CHAPTER 12

INTRODUCTION TO THIN FILMS

INTRODUCTION

A bulk solid material is easily recognised by its three dimensions, i.e. by its length, breadth and thickness. As one goes on decreasing the thickness eventually it reduces to a nearly two dimensional material which can be called as a " FILM".

These solid films can be classified on the basis of their thickness as,

a) Thick films:

They are the films with thicknesses several microns or more.

b) Thin films:

They are the films with thicknesses several thousand angstroms.

c) Ultra thin films:

They are the films with thicknesses less than a thousand angstrom.

A given material tends to behave quite differently in its bulk form from its thin film form. The main reasons attributed to this behaviour are:

1. Much large (100 times or more) surface to volume ratio accompanied by larger imbalance between atomic forces at the surfaces as compared to the normal one in the bulk polycrystalline and single crystalline samples. This is why the films exhibit some interesting specific surface and size dependent features in conductivity, catalysis, adsorption, surface tension and thermionic emission, etc. Metals such as Na, K and Rubidium which behave as metallic conductors in bulk state exhibit semiconducting properties in thin film form[1].
2. Much larger variations in the structure and concentration of defects as compared to those normally found in bulk polycrystalline and single crystalline samples. That is why various properties of thin films are also found dependent on the techniques, conditions and parameters used and adopted in the film preparation.

HISTORY AND DEVELOPMENT

While non solid films and the associated phenomenon of interference colours have been studied for over three centuries, thin solid films were probably first obtained by electrolysis in 1838. In the recorded literature, however, Bunsen and Grove obtained metal films in 1852 by means of a chemical reaction and by glow-discharge sputtering, respectively. Faraday obtained metal films in 1857 by thermal evaporation on explosion of a current carrying wire. The free evaporation and condensation of thin films in vacuum were probably first observed by Edison and then by Fleming in 1883 who reported a metal film formed on inside of a carbon filament lamp envelope. The possibility of depositing thin films of metals by Joule heating of platinum wire was discovered in 1887 by Nahrwold and was adapted by Kundt in 1888 for the purpose of measuring refractive indices of the metal films.

The rapid growth of thin film technology started during the time of second world war when vacuum evaporated metal and dielectric films were used in optics for mirrors and antireflection coatings, respectively.

The technology and understanding of films less than 1 micron thick have made tremendous advances in the last decade, primarily because of the industrial demand for reliable thin film microelectronic devices to fulfill the urgent needs of sputnik era. In addition to major contributions to a variety of new and future scientifically based technologies, thin film studies have directly or indirectly advanced many new areas of research in solid-state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of films.

THIN FILM TECHNOLOGY

The demand for ultra high vacuum conditions for vacuum evaporation has been largely responsible for the growth of a highly specialized and precision based vacuum industry. In addition to the conventional oil pumps, variety of high speed and of oil free, getter ion, sublimation and cryogenic pumps have emerged.

A multitude of techniques have been developed to prepare polycrystalline and nearly single-crystalline films of all types of materials. Deposition rates may range from a fraction of an angstrom to thousands of angstrom per second. The thermal evaporation may be carried out at different rates of evaporation from one or more source, with a high uniformity of film thickness over a large surface (such as that of artificial satellite).

Examples of successful industrial processes are the use of thermal evaporation of Al for aluminization of foils, inert and reactive sputtering of Ta for thin-film microminiaturized resistors and capacitors and chemical deposition of Nb_3Sn on foils for the winding of superconducting magnets.

Several micro analytical techniques have been improved and others invented to determine the composition and microstructure of thin films. Electron diffraction and electron microscopy which owe their present high level of sophistication to the availability of thin films, are now responsible for much of the understanding of the structure of thin films themselves. Among various by products in terms of new 'analytical techniques, that of the Moivre fringes is significant since it is capable of revealing images of lattice and lattice defects down to a dimension of few angstroms.

IMPORTANCE OF THIN FILMS

Properties of thin films differ greatly from those of the same bulk material chiefly because of their extremely small thickness, large surface to volume ratio and unique physical structure which is a direct consequence of the growth process. Some of the phenomena resulting due to the small thickness are optical interference, high resistivity, low temperature coefficient of resistance, increase in critical magnetic field and in critical temperature of a superconductor, the planar magnetization, electronic tunneling through an insulating layer, etc. The high surface to volume ratio of a thin film is known to influence gas adsorption, diffusion and catalytic activity to a significant extent. Due to metastable disordered structure in thin films of certain materials, it is found possible to enhance superconducting transition temperature, hardness, corrosion resistance, thermopower and optical absorption.

Thus, because of the properties of thin films different from those of bulk materials and also due to the possibility of their preparation to obtain desired properties, thin films find their applications in many fields.

