TOOLS TO ORGANIZE TWO DIMENSIONAL MOLECULAR ASSEMBLES:
LANGMUIR-BLODGETT FILM AND SPIN COATING TECHNIQUES
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CHAPTER 1

GENERAL DISCUSSION ON THIN FILM

1.1 INTRODUCTION

The study or research on thin film comes under a huge area of science called “MATERIAL SCIENCE” and the journey of material science is as old as human civilization.Basically material science deals with, how processing of a material effects its structure, thus its property and performance for suitable application. Now a days, the popularity of material science enhanced drastically because of the development of NANOTECHNOLOGY. In our present topic of project we will study about a two dimensional nano structure (one dimension is confined) i.e, THIN FILM which has a vast importance and applications in various field. The size of thin film is of the order of few nanometer to micrometer.

Thin film is generally made by coating of material (with varying thickness of nano to micrometer) on solid substrate .The coating material is may be organic, inorganic or polymeric in nature. But now a days nano particles and quantum dots are also being used as coating material for specific field of application. The solid substrate which are used generally are ordinary glass slide, quartz substrate, ITO coated glass, etc.

1.2 NEED OF THIN FILM AND ITS APPLICATIONS

It was 1965, when E. Moore told that “the number of transistors that can be packed in to a given unit of space will be roughly doubled in every two years”. From the era of diode bulb and triode bulb the main aim was to increase the computing power and packing density. Which means, at the electronics level how small we can go i.e, decrease the size of the basic building blocks of electronics circuit as small as possible. To keep Moore’s law alive, development of nanotechnology play a key role. The topic of our discussion i.e, thin film has the same motive and has great application in various field.

The name of few technological applications where thin film is used are-
Displays, Detectors, sensors, photo switch, photography, O-LED, electronics circuit components etc.
1.3 THICKNESS OF A THIN FILM

Though we know, the size of the thin film is of the order of nano to micrometer but we can define the thinness or thickness of ‘thin film’ such that the property of the material should be effected compared to the bulk structure of that particular material.

1.4 ANALYSIS OF STRUCTURAL CHANGE AND ITS INFLUENCE ON THE PROPERTY OF THIN FILM

If we gradually go from bulk structure of a particular material to its nano structure, we will see, depending on the size, the arrangement of the atoms and molecules will change. Hence, depending on the structure, property of the material will also change.

In nano level the aspect ratio i.e the surface area to volume ratio increases greatly, from what it was in bulk structure. For example if we break a box into two parts, then two new surface will create. In the similar way, undergoing from bulk to nano level the surface area increases rapidly. Which means whatever the number of surface atoms at the bulk structure, now in nano structure it will much more in number with respect to its volume. Which effects the property of the material.

Also, due to the structural change of the material undergoing from bulk to nano dimension, the delocalization of valance electrons occurs and the extent of this kind of delocalization varies with size.

The above mentioned reason can lead to change in various physical and chemical properties depending on size such as Optical property (colour changes with size), band gap (increases with decreasing size and conductivity changes), melting point (decreases with size because loosely bound electron at the surface needed less energy to escape from the atom), specific heat, surface reactivity etc. Depending on the changes in properties, materials assembled onto nanoscale are very promising with respect to technological application.

1.5 THIN FILM DEPOSITION TECHNIQUES

Since we are in nano dimension we cannot fabricate thin film manually. There are various sophisticated techniques available for fabrication of thin film which are as follows-
1. Langmuir-Blodgett (LB) technique,

2. Spin coating technique,

3. Layer by-Layer (LbL) self-assembled technique,

4. Vapor deposition technique,

5. Molecular Beam Epitaxy,

6. Lithography, etc.

In our present study we will learn about first two techniques as listed above which are LB and spin coating.
CHAPTER 2
LANGMUIR BLODGETT TECHNIQUE

