Chapter 2

General Review, Aim and Objective
Abstract

This chapter highlights the research activities and scientific developments occur in the field of ultra thin films of organic molecule prepared by Langmuir- Blodgett and Layer by Layer (LbL) technique. Also contains aim and main objective of the research work.
2.1: Introduction:
Deposition of thin films at the air-water interface has been studied for almost a century. Some of the techniques developed during the past five decades are widely used in the industries. The field of material Science has been an extended interest on scientific and engineering research because of large optical anisotropy and fundamental success of molecular engineering in creating a new class of materials that allies organic, polymeric and even biological components with appropriate physical and optical properties. Thus the thin film studies have directly or indirectly achieved advanced growth in 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 the film [1]. In 1990s, the creation of molecularly controlled nanostructured films was dominated by the Langmuir-Blodgett (LB) technique, in which monolayers are formed on air-water surface interface [2] and then transferred to a solid substrate [3-4]. In addition, these films are widely used in the preparation of various models mimicking biological membranes [5]. Kuhn and his group performed initial work on synthetic nanoscale heterostructures of organic molecules in the 1960s using the LB technique [6]. In 1891, Agnes Pockels first prepared ordered monolayer at the air-water interface [7] and using Pockle’s idea Ketherene Blodgett made several experiments on ordered multilayers and published his research on 1935 [8]. Irving Langmuir developed the first theoretical basis on surface science [9] for which he was awarded nobel prize in 1932. Irving Langmuir carried out a systematic study of the monolayer on various amphiphilic materials at the air-water interface. Langmuir along with Ketherene Blodgett developed the basic methodology to transfer the floating Langmuir monolayer from the air-water interface onto a solid substrate. Hence for the methodology of transferring the monolayer from the air-water interface onto a solid substrate was named after them and referred to as Langmuir-Blodgett (LB) technique. The mono and multilayer film on the solid substrate was named as Langmuir-Blodgett (LB) film. Early research activities on Langmuir-Blodgett (LB) films has been summarized by G.L.Gains [10], G.G.Roberts [11], I.R.Peterson [12], K.Ulman [13], R.H.Tradegold [14] and more recently M.C.Petty [15]. Extensive research activities and technological applications of Langmuir-Blodgett film have been started over last 15 years. Their precise thickness, coupled with a high degree
of control over their molecular architectures have now been firmly established a role of these organic multilayer LB film in thin film technology. The LB technique of thin film deposition is one of the few thin film technologies that actually permit the manipulation of materials at the molecular level. The LB technique requires special equipment and has severe limitations that are often expensive and difficult to maintain. This technique is also limited by substrate selection with respect to size and topology [16] as well as film quality and stability. It was therefore desirable to develop a simple approach that would yield nanostructured films with good positioning of individual layers, but whose fabrication would be largely independent of the nature, size, and topology of the substrate. Another novel and eclectic topic is the so called layer-by-layer (LbL) technique. This approach is based on the alternating adsorption of materials containing complementary anion and cation pairs. Thereby ultra thin layers and films can be assembled with different techniques and chemical modifications.

It is about over 20 years since layer-by-layer (LbL) assembly was introduced as yet another method to functionalize surfaces and to fabricate thin films which is solution based method to grow hybrid organic/inorganic thin films. It provides structure control for the integration of light-absorbing and semiconducting materials on the scale of nanometers and necessary for the fabrication of efficient cell structures. Starting with simple bola-shaped amphiphiles [17] and it was quickly extended to simple polyelectrolytes [18], and functional macromolecules including proteins [19-20] or DNA [21-22]. Eventually, in 1994, biological nanoparticles [23] and inorganic nanoparticles [24-25], including magnetic [26] and gold [27] nanoparticles, were added to the list of possible multilayer film constituents.

