

# *INTRODUCTION*

# CHAPTER 1

## INTRODUCTION

### 1.1 INTRODUCTION

Development of new materials is essential for growth of civilization. Advantages in technology are possible only through the availability of special materials for specific applications. In earlier times, the only processed materials known to mankind were metals and their alloys which were mainly used for their mechanical properties. New materials which came up latter such as semiconductors, polymers, ceramics and composites have had tremendous impact on civilization (**Vijaya & Rangarajan; 2004**).

Thin films science and technology plays an important role in the high-tech industries. Thin film technology has been developed primarily for the need of the integrated circuit industry. The demand for development of smaller and smaller devices with higher speed especially in new generation of integrated circuits requires advanced materials and new processing techniques suitable for future giga scale integration (GSI) technology. The term “Thin film” is broad, not really specifying a maximum thickness, while having an inherent minimum, an atomic layer with nanometer (monolayer) to several micrometer thickness.

The history of thin films probably started about three centuries ago, with the observation of the fascinating colours of thin films of oil floating on the surface of water. Thin solid films were obtained first by electrolysis in 1838. Historically, thin films have been used for more than a half century in making electronic devices, optical coatings, instrument hard coatings and decorative parts. The thin film is a traditional well-established technology. However, thin film technology is still being developed on daily basis since it is a key in the twenty-first century development of new materials and/or man-made super lattices (**Kiyotaka Wasa et al., 2004**).

Any coating less than about 1 $\mu$ m (1000nm) can be called a thin film. Thin films are very important materials in microelectronics, optoelectronics and several other technologically important fields. When a coating is to be called a thin film some necessary conditions have to be satisfied. The material or coating should be on a clean

surface, called substrate. In other words, a layer of substance having a thickness less than 1 micro meter on a substrate can be called as a thin film. Thin films are fabricated by the deposition of individual atoms on a substrate. A thin film is defined as a low-dimensional material created by condensing one by one atomic/ molecular/ ionic species of matter.

The obvious reasons for preparing materials in the thin film form and studying their properties is that, two film surfaces are very close to each other and they can have a decisive influence on the internal physical properties. These properties differ in a profound way from those of bulk material. A thin film can be treated as a two dimensional specimen because its third dimension namely, the thickness is very small compared with the other two dimensions. When a material is in the form of a thin film its physical properties are drastically different from its bulk habit. The physical properties based on the thickness have made thin films more important in technology. In thin films, the quantity of the material associated is smaller than for bulk material, this makes the material lighter and less costlier. If a bulk material is needed the device becomes heavier. Hence the microelectronics and optoelectronic industries utilize different materials in their thin film form. Besides these, other technologically important thin film applications are in the magnetic sensors, gas sensors, antireflection coatings corrosion protection paintings, wear resistance etc (**Muraleedhara Varrier et al., 2011**).

Films are used for a wide variety of purposes, nearly as many as there are types of thin films. Some of its applications are given below,

- Thin films are the backbone of the electronics and optoelectronics industries, where diodes and devices are formed from thin layers of semiconductors or layers of electroluminescent materials.
- Thin films are the building blocks used to make the devices that are rapidly becoming the centers of our lives: from computers to cell phones and electronic displays.
- Thin films are the basis of a growing variety of sensors: from medical sensors used by the diabetics to measure glucose to home pregnancy tests, or for terrestrial applications such as humidity sensors, to military sensors for the detection of poison or biological agents (**Manuel P Soriaga et al., 2002**).

## 1.2 POLYMER THIN FILMS

Modern polymer science owes its development to present level because of original, innovative and highly intellectual thoughts of many scientists and technologists. Polymers belong to a relatively new branch of science although these substances did exist since the first life began on the earth. There has been tremendous development in polymers in past 70 years or so and as on today it is impossible to think of world without polymeric materials that we use in our day-to-day life. The use of synthetic polymers is increasing rapidly year by year and in many applications they are replacing conventional materials like metals, ceramics, wood, natural fibers such as cotton and wool etc (**Bahadur & Sastry, 2003**).