2.1 BASIC INTRODUCTION OF LANGMUIR BLODGETT TECHNIQUE

The work on LB film has been intensified in recent year, after 71 years of Katherine Blodgett’s successful transfer of a monolayer of some organic molecules from water surface to a glass plate. LB technique is the most elegant method of obtaining highly organized molecular assemblies which have their potential applications in sensors, optoelectronic, optical signal processing, digital optical switching devices and as models mimicking biological membranes. The work on LB film has done by Hans Kuhn and his co-workers. The role of $\pi$-electron conjugation, ultra structure as well as domain structure and also the electrical and optical properties of such films is the topic of interest. These kind of detailed investigations are required for the point of view of their applications. The most attractive features of LB film is the inherent control over the alignment of molecules and the thickness of the film.

2.2 HISTORICAL BACKGROUND OF LB TECHNIQUE

Before talking about the history of LB film, it is necessary to mention a name who first started to think about the matter of thin film at the air water interface. In 1774, an American scientist named Benjamin Franklin reported to the British Royal Society that

"At length at Clapman where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface. the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leeside, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."

After observing the oil layer at water Benjamin Franklin comes to a simple conclusion that if a teaspoonful (2 ml) of oil is spread over an area of half an acre, the thickness of the film on the surface of water must be less than 2 nm.

After almost 100 years of this incident Lord Rayleigh suspected that the maximum extension of an oil film on water represents a layer of one molecular thickness. In this time the foundation of characterising the mono layer on the air water interface was introduced by a German woman, Agnes Pockles. Publication of Pockels's work in 1891 set the stage for Langmuir to take the legacy put forward and helped him to start qualitative research on fatty acid, ester and alcohol monolayers. Irving Langmuir was the first to perform systematic studies on floating monolayers on water in the late 1910's and early 1920's. This floating monolayer on water is called ‘Langmuir film’. These studies led to him being
awarded the Nobel prize. The first successful transfer of mono layer from air-water surface to solid surface is done by Katherine Blodgett and the formed film is termed as ‘Langmuir Blodgett film’.

After pioneering work by Langmuir and Blodgett, it took half a century to realize the opportunity of the work all around the world. The first international conference on LB is held on 1979 since then the LB technique become popularised among the researchers. Now LB films are used in various practical applications. However, to use the LB film in practical field, it needs detailed study of Langmuir and Langmuir Blodgett film at the very basic level.

2.3 SUITABLE MATERIAL FOR LB FILM

Generally the materials which have long hydro carbon chain or alkyl chain attached with mother chromophore are compatible for LB film. These types of molecules are known as amphiphilic molecules. The amphiphilic molecules consists of two parts. One is hydrophobic tail (water hating) part, which is basically an alkyl chain. Another is hydrophilic head (water loving) group, which may be a hydroxyl group (-OH), a carboxylic acid group (-COOH), amine group (-NH2), aldehyde group (-CHO), metal ion group, etc. For the formation of proper monolayer at the air-water interface a balance between hydrophilic interaction and hydrophobic interaction is required which is called amphiphatic balance. The molecules attached by long hydrocarbon chain have different kinds of property such as conducting, semi conducting, lasing action, gas sensing, pyro-electric etc. Examples of such type of molecules are Stearic acid (SA), Arachidic acid (AA) and Zinc (Arachidate)2. Fig-1 shows the diagram of LB compatible material.

![Diagram of LB compatible material](image)

Fig-1: Ideal LB compatible material
Recently it is observed that the molecules which do not have any hydrophobic chain i.e non-amphiphilic molecules also can be used for formation of LB film. Non-amphiphilic molecules mixed with a long chain fatty acid such as stearic acid or arachidic acid or with an inert polymer matrix such as polymethyl methacrylate or polystyrene forms excellent LB film. In this case fatty acid or polymer acts as building block for the arrangement of molecule at the air water interface. Non-amphiphilic molecules are easily available and they have wide range of variety having different types of properties. Also the quality of this non-amphiphilic LB film is very much comparable to the LB film which is made from amphiphilic molecule as far the spectroscopic and aggregating properties are concerned. which is advantageous for application.