Layer-by-layer (LbL) method was first developed and introduced by Iler at Dupont, for the fabrication of multilayers by alternating deposition of positively and negatively charged colloid particles [28] (paper published in1966) and first performed and established by Decher and co-workers [29] at the beginning of the 1990s that initiated new attention to the topic. The main idea of LbL method is to utilize electrostatic interactions to deposit the material in controllable manner. Several steps are repeated consecutively to obtain desired number of layers. When immersed in a solution of positively charged polyelectrolyte, such as poly(diallyldimethylammonium chloride)
(PDDA), poly(allylamine hydrochloride) (PAH), or polyethylenimine (PEI), and subsequently rinsed by pure water (the aim of rinsing is the removal of loosely adsorbed polyelectrolyte from the substrate), the net charge of the substrate's surface becomes positive because of the adsorption and overcompensation of polyelectrolyte with opposite charges. Subsequent execution of the analogous procedure with a negatively charged polyelectrolyte solution, such as poly (styrene sulfonate) (PSS), poly(vinyl sulfate), or poly(acrylic acid) (PAA), leads to the net surface charge reversal on the substrate that occurs with each adsorption step leads to the polyanion conformation and layer interpenetration [16] and bringing it back to the starting point. In theory, there are no limitations with respect to substrate size and topology due to the fact that the process involves adsorption from a solution. Nanolayer films have been created on objects of a variety of different sizes. However, this method is robust and is easy to fabricate heterostructures films. The layer thickness can be controlled precisely, and the fabricated film has high durability. The LbL technique is not only applicable for polyelectrolyte/polyelectrolyte systems but also in any type of charged species, including inorganic molecular clusters [30-31], nanoparticles (NPs) [32], nanotubes and nanowires [33-34], nanoplates [35-36], organic dyes [37], dendrimers [38], porphyrins [39], biological polysaccharides, [40-41], polypeptides [42-43], nucleic acids and DNA [44], proteins [45-48], and viruses [49] can be successfully used as components to prepare LbL films. The list of materials is not limited for polymeric materials; charged inorganic substances, including colloidal nanoparticles [50] clay [51] nanosheets [52] modified zeolite crystals [53] two-dimensional perovskite [54] and polyoxometalates [55] bolaamphiphile monolayers [56] lipid bilayers [57] and stacked dye molecules [58] are appropriate for LbL method as well.

The LbL assembly technique has become wide range of potential applications for fabrication of thin films and has been practiced by numerous research groups worldwide. These are including such diverse areas as drug delivery systems [59], biomedical applications [60], food applications [61], micropatterning [62] and solar-energy conversion [63].
2.2. International Level Research Activities on Ultra Thin Film of Organic materials:

Thin films have been of great interest for more than a hundred years because of their technological applications in the fields of optoelectronic, photonic and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. In addition, optical and electrically active as well as magnetic thin films can be usefully employed in sensor, transistors, solar cell, magneto-optic memories, magneto-optic discs, thin film electro acoustic devices as well as other emerging cutting technology [64].

The properties of material significantly differ when analyzed in the form of thin films. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films of organic and inorganic materials are now being extensively studied by the researchers around the world for their possible application in modern technology [65-66].

There are several research groups throughout the world working on various aspects of thin films prepared by LB and LbL technique. The Langmuir-Blodgett (LB) technique offers the possibilities of a highly ordered mono and multilayer and realizes that the construction of molecular architectures which allow the study of physical phenomenon on a molecular scale. The ‘modern’ era of Langmuir-Blodgett (LB) film research activities was actually initiated from the early 1970’s with the pioneering works of Kuhn and his co-workers. In the recent times Dr. Thomas J.Pinnavaya Department of chemistry and Material Science, Michigan State University, USA, Dr. Harry Finklea Department of chemistry Virginia University, USA. are working on the practical applications of Layer by Layer Self Assembled Monolayers. Research team at university of Leicester is working on a new technique for growing nano-ordered films which could have extraordinary implications in electronics and molecular engineering. Dr Andrew Ellis and Dr. Shengfu Yang, Professor Chris Binnus and Dr. Klaus von Haeften and their groups are working on developing this technique in order to get assembled structures of nano order that cannot be achieved by conventional methods of film fabrication. Apart from this almost every country in this world is now interested in this field and is working on the
electrical and photophysical characteristics of LbL films. Thin films prepared by different processes have shown remarkable capability for the immobilization of proteins and cells and subsequent application in biocatalysis, drug delivery, and tissue engineering [67-70] etc. Many schemes have been developed where LB and LbL films can be utilized in conjunction with more conventional microfabrication technique to extend the capability of microelectronic devices, as constituents of various chemical sensors, transducers and also for numerous biological, technical applications.

