MATERIALS AND METHODS

CHAPTER 3

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3.1 INTRODUCTION

The selection of specific material for coating generally depends upon the advantage and application of that material. Thin film polymeric materials are of growing importance in technical applications of microelectronics, optics, optoelectronics, etc, and hence in this research work thin polymeric materials have been analysed. Thin films can be deposited atom by atom on variety of substrates. For this purpose various preparative techniques have been developed. Newer methods are also being evolved to improve the quality of the deposit with maximum reproducible properties and minimum variation in their composition, and for each coating material suitable deposition techniques are adopted. Depending on the field of application the deposition technology has to match a broad spectrum of requirement in order to meet the desired functional parameters. Among the various available physical and chemical methods, chemical bath deposition and spin coating method has been followed in this research work.

3.2 MATERIAL SELECTION

Selection of the best film for any particular use is a matter of matching film properties against the end use performance required. Polystyrene, poly(methyl methacrylate) have been chosen for thin film coating in this work. Poly(methyl methacrylate) is a clear transparent, thermoplastic with good optical, electrical, and mechanical properties. The main feature of this plastic is its optical clarity and it is an excellent substitute for glass. It is also used in optical fibers, contact lens, lighting fixtures and automobile surface coatings. It has an excellent outdoor life period and good strength.

Polystyrene is also a clear, transparent thermoplastic material, capable of transmitting slightly more than 90 percent of white light. Many important and novel use of polystyrene depends upon its optical properties. The light transmission of this plastic is not quite as high as that of PMMA, but it is slightly better than that of glass plate. Thus like poly(methyl methacrylate) the exceptional clarity and transparency of polystyrene lead to such uses as "un- breakable glass" for gauges, windows and lenses.

The two polymers, PMMA and PS are blended with each other so as to yield a composite thin film with desired properties. Immiscible blends are known to have properties, which combine those of both the polymers, and to have segregated structures with domains predominantly formed from the individual homopolymers. PS/PMMA blend is well-known immiscible combination for which bulk and surface phase separation has been observed. Among the commercially available polymers, polystyrene, poly(methylmethacrylate) is a good material of choice. However due to the low entropy of mixing, polymeric blends are mostly incompatible and phase separate under appropriate conditions. Especially for thin films, since the surface area-to- volume ratio of polymer blend film is relatively large, the presence of both air/polymer and substrate/ polymer interface play an important role in determining the morphology of polymer blend thin films. For ultra thin films the additional presence of a surface leads to behaviour, which is very different from bulk systems (**Krausch, 1995**).

PS/PMMA composite is a good classic model system for polymer phase segregation studies, but they also have direct technological relevance. Thin films of PS-PMMA copolymers are currently being investigated for possible use in the fabrication of high density magnetic storage media, while phase separated PS/PMMA blend thin films have been proposed as antireflection coatings (**Walheim et al., 1999**). Thin films of PS/PMMA blends with a surface consisting of pure PS and pure PMMA in adjacent micron-scale domain, and can be used as substrates for competitive protein absorption studies also.

3.3 CHOICE OF THE SUBSTRATE

The substrate surface usually provide template for subsequent deposition and growth of thin films. In addition surface also serve as the vehicle for imparting interfacial structural, mechanical and physical properties of thin films **(Milton ohring, 2006).** The microstructure of thin films is strongly depend on the kind of substrate i.e. roughness, crystalline structure and the chemical state of the surface. Unfortunately, an ideal substrate does not exist. Specific applications require different substrate materials which offer an acceptable compromise for the purpose on hand.

Ideally the substrate should provide only mechanical support but not interact with the film except for sufficient adhesion. In practice, however the substrate exerts considerable influence on the thin film characteristics. The various substrate requirements are, atomically smooth surfaces, inertness to chemicals used in processing, high volume and surface resistivity, high thermal conductivity, coefficient of thermal expansion similar to film, high mechanical strength, high thermal shock resistance, zero porosity, good dimensional tolerance, excellent scribing, cutting, module- separation properties and low cost. There are a number of materials like glass, ceramics and quartz available for use as thin film substrates. Glass plates fulfil these varied requirements best and hence is preferred in this work (**Maissel and Glang, 1983**).