To meet the growing demand of modern ages newer polymer are being synthesized everyday. The term polymer was first used by Berzelius in 1827, but the concept of polymer as macromolecule with high molecular weight was introduced by the German scientist Hermann Staudinger. The word “*polymer*” is derived from the Greek, “*poly*” or many, and “*mers*” or parts. However, a polymer molecule may be defined as a number of repeating chemical units held together by covalent bonds. This definition is necessary to distinguish polymers from crystals or liquids wherein repeating units are held together by ionic bonds or by hydrogen bonds. (**Arora et al., 2003**). Certain polymers such as proteins, Cellulose and Silk are found in nature, while many others, including polystyrene, polyethylene and nylon are produced only by synthetic routes (**Joel R. Fried, 2000**).

Polymer thin films are an emerging area driven by their enormous technological potential and the intellectually challenging academic problems associated with them. Polymers are made of large size molecules called macromolecules within each molecule, the atoms are bonded by covalent bonds. The macromolecules are in the form of long chains. The backbone of a polymer chain is a string of carbon atoms with a strong carbon-carbon bond. The other two electrons of the carbon atom will form strong bonds with other atoms or radicals positioned adjacent to the carbon-carbon chain. The larger

molecular chain may be thought of as made up of identical structural units called *mer* units or *mers*. A single *mer* is called a monomer and several *mers* form a *polymer*.

In the modern world, polymer thin films are utilized for a lot of technological applications in diverse fields such as surface coatings, micro and opto-electronics, holography, biosensors, etc. In thin films, substrate interaction, interfacial effects and confinement alter the kinetics of phase segregation and phase equilibrium. The presence of surface and an interface make them exhibit properties not generally detected in bulk materials. The theoretical understanding of the thermodynamic properties of these thin films can be improved by accurate analysis of the topographical and morphological features manifested by them and this, in turn, can lead to new outlooks and applications (Kailas et al., 2005).

### **1.2.1 ADVANTAGES OF POLYMER OVER OTHER COATING MATERIALS**

Development of polymer electronic devices is one of the most interesting and required in the recent year industrial technology. Polymeric material has various characteristics which can be controlled and monitored. These characteristics including, light weight, mechanical flexibility, high dielectric strength, fracture tolerance, high chemical resistance, easy processibility, low manufacturing cost. Moreover they can be configured onto any conceivable shape like thin sheets, thin films, thin tapes, thin fibers, etc. and their properties can be tailored to suit many applications (Abbass A Hashim, 2010).

The technological advancements in the industrial sector across the world have intensified the demand for high performance polymer coatings during the past few decades. The control of utilization of hazardous air pollutants, heavy metals as well as waste minimization has posed a significant challenge before the coating technologies and urged mankind to evolve eco-compliant high performance coating materials. Specialty polymeric coatings can be categorized as a special class of coatings that are engineered and designed to provide aesthetic sense and high performance surface protection under

specific environmental conditions. The characteristic features of these polymer coatings are

1. Their ability to withstand stress, strain exerted by different kinds of exposure in aggressive environments.
2. They can protect the metallic, concrete and other structures from corrosion and erosion.
3. Aesthetic retention (**Faiz Mohammad, 2007**)

### **1.2.2 UTILITY OF POLYMERIC MATERIALS IN VARIOUS FIELDS**

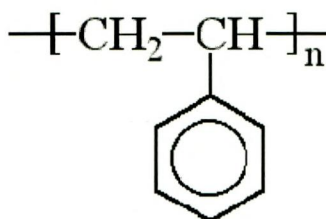
Polymers have applications in almost all fields. Plastics have virtually replaced all other types of materials like metals and inorganic dielectrics (glass) in many industrial and household applications. Polymeric and other organic thin films and multilayers are important for a wide range of applications, including electronics, optoelectronics and sensors, protective and optical coatings and membranes for diverse fields from engineering and material science to medicine. They are usually good electrical and thermal insulators. They are used as packing materials, thermal insulators, containers, coatings, adhesives, wires, etc. (**Vijaya & Rangarajan, 2004**).

They have low electrical conductivity, low dielectric loss and good chemical stability even at high temperatures. Hence they are particularly suited for the component industry for insulation, interconnection etc. In recent years, polymers find increasing applications in the electronic industry for preparation of different devices like electret microphones, disk recording cartridges, infrared detectors etc. also polymer films are used as anticorrosion coatings because of their chemical inertness (**M.Tamura et al., 1975**).

Considering some of the above applications, in this present research work polystyrene and poly(methyl methacrylate) has been chosen as coating constituents.