2.4 FORMATION OF LB FILM

The formation of LB film is divided into two parts one is Langmuir film and another is Langmuir-blodgett film. Basically, the molecular assembly formed at water surface is called the Langmuir monolayer. when the film produced at air-water interface shifted at solid substrate then it is called Langmuir-Blodgett film. Here, two types of films are discussed separately.

2.4.1 LANGMUIR FILM

The Langmuir monolayer formed at air-water interface or in any suitable liquid such as benzene needs sophisticated instrument and extreme precautions. The instrument required for assembling molecule at water surface is known as LB film deposition instrument. The essential part of this LB deposition instrument is Teflon coated trough which is filled up with distilled and deionised water. There is a Teflon coated barrier at the one end of the trough which can move through the water without going deep into the water.
Fig1-Schematic diagram of LB monolayer on LB trough

Fig-2 LB film deposition instrument
The liquid surface pressure measurements has been done by Wilhelmy plate attached to an electronic microbalance and then the reading is fed to a micro computer through an interface. The Wilhelmy technique of measuring the surface pressure is done by a thin paper which semi-immersed on subphase and attached to the microbalance vertically above it.

Now, to make LB film, first take LB compatible material then dissolve it into highly volatile and water insoluble medium (e.g. CCl₄) and makes dilute solution. Now few micro liters of this solution is spread at the water surface (air-water interface) with a controlled manner by a micro syringe and allow the solvent to be evaporated. Now the molecule at the 2D water surface starts move randomly as the gas molecule moves in 3D. This situation on the water surface is termed as gas phase and the molecules are loosely packed in this condition. In this gas phase, each molecule occupy a large molecular area (A) and the surface pressure is also quite low. Now if the barrier is start to move through the water surface by computer controlled technique, the molecules start to come closer. In this way surface pressure is gradually increased and correspondingly phase change occur from gaseous to liquid and finally to solid as shown in fig-3 and fig-4 and fig-5. At low molecular area and high surface pressure this solid phase typically has a 2-D lattice structure on water surface. Further pressure cause breakdown of the film as shown in fig-3. The highly organised 2D lattice formed at the water surface is called Langmuir film according to the name of Irving Langmuir who has immense contribution in this field.

![Fig-3 Different phases of monolayer formation](image-url)
The surface pressure-area per molecule (π-A) isotherm is important to investigate the surface behaviour of LB material on the air-water interface and the surface pressure is estimated for the stable LB film which is an important parameter for LB film deposition.

2.4.2 LANGMUIR BLODGETT FILM

Apart from the study of intermolecular distance from the Langmuir monolayer, the monolayer from water surface also can be transferred into solid substrate and, mono or multi layer of controlled thickness can be formed. These are highly organised and defect free film of molecular dimension. The properties of the film depend on fabrication procedure. Now, the transfer of Langmuir monolayer from air-water interface into solid substrate has been done by dipping the substrate vertically through the spread monolayer at a constant surface pressure which results in well ordered mono or multi layered film on to the solid substrate as shown in figure-6. K. Blodgett and I. Langmuir first invented this method. The film obtained by this process is called Langmuir-Blodgett film.
Depending on the nature of substrate and spread monolayer, the LB film shows different structure. If the substrate is hydrophilic then monolayer is transferred by up stroke. Then hydrophilic head group of the monolayer interacts with the surface of the substrate. Now if the substrate is hydrophobic then monolayer is first transferred by down stroke. Now hydrophobic tail group will interact with the surface of substrate. Hydrophilic substrate becomes hydrophobic after the transfer of first monolayer by up stroke. Thus second layer will be transferred by down stroke. This type of deposition is called Y-type deposition. In this way multilayers are prepared on a solid surface. This is the most stable film deposition process as the interaction between adjacent monolayers are of same type as hydrophilic-hydrophilic or hydrophobic-hydrophobic.