3.4 SUBSTRATE CLEANING

Almost all depositions are made of some solid substrates such as glass, quartz, ceramics, mica, minerals, metals, etc. the most important consideration in all these cases is that the deposit layers must be adherent to the substrate and these should not peel off from the substrate under the normal condition of stress and strain, mechanical or thermal changes to which the deposits are exposed during their uses. A poor adhesion of deposit to a substrate is primarily caused by the presence of impurities at the substrate surface **(Goswami, 2005).** The cleanliness of the substrate surface exerts a decisive influence on film growth and adhesion. A thoroughly cleaned substrate is a prerequisite for the preparation of films with reproducible properties. Residues from manufacturing and packaging, lint, fingerprints, oil and airborne particulate matter are examples of frequently encountered contaminants.

Hence all the glass wares were washed with ordinary distilled water. Then they were rinsed with Extran and washed completely with distilled water followed by de-ionized water. The blue star glass plates of dimension (75mmx25mmx1mm) were washed with distilled water and immersed in HNO_3 for half an hour and washed with distilled water. The substrates were dipped in HCL for the same period. After that the slides were rinsed using soap solution and distilled water. Finally the substrates were allowed to dry in a hot air oven for about an hour at a temperature of 100°C. Thus the substrates required for film coating in this study have been prepared.

3.5 THIN FILM FORMATION TECHNIQUES

Thin film formation is an act of applying material onto a substrate or previously deposited layer. Thin film of a material is created by the random nucleation and growth process of individually condensing/ reacting atomic/ ionic/ molecular species on a substrate. The structural, chemical, metallurgical and physical properties of such materials are strongly dependent on a large number of deposition parameters. Any thin film deposition process involves three main steps

- Production of the appropriate atomic, molecular or ionic species.
- Transport of these species to the substrate through a medium.
- Condensation on the substrate, either directly via a chemical and/ or electrochemical reaction, to form a solid deposit. **(Kiyotaka Wasa et al., 2004)**.

A wide choice of preparation techniques is open to the scientist who is interested in thin films. Broadly these methods may be divided into two classes, Physical method and Chemical method.

A) PHYSICAL METHOD

In this process depositions happen because of a physical reaction. The objective of this deposition process is to controllably transfer atoms from a source to a substrate where film formation and growth proceed automatically. Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film. Commercial physical deposition system tends to require a low-pressure vapour environment to function properly; most can be classified as Physical Vapour Deposition (PVD).Two most important physical vapour deposition process are, Evaporation and Sputtering.

Evaporation process comprises evaporating source material in a vacuum chamber below $1x10^{-6}$ torr and condensing the evaporated particles on a substrate. This method is also known as "vacuum deposition". Several types of evaporation process are

- Laser ablation evaporation
- Thermal evaporation

- Molecular beam epitaxy.

In sputtering process, a solid surface is bombarded with energetic particles such as accelerated ions, surface atoms of the solids are scattered backward due to collisions between the surface atoms and the energetic particles. The target can be kept at a relatively low temperature than evaporation, making this one of the most flexible deposition techniques. Several sputtering systems proposed for thin film deposition are given below,

- RF sputtering
- DC diode sputtering
- Magnetron sputtering
- Ion beam sputtering (**Kiyotaka Wasa & Shigeru Hayakawa, 1992**).

B) CHEMICAL METHOD

This process exploits the creation of solid materials directly from chemical reactions in gas and or/ liquid compositions or with the substrate material. Here a fluid precursor undergoes chemical changes at a solid surface, leaving a solid layer. The film is formed by a chemical reaction on the surface of the substrate. Since the fluid surrounds the solid object, deposition happen in every surface, with little regard to direction. Thin films formed by chemical deposition techniques tend to be conformal rather than directional.