2.2.1: Thin film used as biosensors

There has been an extended interest on biosensors for rapid and reliable detection of biological particles or molecules mainly enzyme, lipid, membrane etc. In addition, microorganisms, animal or plant whole cells and tissue slices can also be incorporated in the biosensing system. An optical biosensor is a compact analytical device, having biological sensing element, integrated or connected to an optical transducer system. The working principle of biosensors is mainly based on adsorption of biological molecule to be detected on a sensitive surface, made of a thin film modified with receptor probes. Immobilized enzymes possess a number of advantageous features to make enzyme films as biosensors, is of two types viz oxyreductase biosensors and nanoxyreductase biosensors. The thin film acts as a physicochemical (optical, mechanical, magnetic, or electrical) transducer, which converts the signal resulting from the recognition of the biological analyte into another measurable signal. These biosensors are complex structures of thin films, which give enormous functionalities to the sensors.

Polyaniline based Langmuir-Blodgett film has been used as a cholesterol biosensor. Cholesterol oxides (ChOx) has been covalently linked to Langmuir-Blodgett (LB) monolayers of polyaniline (PAN)-stearic acid (SA) prepare onto a indium-tin-oxide (ITO) coated glass plates [71].

Bazan et al. developed an energy transfer based DNA sensor that possessed high signal amplification due to efficient energy transfer from a cationic conjugated polymer to a dye labelled probe molecule [72]. Caruso et al. [73] were the first to prepare an immunosensor by embedding anti-immunoglobulin G (anti-IgG) monoclonal antibodies into LbL films. The unique advantages of immunosensors prepared by LbL methods
including low unspecific background reactivity, high sensitivity, and good response linearity over a large magnitude of antigen concentrations are further disclosed by Diederich et al. [74]. Rusling and co-workers applied the DNA sensors to the detection of chemical toxicity [75-77].

An enzymatic glucose sensor based on hybrid organic-inorganic Langmuir-Blodgett films has been developed. In this sensor glucose oxidase (GOx) can be immobilized in hybrid LB films consisting of octadecyl trimethyl ammonium (ODTA) and nano-sized prussian blue (PB) clusters. These ODTA/PB/GOx LB films showed a glucose sensing action at a very low operating system. Olivera and his group developed phytic acid based on mixed phytase- lipid Langmuir- Blodgett films [78]. It is sure that the materials used in the innovative fabrication of biosensors improve the novel design and result in enhancement of the sensitivity and specificity of the miniaturized device.

2.2.2: Thin film as optoelectronic devices.