There are another ways available for formation of multilayers these are X type deposition and Z type deposition. If the deposition occur by down stroke only then technique is called X-type deposition and if the deposition occur by up stroke only then technique is called Z-type deposition as shown in fig-7.
Here in both cases i.e x and z type technique the films are less stable than y-type since the interaction is hydrophobic-hydrophilic.

2.5 CHARACTERISATION

The quality of the Langmuir-Blodgett films largely depends on the parameters like pH of subphase, temperature, speed of dipping, way of spreading the materials, surface pressure of lifting, speed of compression of the barrier. The characteristics of LB films are studied by UV-Vis absorption spectroscopy, Fluorescence spectroscopy, X-ray diffraction, Electron and neutron diffraction, Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Electron Spin Resonance (ESR), Raman Spectroscopy, Optical harmonic generation, Infra Red Spectroscopy, Pyroelectric, AES, SIMS, ESCA, Surface potential, Scanning transmission microscopy (STM), Brewster angle microscopy (BAM), Transmission electron microscopy (TEM) etc (R. H. Tredgold, 1994).

2.6 APPLICATIONS

The two dimensional assembly obtained by LB technique has various kind of applications such as organic conductors, organic diodes, organic field effect transistors, LEDS, sensors, rectifiers etc. Some specific applications of LB film with their constituents compounds are mentioned below:-


- The scientists named Kai Xiao, Yunqi Liu, Xuebin Huang, Yu Xu, Gui Yu and Daoben Zhu made Field effect transistors based on Langmuir-Blodgett films with Phthalocyanine derivatives as semiconductor layers (july 26, 2003)
- The scientists named Guofeng Xu, Zhenan Bao, and John T. Groves made field effect transistor based on LB films with Regioregular poly(3-hexylthiophene) (Jan 6, 2000).


2.7 CONCLUSION

Langmuir-Blodgett technique is a sophisticated process for preparing ultrathin organic, metallorganic, polymeric layers with desired characteristics which is not found in any other technique. Nowadays, the concept of storing and even processing information on a molecular or nearly molecular scale attract the research workers largely to work with this technique. To extract information at the molecular level by this method one has to arrange some special molecules in an ordered manner. Development of LB films for practical application is a challenge, requiring an interdisciplinary outlook and the process can be progressed with the collaboration of physicists, chemists, biologists, material scientists and computing specialists.
CHAPTER 3

SPIN COATING

3.1 INTRODUCTION

Spin coating is currently the predominant technique employed to produce uniform thin films of photosensitive organic materials with thickness of the order of micrometers and nanometers. Spin coating was first studied for coating of paint and pitch. The pioneering analysis of spin coating was performed more than fifty years ago by Emil et al., who considered the spreading of a thin axisymmetric film of Newtonian fluid on a planner substrate rotating with constant angular velocity. In many cases the coating material is polymeric and is applied in the form of a solution from which the solvent evaporates. This process is frequently used in the manufacture of integrated circuits, optical mirrors, color television screens and magnetic disk for data storage.

3.2 MODELING OF SPIN COATING

First of all the sample is prepared by dissolving the desired molecule (which is chosen for formation of film) with a solvent. For example, for formation of film like clay hectorite we can use Methanol as a solvent and after stirring the solution in well manner (say for 24 hours), the sample is made ready for preparation of the film. The machine used in spin coating technique is called spin coater. Now a solid substrate such as cover slip is settled on the spin coater in such a way that while rotation the substrate is not flown away from the settled place. This is done by a motor pump, which sucked the slide tightly while it is in motion. As a result the slide is get stucked. When the slide starts to rotate the coating process with the prepared sample get started. Generally, the sample is poured on the slide by a syringe. The number of rotation and the time of rotation can be set manually.

Centrifugal force due to rotation drives the liquid radially outward. The film thins by the combination of outward fluid flow and evaporation.
3.3 KEY STAGES

The technique of the spin coating can be effectively modelled by dividing whole process into four stages as shown in figure -iii, which are :- deposition , spin up(increase in rpm) , spin-off (decrease in rpm) , evaporation of solvents . First three stages are commonly sequential, but spin-off and evaporation stage usually overlap. Flow controlled or spin-off and evaporation stage are most important stage for maintaining coating thickness.