### 1.3 POLYSTYRENE

Polystyrene, also known as polyvinyl benzene is the simplest aromatic hydrocarbon which has the following structure



Polystyrene is one of those polymers that are all over the place. Polystyrene is an inexpensive and hard plastic. Polystyrene (PS) is a clear, colorless polymer used extensively for low-cost applications. It is available commercially in both pellet and sheet form. Styrene was obtained by steam distillation of resin from the tree *styrax officinalis* and also produced from ethylene and benzene. In 1920's German Scientist Hermann Staudinger gave the name styrene. Polystyrene is produced by the polymerization of the styrene monomer. Styrene is of particular value in industry in view of its widespread use in synthetic elastomer manufacture and because of its remarkably good electrical insulation properties. Although styrene has been polymerized commercially by all known methods of polymerization, it is largely economic forces which determine which method is used. Polystyrene is mostly of the atactic variety and hence is amorphous in nature. Polystyrene generally consists of linear molecules and is chemically inert.

#### Properties

- The linear polystyrene exists as a hard, rigid, brittle and transparent, glass like thermoplastic resin.
- Molecular weight of repeat unit is 104.1g/mol and it has the glass transition temperature of 100°C.
- Melting point of polystyrene is 240°C and its density is 1.047g/cm<sup>3</sup>.

- Polystyrene softens slightly above 100°C and becomes a viscous fluid at temperatures around 185°C.
- Polystyrene is highly transparent and is able to transmit about 90% of visible light.
- It also possess good electrical insulation characteristics. It is also having low moisture absorption; hence the electrical properties are maintained in humid conditions.
- Polystyrene is resistant to acids, alkalis, alcohols and to vegetable oils, fats or waxes. It is readily soluble in aromatic and chlorinated hydrocarbons and many esters and ketones, whereas it is swelled but not dissolved by aliphatic hydrocarbons and acetone.
- Due to low cost, good modulability together with its transparency and colourability this material is having widespread applications.
- Polystyrene has also been fabricated into a wide variety of extruded shapes, including films, monofilaments and oriented sheets (**Arora et al., 2003**).

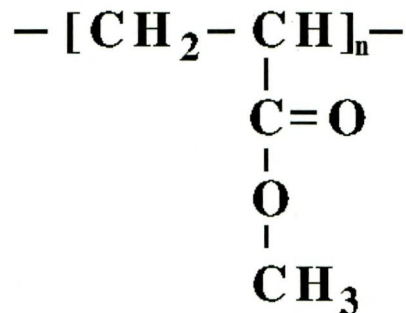
## **Applications**

- ❖ Polystyrene finds wide application in making household goods, lenses, plastic moulds, toys, wood laminates, films, battery boxes and electrical components.
- ❖ Many important and novel uses of polystyrene depend upon its optical properties. Thus, like poly(methyl methacrylate), the exceptional clarity and transparency of polystyrene leads to such uses as “un-breakable glass” for gauges, windows and lenses, as well as in countless specialties and novelties
- ❖ It has high refractive index (1.60) which, combine with its clarity allows polystyrene to bend light around corners, so it is used for the edge-lighting of indicators and dials.
- ❖ Polystyrene has fair light stability for all uses except those involving exposure to sunshine or ultraviolet light for a long time.
- ❖ Because of its excellent electrical characteristics, extremely low moisture absorption and good dimensional stability, polystyrene is widely used in the

manufacture of capacitors, insulators, coils, cables, radomes and many other components for electrical industry.

#### 1.4 POLY(METHYLMETHACRYLATE)

Poly(methyl methacrylate) (PMMA) is a commercially important vinyl polymer. This polymer has the following structure



Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic, often used as a lightweight or shatter-resistant alternative to glass. It is sometimes called acrylic glass. Chemically, it is the synthetic polymer of methyl methacrylate. The material was developed in 1928 in various laboratories, and was first brought to market in 1933 by the Rohm and Haas Company, under the trademark Plexiglas. The methacrylate ester polymers are exceptionally clear, hard, glass plastics. They soften at temperature over 120°C, this permits fabrication of molding and extrusion techniques. PMMA is widely used sometimes with plasticizer and or small amount of other esters as copolymers.

The monomer methyl methacrylate is produced from acetone. PMMA is prepared by radical polymerization in bulk or suspension. It is often preferred because of its moderate properties, easy handling and processing, and low cost, but behaves in a brittle manner when loaded, especially under an impact force, and is more prone to scratching than conventional inorganic glass.