VAPOR GROWTH AND EPITAXY

The vapour deposition and epitaxial methods of preparing thin films provide a general platform easily susceptible to development of theory of thin film growth. When an atom impinges on a surface it selects for itself a position which is compatible (in terms of potential energy) with the surrounding conditions. The position of the deposited atoms are governed by the positions of the atoms in the very beginning on the initial surface and by positions of the atoms of the successive layers of the crystals as the growth proceeds. As soon as the growing deposit reaches a thickness of about four to five atom layers, the substrate surface, in general, will have no influence on further growth of the deposit. As it is quite often the growth takes place simultaneously on two or more layers and hence the atom at the junction will not be in a maximum stable condition, thereby giving rise to crystal defects such as dislocations, stacking faults, twins etc.

Pashley[2], Hirten & Pound[3], Rhodin and Walton[4], Baner[5] and Van der Merwe[6] and Pashley et al[7] have suggested that the vapour phase deposits grow in the form of grains on individual sites on a surface and as growth proceeds the grain grow until they touch one another. Some of them coalesce with one another like liquid drops. When coalescence nearly completes there still remain what are known as channels which will be filled only during further growth of deposit to give rise to a smooth and continuous film. In certain materials the " island structure" persists upto a large thickness. During the initial stages of film growth, i.e., when islands are quite small, they are observed to be perfect single crystals. But when islands become large enough so that they touch at grain boundaries, lattice defects will be incorporated in the film unless islands coalesce to form a single grain.

The term epitaxy (arrangement on) was first introduced by Royer[8,9] to denote the phenomenon of oriented overgrowth of one crystal on to the other. The nature of the substrate bears a great influence on the epitaxial growth of films, their structures, their orientations and hence their properties. However, other parameters like substrate temperature, impurities, deposition rate, thickness, electric field, etc. also affect the epitaxial growth.

STRUCTURE OF THIN FILMS

Solids, including thin films can be classified into forms, namely, crystalline and amorphous phases. Crystalline solids can be sub-divided as single crystalline and polycrystalline with or without any preferred orientation. Amorphous materials do not have any such ordered arrangement of atoms or ions. The thin films of most of the materials assume the same crystal structure as that of the bulk materials. However, the structural order, as for example, size and orientation of the crystallites, departs considerably from that of the bulk.

CHARACTERIZATION OF THIN FILMS

Thin films have been assuming increasingly complex structures in view of their applications which demand tailor-made properties. As a result sophisticated characterization techniques have emerged for the understanding of the multifaceted properties of thin films. No single technique is sufficient to characterize a film completely even in any one domain; for example, crystal structure, chemical nature, etc. Table I below shows a few aspects of thin film characterization, namely, surface topography, surface and bulk structure and chemical analysis with their corresponding techniques.

TABLE – 1

Important Film Properties and Characterization Techniques

Film property	Characterization technique
Topography	1. Stylus 2. SEM (Scanning Electron Microscopy) 3. TEM (Transmission Electron Microscopy) in the replica mode
Crystal Structure	1. XRD (X-ray Diffraction) 2. TEM
Surface Structure	1. LEED (Low Energy Electron Diffraction) 2. RHEED (Reflection High Energy Electron Diffraction) 3. FEM / FIM / APFIM (Field Emission Microscope / Field Ion Microscopy / Atom Probe Field Ion Microscopy)
Chemical Analysis	1. EPM (Electron Probe Micro Analysis) 2. AES (Auger Electron Spectroscopy) 3. SAM (Scanning Auger Microprobe) 4. ESCA (Electron Spectroscopy for Chemical Analysis) 5. ISS (Ion Scattering Spectroscopy) 6. SIMS (Secondary Ion Mass Spectrometry) 7. RBS (Rutherford Back Scattering)

APPLICATIONS OF THIN FILMS

Thin film technology plays a key role in many segments of industry today. The main application of thin films can be very broadly classified as follows:

1) Optical
2) Magnetic
3) Electronic
4) Thermoelectric

1) **Thin Film Optics**[10]

For over two decades, metallic and dielectric thin films have found diverse applications in technical optics. Metallic mirrors, antireflection coatings, dielectric high reflecting mirrors, semi-transparent mirrors, interference filters, etc. are the outcome of the development of thin film technology.

1(a) Mirror coatings :

They are extensively used in optical instruments for visible as well as infrared regions. Evaporated Al films possess good adhesion, durability and high reflecting properties and they are corrosion resistant and free from tarnishing. Purity of the material and rate of evaporation influence the reflectivity property to a large extent. At 140 nm if the surface is coated with SiO it gives protective coating to the mirrors.

1(b) Semitransparent mirrors and Beam splitters :

Optical semi-reflectors are widely used in interferometers, range finders, optical gunsights and lasers. The requirement of partial transmission or reflection of incident light depends on the application of these components. They are produced out of metals, semimetals and dielectric films of varying thickness. For examples, the beam splitters which reflect 20%, 30%, 40% and over 40% in visible region are single layers of SiO, ZnS, TiO_2 and Al, respectively.

1(c) Antireflection coatings or bloomings :

In multicomponent optical instruments considerable amount of light is wasted by reflection at each glass-air interface. It is possible to improve the brightness and contrast of optical image by reducing unwanted reflections. Antireflection coatings would reduce the reflectance and add to transmittance. These also avoid formation of ghost images on image plane. MgF_2 is used for antireflection single layers as it also possesses high mechanical strength and durability.