Chemical deposition is further classified as follows,

- ➢ Plating
    - ✓ Electroplating
    - ✓ Electrolessplating
- ➢ Chemical Vapour Deposition (CVD)
    - ✓ Low pressure CVD (LPCVD)
    - ✓ Plasma Enhanced CVD (PECVD)
    - ✓ Atmosphere-Pressure CVD (APCVD)
    - ✓ Metal Organic CVD (MOCVD)
- ➢ Anodic Oxidation

Plating relies on liquid precursors often solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution, but by far the most commercially important process is Electroplating. Chemical vapour deposition (CVD) method makes use of some of the principles involved in vapour phase transport reactions. It is used to obtain very pure films and it does not require vacuum or unusual electric power as it was practiced commercially prior to PVD. The films are formed by decomposition of gaseous molecules. This is an Electrolytic method of producing oxide films on the surface of metals. These metals form the anode that dips into a liquid electrolyte such as salt or acid solution. Oxide ions are attracted to the anode to form a thin layer. On increasing the field strength more oxide ions diffuse through the oxide layer to the metal surface and hence oxide layer grows thicker.

3.6 TECHNIQUES ADOPTED IN THIS STUDY

1). CHEMICAL BATH DEPOSITION

The Chemical bath deposition (CBD) method is one of the cheapest method to deposit thin films and nanomaterials, as it does not require 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. It is well known that the chemical bath deposition (CBD) is an economical growth technique that can deposit homogeneous stoichiometric films with high purity on non-planar substrates, which has been proved by growth of single- or poly-crystalline oxide thin films

The major advantage of CBD is that it requires only solution containers and substrate mounting devices. The one drawback of this method is the wastage of solution after every deposition. Among various deposition techniques, chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The chemical bath deposition method is one of the simplest method for preparing highly efficient thin films in a simple manner. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution, and topographical and chemical nature of the substrate.

The chemical bath deposition involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution. In the chemical bath deposition procedure, the substrate is immersed in an aqueous solution containing the precursors. While chemical bath deposition (CBD) is widely used in the laboratory and industry for the creation of thin films and nanostructures for semiconductors and photovoltaic.

2). SPIN COATING

Spin coating is used widely for depositing thin polymer layers on flat solid substrate. Spin coating is a procedure used to apply uniform thin films to flat substrates. A known 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. The machine used for spin coating is called a spin coater, or simply spinner.

Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. Stages of spin coating are, deposition of the coating fluid onto the wafer or substrate, acceleration of the substrate up to its desired final rotation speed, spinning of the substrate at a constant rate; fluid viscous forces dominate the fluid thinning behavior and solvent evaporation dominates the coating thinning behavior. Some variable process parameters involved in spin coating are, solution viscosity, solid content, angular speed, and spin time.

Although many polymers with a wide range of weights may be spin-coated, one of the easiest and most typical polymers to spin-coat is poly(methyl methacrylate) (PMMA) with a moderate molecular weight, dissolved in a solvent with some moderate polarity. Both the choice of solvent and especially the molecular weight of the polymer significantly affect the viscosity of the solution and thus the thickness of the resultant coating.

Many other polymers, such as polystyrene or more polar polymers such as polysulfones or polyetherimides, can also be spin-coated. Some polymers are more difficult to coat than others. Although strict control over the laboratory environment is the best way to improve coating quality, when this is difficult or infeasible one quick-fix to significantly improve film quality is to gently spray a dry inert gas (such as nitrogen, or preferably argon) over the sample during coating while heating the sample with an infrared heat lamp (available at most hardware stores). This lamp significantly reduces the local humidity while simultaneously increasing the rate of solvent evaporation so that the sample does not have a chance to absorb moisture.

3.7 EXPERIMENTAL DETAILS

3.7.1 CHEMICALS AND GLASSWARES USED

Polystyrene (99% purity), poly(methyl methacrylate) (>99% purity), Ethyl methyl ketone GR (>99% purity- Merck), Toluene GR (>99% purity- Merck), were used to prepare polymer precursor solution. HCl GR (>40% purity- Merck), HNO_3 GR (>60% purity- Merck), Acetone GR (>99% purity- Merck), double distilled water and Extran were used to clean the microscopic glass slides. Glass wares used for film coating are blue star glass slides with 75mmx 25mmx 1mm dimension, beakers, conical flasks and measuring jar.