In recent year’s development on organic light emitting diodes (OLEDs) have earned considerable attention compared to conventional inorganic LEDs. The organic devices offer specific advantages and are expected to yield new applications, such as large-area flexible displays with full color and low cost. Among conducting polymers a certain class has electroluminescent properties that is they emit light when exposed to electricity. The main advantage of these materials over conventional luminescent materials are the tunneling of emission wavelength by chemical modification, low operating voltage, flexibility, easy processing, low cost of making large devices and output colours in whole visible spectrum. Several p-type conducting polymers have been tested in LB and LbL films [79-83] and it is widely used as hole injecting electrodes, like polypyrrole, polythiopene derivatives and polyaniline, which have greater tendency for injecting and transporting holes than for electrons. The relatively ordered nature of LB arrays of molecules may be exploited in light emitting structures. The technique of improvising the efficiency of the optical LED by using insulating LB layers was demonstrated by M. C. Petty, in which both the emissive layer and the hole transport layer were deposited by thermal evaporation technique. Also to improve the lifetime of
the OLED, several experiments of MEH-PPV LB films have been done by Petty et. al [84]. In a more recent work, effort was made by M. C. Petty in order to increase the electron-injection of hybrid of pyridine and oxadiazole [84]. Recently, Rubner has used the LbL assembly method to develop new processing techniques that can be utilized to manipulate organic systems at the molecular level [85]. The idea is that the ability to manipulate the manner in which molecules organize at the molecular and supermolecular level will make it possible to likewise control and tailor specific properties at this nanoscale level.

Several conducting polymers such as polyacetylene, polythiopene, polyindole, polypyrrole, polyaniline etc. have also been reported as the electrode materials for rechargeable batteries [86]. These batteries exhibit the same voltage and current as their bulky counterparts, but their thinner dimensions allow for greater applications such as making thinner electronic devices, like cell phones, laptops and even implantable medical devices and reducing the weight of common devices that are run on battery power because of the batteries high energy density.

2.2.3 Applications of ultra thin films in Drug Delivery:

Ultra-thin films (hundreds of nanometers or less) are a prime example of a high-tech application that requires such nanoscale characterization. Optimizing thin film properties requires a well-understood relationship between processing parameters, modeling, and model confirmation through novel testing techniques.

The history of drug delivery teaches us that it was discovered accidentally and from then on various technologies for drug storage and release have been developed. It started with macroscopic delivery devices. In 1960 micro delivery systems were adopted and available clinically in the 1980s. The nano era started in the middle of 1970 and introduced in targeted polymer-drug conjugates and in surface controlled drug delivery system [59]. A major challenge in the development of advanced drug formulations is the elaboration of delivery systems, capable of providing sustained release of bioactive materials. The field has been growing rapidly, and many researchers have contributed to the development of new LbL drug delivery systems [87-89]. For example polycyclodextrins (PolyCDs) with charged groups can be used to sequester hydrophobic
drugs such as anti-inflammatory agents, and subsequently can be layered in multilayer thin films to create stable thin films [90]. Micelles, liposomes or other colloidal carriers and nanomaterials such as nanoparticles may also be used as drug carriers that can be directly introduced into multilayer thin films [91-94]. Thin film fabricated out of micro capsules containing pyrene as a model drug. Microcapsules were fabricated by the layer-by-layer approach [95-98] on melamine formaldehyde (MF) particles with pyrene and chitosan. Mueller et al. [99] constructed LbL thin films consisting of PEI and PAA. It was demonstrated that adsorption of a positively charged protein took place at pH 7.3, where the outermost layer of the film was negatively charged. Complete desorption was obtained at pH 4, where the external layer was neutral. Paula T. Hammond, Department of Chemical Engineering, Koch Institute of Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, is working in the field of drug delivery using the ultra thin film of bio active materials prepared through LbL technique.[100] Ultra thin films prepared by different process have been extensively used in the drug formulation and gene delivery [101-104]. Another exciting area in which ultrathin films have a true potential is regenerative medicine and tissue engineering [105-108]. M.C.Petty currently heads the Molecular Electronics Research Group and co-directs the University of Durham Centre for Molecular and Nanoscale Electronics has established an international reputation in the area of ultra-thin and nano-scale organic films and the exploitation of their optical, electro-optical and biological properties.