1(d) High Reflecting Mirrors :

They find very useful applications in interferrometers and lasers. With advancement in coating technology, it has become possible to produce mirrors which approach 100% reflectivity. They are based on the principle of interference between the light waves reflected from the front and back surfaces of multilayers. Alternate stackings of ZnS and MgF_2 can produce these mirrors for any spectral religion required.

1(e) Interference Filters :

Interference filters of sandwich type have low transmission due to absorption by Ag layers. Now a days, half band width filters are produced which are called cold mirrors and are positioned behind a tungsten projection lamp in motion-picture projectors.

1(f) Opthalmic Coating :

Evaporated thin films are used in opthalmic industry for various purpose. Iron oxide is an important material for this purpose.

2) Thin Films In Magnetic Application[11,12]

Magnetic films are prepared mainly by electrodeposition and vacuum evaporation. As compared to plating, vacuum deposition provides better control of the product. The first magnetic film was prepared in 1951 by Drigo using electroplating, while first evaporated magnetic film was prepared by Blois[13] in 1955.

The need for magnetic film arose with the development of high speed computers and their need for large memories. In initial stages, magnetic drums were used for information storage, which were slow and had limited memory.Thin magnetic films have several advantages over the cores to provide similar functions.

It was correctly predicted by Kittel[14] that a critical thickness exists below which a thin magnetic layer becomes a single domain. As a result the magnetic direction reversal time becomes less than 10^{-9} seconds. This property is possessed by some of the permalloys containing 80% Nickel and 20% Iron. In addition to fast magnetisation reversal, the geometry of the magnetic film permits large scale inexpensive computer memory device construction.

Current research in this field is aimed at obtaining fast switching with minimum input pulse. Simultaneously maximum change in magnetic induction is desirable to produce a high signal to noise ratio in the read out.

3) **Thin Film Electronics**

Thin film circuits are smaller, less expensive and potentially more reliable as compared to conventionally built circuits. They are more flexible and permit the fabrication of parts with closer tolerance. Passive components (resistors and capacitors) and inter-connecting patterns are evaporated on to glass or ceramic substrates.

3(a) Interconnections and Thin Film Resistors :

Aluminium which is generally used for connections is fairly reactive with many systems. Pt films sandwiched between the substrate and Al film is highly resistant to solid state diffusion of the latter. Au-Mo films are gaining popularity for use in interconnections.

For precision resistors, Chromium[15] and Nichrome[16] films are usually vacuum evaporated. Resistivity of refractory and semirefractory metal films can be increased 10 to 100 times by decreasing their grain size by depositing them in presence of a partial pressure of oxygen by vapor quenching.

The most promising material for production purpose is sputtered TaN[17] film which can be protected from aging by anodisation and at the same time trimmed accurately. Metal dielectric mixture, called cermets[18], such as those of Au and Cr with SiO_2 yield films of high resistivities.

3(b) Thin Film Capacitors :

Thin film capacitor dielectrics are associated with an increase in capacitance per unit area for material of a given dielectric constant. Among evaporated films, Silicon Monoxide[19] is widely used as a thin film capacitor dielectric. Organic polymers are also used as thin film dielectrics in some applications.

3(c) Thin Film active devices[20] :

The deposition of the thin film active devices such as transistors, diodes and photoconductors along with passive components on an inexpensive insulating substrate is a potential alternative to monolithic circuits. Thin film photoconductors used in photoconductive cells, image sensor arrays and devices such as television camera tubes and electrostatic copying machines are made of CdS, CdSe, amorphous Se, etc.

3(d) Thin Film Superconductors[21] :

The disappearance of the electric resistance of mercury at helium temperature was first observed by Kemmerlingh Onnes' in 1911. He called this phenomenon "superconductivity". Since then, a large number of metals, alloys and compounds have been found to be superconductive. Thin film studies have opened many new and fascinating areas of solid state research such as superconductive tunneling. Superconducting thin film devices have numerous applications. A few of them are cryotrons, computer memory devices, superconducting magnets and superconducting detectors.

PROPERTIES OF THIN FILMS

Various properties of thin films that can be studied can be generally listed as below:

1) Mechanical properties
2) Optical properties

3) Magnetic properties

4) Electrical

5) Thermoelectric and other transport properties

The structure of a thin film plays a very important role in determining its properties. Both of these depend on various experimental parameters that are involved in the film preparation. The important experimental parameters in this regard are :

**nature of the substrate

** the substrate temperature

** rate of deposition

** vapor pressure of the depositing species

** ambient pressure

By suitably controlling these parameters, one can prepare a film of required structure and hence the required properties.

The present work deals with the study of the electrical and optical properties of $BiSbTe_3$ thin films with film thickness and heat treatment as effective parameters. The importance of this material in thin film thermoelectric application and its preparation technique, along with the results of the electrical and optical study are discussed in Chapter 13.

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