3.7.2 EXPERIMENTAL PROCEDURE FOR CHEMICAL BATH DEPOSITION

Thin films of polystyrene and poly(methyl methacrylate) were deposited on highly clean glass substrates. The solution was prepared in a glass beaker by dissolving known quantities of PS and PMMA separately in different solvents at room temperature to yield different molar solutions. Then the solution was heated to 40˚C to ensure a homogeneous mixing of solvent. Similarly the blend of both PS and PMMA solution were prepared by dissolving these two polymers in a common solvent and the solution was heated to 40˚C to ensure the complete mixing of these two polymers. Then the solution was filtered using 0.5μm Whatman filter papers to remove any undissolved impurities and dust before use. Thin films were prepared using Constant temperature water bath with digital proportional temperature controller. The beakers with PS, PMMA and PS/PMMA solutions were kept in water bath. The rate of growth and thickness of the film depend on the nature of the substrate, the concentration and temperature of the solution and also the time for which the substrate is left immersed in the solution. The chemical bath setup used in this work is shown in plate. 1. Various solvents have been used to deposit polymer film, but only the following best coated films characteristics have been analysed.

Sample I: 4.5 mole of PS dissolved in 100 ml mixture of Ethyl methyl ketone and Toluene.

Sample II: 2 mole of PMMA dissolved in 100 ml Ethyl methyl ketone.

Sample III: 4.5 mole of PMMA and 2 mole of PS dissolved in 100 ml Ethyl methyl ketone.

After the film deposition, coated substrates were taken out and annealed at 80°C for one hour to remove all the traces of solvent.

3.7.3 EXPERIMENTAL PROCEDURE FOR SPIN COATING

Although may polymers with wide range of molecular weights may be spin coated, one of the easiest and most typical polymers to spin-coat is poly(methyl methacrylate) with a moderate molecular weight, dissolved in solvent with moderate polarity. Known quantity of PMMA is dissolved in dichloromethane and toluene at room temperature. The solution was then kept in water bath at 40°C to yield a homogeneous solution. Prior to spin coating, the polymer solution was filtered to remove dust and undissolved impurities with 0.5µm Whatman filter paper. Spin coating was carried out using SCU 2007 A spin coating unit, in a clean room environment and for coating one-inch square glass plates cut from microscope slides were used as substrates. The glass plate is placed upon the spin-coating apparatus and then coated liberally with the polymer solution by use of syringe. During the first stage, the plate is spun at a low to moderate speed 500–1000 rpm for 5–10 seconds to evenly spread the solution. The thickness of the coating is then determined and controlled during the second stage by spinning the coating at a higher speed, between 2500–3000 rpm for time duration less than one minute. These conditions will typically produce high quality coatings of thickness between 2 and 10 micrometers. Spin coater is shown in plate. 2.

Once spin-coating is complete, the plate is placed quickly in a muffle furnace (heated to around 100 °C) for a few hours to initially evaporate solvent and solidify the coating.

3.8 FILM THICKNESS MEASUREMENT

Thickness of a film is among the first quoted attribute of its nature. The reason is that thin film properties usually depend on thickness and it plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the film thickness and the deposition parameters are kept constant. Historically the use of films in optical applications spurred the development of techniques capable of measuring film thickness with high accuracy **(Milton ohring, 2006).** Many methods are either commercially available or experimentally adapted for real time monitoring of film thickness during growth.

Various types of optical interference phenomena have been found to be most useful for the measurement of film thickness, in addition to interference phenomenon, there are other optical techniques which can be used to measure thickness. Examples are ellipsometry and absorption spectroscopy. In addition to the optical techniques there are mechanical, electrical and magnetic techniques which have been used for film-thickness measurements. Electrical methods of measuring film thickness involve film resistance method, capacitance monitor and ionization method. Film thickness can also be measured mechanically by means of the following techniques such as profilometry, quartz crystal microbalance, microbalance gravimetric and ultrasonic multilayer film technology, etc. Among these the one that has found the widest acceptance is the microbalance gravimetric technique. (**Maissel and Glang,1983**).