Poly(methyl methacrylate) (PMMA) is a clear, colorless polymer used extensively for optical applications. It is available commercially in both pellet and sheet form. Outstanding properties include weatherability and scratch resistance.

## Properties

- PMMA is a strong and lightweight material. It has a density of 1.17–1.20 g/cm<sup>3</sup>, which is less than half that of glass.
- It also has good impact strength, higher than both glass and polystyrene
- Molecular weight of repeat unit is 100.12g/mol and it has the glass transition temperature of 114°C.
- Melting point of polystyrene is 160°C and its density is 1.188g/cm<sup>3</sup>.
- Commercially produced PMMA is a thermoplastic that softens at 120°C.
- It is amorphous by nature, owing to the presence of bulky side groups in the molecules.
- PMMA is hard and transparent polymer with good resistance to the effects of light and weathering.
- It is resistant to many chemicals but soluble in organic solvents such as ketones, chlorinated hydrocarbons and esters.
- PMMA transmits up to 92% of visible light and gives a reflection of about 4% from each of its surfaces on account of its refractive index (1.4914 at 587.6 nm).
- Its environmental stability is superior to most other plastics such as polystyrene and polyethylene, and PMMA is therefore often the material of choice for outdoor applications (**Gowariker et al., 2009**).

## Applications

PMMA is a versatile material and has been used in a wide range of fields and applications.

- ❖ It is an excellent substitute for glass. PMMA acrylic glass is commonly used for constructing residential and commercial aquariums.
- ❖ Poly(methyl methacrylate) has drawn tremendous interest due to its optical properties and its possible use in non-linear optics.
- ❖ PMMA is used to make attractive sign boards and durable lenses for automobile lighting.
- ❖ Historically, PMMA was an important improvement in the design of aircraft windows.

- ❖ Daylight redirection-Laser cut acrylic panels have been used to redirect sunlight into a light pipe or tubular skylight and, from there, to spread it into a room.
- ❖ PMMA has a good degree of compatibility with human tissue, and can be used as intraocular lenses in the human eye when the original lens has been removed in the treatment of cataracts.
- ❖ PMMA was used in Laser Disc optical media. (CDs and DVDs).
- ❖ Plastic optical fiber used for short distance communication is made from PMMA, and perfluorinated PMMA, clad with fluorinated PMMA, in situations where its flexibility and cheaper installation costs outweigh its poor heat tolerance and higher attenuation over glass fiber.
- ❖ Poly(methyl methacrylate) (PMMA) polymer films can be used either as a chemically sensitive coating material in implementing biochemical sensors or as a waveguiding layer in guided shear-horizontal surface acoustic wave (SH-SAW) sensor platforms ([http://en.wikipedia.org/wiki/Poly\(methyl\\_methacrylate\)](http://en.wikipedia.org/wiki/Poly(methyl_methacrylate))).

## 1.5 PREPARATION OF POLYMER THIN FILM

Many different methods are used to produce polymers on substrates. Among them Chemical Bath Deposition (CBD) and Spin coating are widely used because of their ease of processing, and the same is adopted in this present work. Sorption of polymer molecules from the dilute solutions on the substrate allows formation of very thin polymer layer, which thickness is comparable with the size of macromolecules.

Spin coating is a fast and easy method to generate thin and homogeneous organic films out of solution. Spin coating is a procedure used to apply uniform thin films to flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater.

The Chemical bath deposition (CBD) method is one of the cheapest method to deposit thin films and nanomaterials, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. In 1933 Bruckman deposited Lead (II) sulfide (PbS) thin film by chemical bath deposition (CBD) or solution grown method.

Synthetic polymers already find widespread applications as replacement structural materials for natural products. Recent efforts have focused on the application of polymers as active functional materials for electronics, optoelectronics and photonics. Specific applications include light emitting diodes (LEDs), photo detectors and solar cells, TFT arrays and memory elements, amplifiers and Lasers. Thus, knowledge and determination of the nature, function and new properties of thin films can be used for the development of new technologies for future applications.

## **1.6 OBJECTIVES OF THE STUDY**

The aim of the present work is

- To prepare PS/PMMA composite thin films by Chemical bath deposition and Spin coating technique on glass substrate.
- To measure the thickness of prepared film.
- To analyze structural, optical and surface properties of the coated thin film using UV-Visible, Photoluminescence, GC-MS, SEM and XRD characterization methods.

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