Deposition:-

During this stage, solution provided to fall on rotating substrates from syringes and the substrate is accelerated to a desired speed. Spreading of the solution takes place due to centrifugal force and height is reduces to the critical height. This is the stage of delivering an excess of the liquid to be coated the surface of the substrate a portion of which is immediately covered or wetted. This stage is ends when delivery ceases.

Spin- up:-

The second stage is when the substrate is accelerated up to its final desired rotation speed. This stage is usually characterized by aggressive fluid expulsion from the wafer surface by the rotational motion. Because of the initial depth of fluid on the wafer surface, spiral vortices may briefly present in this stage ; these would form as a result of the twisting motion caused by the inertia that the top of the fluid layer exerts while the wafer below rotates faster and faster. Eventually, the fluid is thin enough to be completely co-rotating
with the wafer and any evidence of fluid thickness differences is gone. Ultimately, the wafer reaches its desired speed and the fluid is thin enough that the viscous shear drag exactly balances the rotational accelerations.

Stable fluid outflow:-

This stage is also known as spin off or spin down process in which the speed of rotating substrate will get decrease slowly. In this stage when substrate is spinning at a constant rate the fluid viscous force dominate fluid thinning behaviour. Due to fluid outflow in this stage the coating thickness much more reduce.

Evaporation:-

When spin-off stage ends the film drying stage is started. During this stage centrifugal outflow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. In this stage when the substrate is spinning at a constant rate the solvent evaporation dominates the coating thickness behaviour. Here the rate of evaporation mainly depends on the difference in partial pressure of each solvent species between the free surface of the liquid layer and the bulk of the gas flowing nearby.

3.4 ADVANTAGES AND DISADVANTAGES OF SPIN COATING:-

The advantage of spin coating is its ability to quickly and easily produce very uniform film, ranging from few nanometers to micrometers in thickness. Film thickness is easily changed by changing spin speed. It is a low cost and fast operating system. Due to the ability of high spin speeds, the high air flow leads to fast drying times for the formation of the film.

The biggest disadvantage of spin coating is its lack of material efficiency. Typical spin coating processes utilize only 2–5% of the material dispensed onto the substrate, while the remaining 95–98% is flung off in to the coating bowl and disposed. If economically feasible manufacturing costs are to be maintained, a method for improving this material utilization is of primary importance, especially in the flat panel display area.

3.5 APPLICATIONS

Spin coating has been used for several decades for the application of thin films. It is widely used in the manufacture of integrated circuits, optical mirrors, magnetic disk for data storage, device of solar cells, detectors, sensors, VLSI (very large scale integration), nano scale device (quantum dots, carbon nanotubes), DVD and CD ROM, photo resist for patterning wafers in microcircuit production, insulating layers for microcircuit fabrication such as polymers (where it can be used to create thin films with thickness below 10 nm), flat
screen display coatings, antireflection coatings and conductive oxide etc. Some specific applications where spin coating is being used with constituent compounds are listed below:

- Carbon nanotube and metal oxide hybrid materials for gas sensing made by T. Kerdcharoen, C. Wongchoosuk (2013)
- Photoresists are typically comprised of base resin e.g. novolak, bisazide, or epoxy and photoactive compound e.g. DNQ (diazonaphtoquinone) or hexafluoroantimonite salt and solvent e.g. MEK (methyl-ethyl ketone), PGMEA (methoxy-propyl acetate) done by Sami Franssila, Santeri Tuomikoski (2010)

3.6 CONCLUSIONS

From the above mentioned description we get some idea about the spin coating process and the basic physics behind that. Actually spin coating has been universally used in the semiconductor industry long before but hardly any theoretical study has been initiated. An accurate theory of spin coating would permit better design and control of the process in its various applications. For this, the researchers have to take this process in serious note and have to take the initiative to develop the technique in a better way.