Instrument suitable for the Gravimetric determination of small quantities of mass are summarily referred to as microbalance technique. This is one of the oldest methods for film-thickness determination by weighing the substrate before and after deposition of the film. The basic requirement of Gravimetric technique is the weight measurement should be done on the same substrate before and after deposition of the film. Another requirement is that the substrate should not be prone to chipping or other types of material loss and the deposition process should not result in the accumulation of material other than the desired film. The weighing should be very accurate since relatively small difference in large numbers is being sought. The weighing accuracy of

±1 μg, which is attainable with digital balance, barely permits the detection of about micron film thickness. The film thickness (t) has been evaluated from the following relation

$$t = W/\rho A$$

Where,

Weight of the thin film on the glass substrate (W) = Weight after deposition-weight before deposition (g)

ρ = density of the material (gcm^{-3})

A = deposited area (cm^2)

DENVER microbalance with 4-digit accuracy used for measuring the weight of the deposited film during this study is shown in plate 3.

PLATE 1

CHEMICAL BATH SETUP FOR FILM COATING

PLATE 2

SPIN COATING UNIT USED FOR FILM DEPOSITION

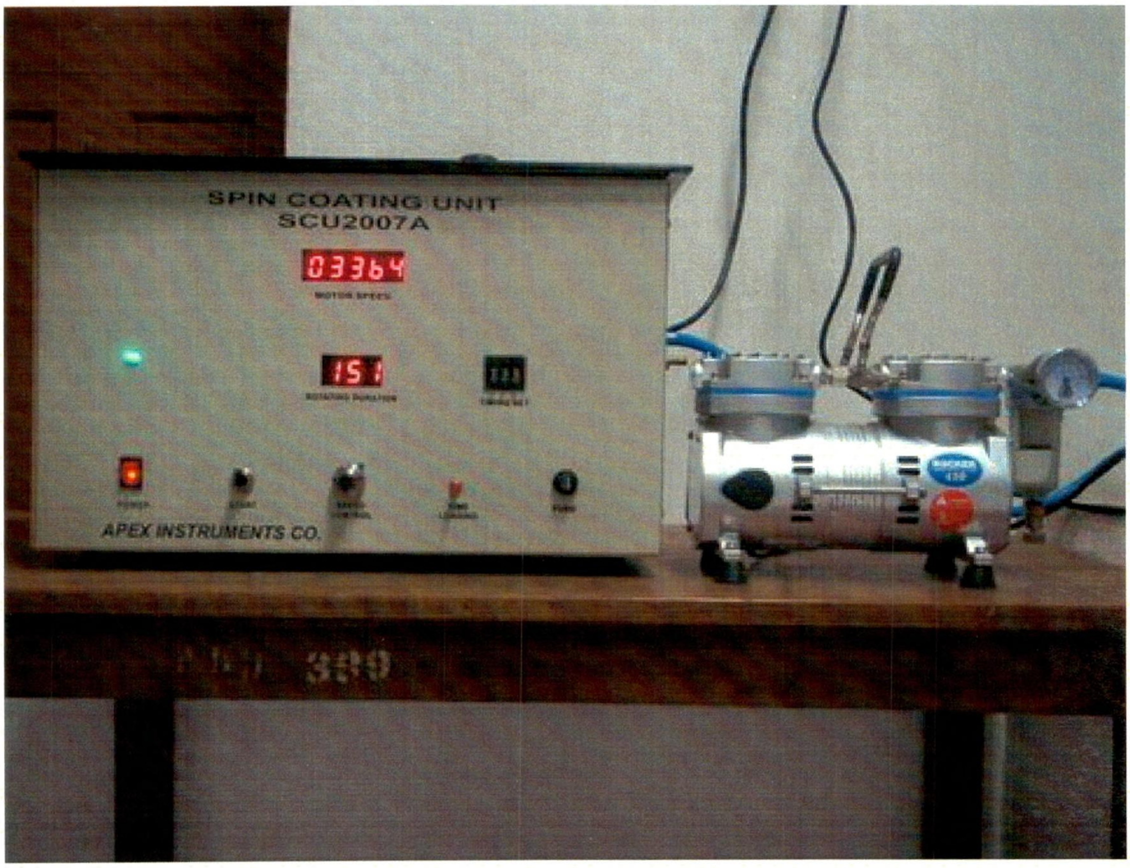

PLATE 3

DIGITAL MICROBALANCE USED FOR THICKNESS MEASUREMENT

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