia, magnesia, thoria and zirconia). A paste to be used usually consists of : 1) a metallic / resistive / dielectric / semiconducting component in finely divided powder form, 2) bonding agent, 3) an organic suspension medium and 4) an organic diluent. Semiconductors like CdS, CdSe, CdTe etc can be deposited by this technique.

f) Chemical bath deposition

Various deposition methods are available for thin film preparation and only few of them are presented in the above article which produce polycrystalline thin films for a variety of applications. Out of these methods, chemical bath deposition (also known as solution growth deposition, controlled precipitation method, electroless deposition or simply chemical deposition) is relatively inexpensive, simple and extremely convenient method for large area deposition of II-VI, IV-VI, III-V and I-III-V compounds / 3-9 /. The method does not require sophisticated and expensive instrumentation like vacuum system and

other cost involving equipments. It can be carried our just in a glass beaker. Only a hot plate and a stirrer are the equipments needed and hence the power consumption is almost negligible / 3-9 /. The starting materials are commonly available and cheap. The chemical bath deposition is ideally suited for large area deposition and can be achieved by using a large volume vessel only. A large number of substrates can be coated in a single attempt with a proper jig design. Positioning the substrates in a design along the walls of the reaction vessel is a simple technique to obtain a large number of coatings. Unlike in electrodeposition, electrical conductivity of the substrate is not a hard and fast requirement. Hence, any insoluble surface to which the solution has free access will be a suitable substrate for deposition. The lower deposition temperature avoids oxidation or corrosion of the metallic substrates. The method results in pinhole free, uniform, adhesive deposits as the solution from which the films are deposited always remains in touch with the substrates. Finally, doping and stoichiometry of the deposits can easily be obtained since the basic building blocks are ions instead of atoms. In a chemical deposition method the film forms slowly which facilitates better orientation of the crystallites with improved grain structure. The quality of the films so obtained is dependent on the deposition conditions such as the bath temperature, stirring rate or speed of the substrate rotation, pH, solution concentration and its purity, quality of the substrates etc.

1.3 The Tin Chalcogenides: A Brief Review

Semiconductors are classified into various groups according to their position in the periodic table. Group IV semiconductors are most widely studied. Growth of the semiconductor technology, in early 1950's, highlighted the limitations of silicon and germanium, of which the character and magnitude of forbidden gap was most disadvantageous. Extension in the range of the energy gaps was sought in compound semiconductors.

IV-VI group semiconductors are attracting a great deal of attention due to their unmatched applications in IR production and detection /10-12/. Among the IV-VI compounds, germanium sulphide, germanium selenide, tin sulphide and tin selenide have the orthorhombic structure with eight atoms per unit cell /12-14/ forming double layer planes normal to the longest axis. SnS and SnSe are isomorphous and crystallize in a rhombic, pseudotetragonal layer structure /12-15/ which is related not only to the NaCl structure, but also to the crystal structure of the hexagonal arsenic.

Tin selenide films are of immense importance because of their use as memory in switching devices. Vacuum deposited amorphous SnSe films have been studied by Baxters /16/ for the electrical switching properties and reported that these films show ovonic type switching. Engelken et al /17/ deposited SnSe films by an electrodeposition and studied their optical and photoconducting properties. Pramanik and Bhattacharya /18/ exploited a chemical method for deposition of SnSe thin films. Electrical and optical absorption properties of SnSe films obtained by evaporation and solid state reactions have been reported by Quan /19,20/. Subba Rao and Choudhari /21/ investigated the

photoconduction and photoelectronic properties of SnSe thin films. A correlation between microstructure and photosensitivity of SnSe films is reported by a number of workers /22-25/. SnSe has highly anisotropic structure with weak interlayer bonding that are stacked along b-axis. The indirect character of the gap of SnSe (~ o.9 eV) is a common property of the orthorhombic IV-VI compounds /26,27/ and has been confirmed by band structure calculations /28,29/. The electrical resistivity of SnSe films decreases with increase in temperature while carrier concentration increases with temperature which indicates predominance of grain boundary potential barrier mechanism in SnSe films. Mobility activation energy is of the order of 0.016 eV whereas the optical absorption studies showed a direct band gap of 1.2 eV /13/. FTO-SnSe heterojunction showed good rectifying behaviour /12/.

SnO_2 is other most interesting material, particularly, in sensor devices /30/. The high transparency combined with mechanical hardness of these films and good environmental stability have opened up a number of applications viz. in solar cells as well as in heat mirrors for architectural windows and solar collectors, special furnaces etc. These are the semiconductors with a wide gap of 3.5 – 4.0 eV /31-33/, having refractive index of about 1.94 and a tetragonal rutile structure. Many techniques have been employed for the deposition of tin oxide films. Among these CVD, spray pyrolytic process, reactive evaporation and reactive sputtering are commonly used methods /34,35/.

SnS is one of the low-cost thin film solar cell materials. Tin sulphide thin films are reported to be obtained by different methods. These films were obtained by the vacuum evaporation /36/,

electrodeposition /37,38/ and as well as by a chemical deposition /39/. As-grown SnS films showed p-type conduction with a resistivity of 13-20 Ω cm, a carrier density of 10^{14} to 10^{15} cm $^{-3}$ and a Hall mobility of 400-500 cm^2/V.s /36/. The coefficient of an optical absorption at the absorption edge is high (10^4 cm^{-1}). The photovoltaic properties, viz. a short circuit current of 7 mA/cm^2, an open circuit voltage of 0.12 V, a fill factor of 35 % and a conversion efficiency of 0.29 % were observed /36/. An electrodeposition of SnS films was carried out at room temperature. The XRD pattern of the sample consists of (013) or (004) reflections/40/. The SEM studies showed loose packing with random distribution of the grains whose average size is about 1μ /40/. The indirect nature of the optical absorption in SnS showed the estimated band gap to be 1.41 eV.

SnS films were also deposited by a chemical bath deposition method from an aqueous alkaline medium. The carrier concentration depends on the alkalinity. Annealing of SnS films above 285 $^{\circ}$C for a short time changes the conductivity to n-type without change in composition whereas annealing for longer duration changes the composition to SnS_2 /39/. Oxidation of the films, by annealing at higher temperature (300-400 $^{\circ}$C) in open air, changes the composition to SnO_2. Nair and Nair /41/ studied the solar absorptance of SnS-Cu_xS thin films for glass-tubular solar collectors. Vyas et al /42/ have grown SnS single crystal by a Bridgeman-Stock-Burger method and carried out the microhardness creep studies.

1.4 The Proposed Work

On going through the literature data and considering the above observations into account a detailed investigation plan of SnS thin films

was worked out in our group. Looking towards limitations of our laboratory and materials aspects of SnS (optical band gap, absorption coefficient, mode of transitions, stability against photo and electrolytic corrosions etc) we thought it to be proper to initialise the thin film studies of this important multifarous material. The work was carried out intentionally through the two successive linked aspects: i) materials synthesis in thin film form and its characterisation and ii) use of as-deposited material in photoelectrochemical (PEC) application. A chemical deposition process was employed for this purpose. The technique works on the principle of an ion-by-ion condensation /3-9/. The preparation parameters such as bath temperature, pH, deposition time, speed of the mechanical churning etc were finalised and kinetics of the growth mechanism is suggested. The films were then characterised through the structural, microscopic, optical and electrical transport properties to obtain information on the materials characteristics viz grain size, lattice parameters, optical absorbance, optical gap, mode of optical transitions, electrical conductivity, activation energies, carrier concentration, mobility, barrier height etc. The SnS films were also obtained onto the stainless steel substrates and the photoelectrochemical (PEC) cells were constructed using SnS films as an active photoelectrode, ferro / ferricynide as an electrolyte and graphite rod as a counter electrode. The various cell characteristics, namely I-V and C-V characteristics in dark, power output curve under constant illumination, photo, spectral and speed responses etc were then examined and evaluated to yield the various cell parameters viz junction quality factors (n_d and n_L), flat band potential (V_{fb}), barrier height (ϕ_B), efficiency (η %), form factor (ff%), series and shurt

resistances (R_s and R_{sh}) etc. A correlation has been made between the film and cell properties.

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