2.3. National level research activities on ultra thin film:

2.3.1: Langmuir – Blodgett technique:
The Langmuir – Blodgett (LB) technique is widely used by several research groups to prepare ultra thin films in all over India. Both photo - physical and electrical characterization of various organic, organometallic, Liquid Crystal and bioactive materials in LB films are currently being investigated by various groups of India [109]. The following research groups in India are currently using this technique in ultra thin film preparation: NPL New Delhi, IACS Kolkata, IIT. Mumbai, BHU. Varanasi, NCL Pune, IIT. Guwahati, Jawahar Lal Nehru Centre for Advanced Scientific Research, Bengaluru, Department of Physics, Department of Chemistry, Tripura University,
Tripura. In the department of spectroscopy, IACS, Kolkata, Professor G. B. Talapatra and his group is mainly concentrating to study the electrical properties, optical properties, ultra structure, bio – sensing properties of LB deposited thin films of organic molecular system [110]. Professor S. S. Major along with his group in the Department of Physics, IIT Bombay are recently investigating morphology, electrical and photo physical characteristics of nano crystalline thin films formed by LB technique [111]. Professor A.J. Pal and his group in the Department of Solid State Physics, IACS, Kolkata is mainly concentrating on the study of photo physical and electrical characterization of ultra thin films and their feasibility in the formation of electronic, photonic memory and switching devices [112]. Professor B.D. Malhotra and his research group in NPL New Delhi has been actively working towards the application of bio sensors, conducting polymers to Schottky Diodes semi conductor devices as well as in the technical development molecular electronic devices [113]. Professor M.K. Sanyal and his group, Surface Science Division, Saha Institute of Nuclear Physics, Calcutta, investigating the growth mechanism and morphology of Langmuir – Blodgett films [114]. The department of physics, Tripura University is working on the feasibility of formation and characterization of molecular assemblies in Langmuir – Blodgett films [115-116].

Our research group in the Department of Chemistry, Tripura University is working on the formation of stable LB films by doping the Organic and charge transfer molecules [117] and changing various LB parameters as well as the pH of the subphase. Dr. K.K.Raina, and his group in Thapar University. Punjab, is working on the film preparation of liquid crystal, bioorganic molecules etc. and studying the morphology, and photophysical properties of the film [118].
2.3.2. Layer by Layer assembled technique:
Besides the worldwide research activity, there are various research groups working with LbL technique to prepare ultrathin films in India. In India, several groups are using Layer by Layer (LbL) technique for fabrication of ultrathin films. Various groups at IACS, Jadavpur, Kolkata have reported papers in this line of work. Other than that, Department of mechanical Engineering IISc, Raman Research Institute, Bangalore, IACS, Kolkata, Institute of Physics, Bhubaneswar, Institute of Technology and Science, Indore, Institute of technology, Roorkee, Institute of medical science and technology, Energy and Research Institute, Barbari, Central Glass and Ceramic Research Institute, Kolkata are also working in this field. Dr. Dipak Kumar Goswami, IOP Bhubaneswar, Dr. K. Krishnamurty Rao, Tata Institute of Fundamental Research (TIFR), IIT Chennai and Dr. D. Bhattacharjee, Dr. S. A. Hussain and his group, Department of Physics, Tripura University, is also carrying out significant research. Several groups in India are also involved in significant research and development in Layer-by-Layer self assembly for example Prof. B. D. Malhotra in NPL New Delhi, Prof. S. S. Major, IIT Bombay, Prof. A. J. Pal, IACS Kolkata V. Bindu, M. Venkataramanan and T. Pradeep, Indian Institute of Technology, Department of Chemistry and Regional Sophisticated Instrumentation Centre, Madras, V. Ramgopal Rao and his group, at Department of Electrical Engineering, Indian Institute of Technology (IIT), Mumbai, Prof. S. P. Moulik at Centre for Surface Science, Department of Chemistry, Jadavpur University.

2.4. Aims and objective of the research work:
Thin films down to monolayer thicknesses are of scientific and engineering interest since decades with a high potential for and an increase in application. Both organic and inorganic materials are deposited in thin and ultra thin film form on a huge variety of substrate materials. Depending on the combination of substrate and thin film material, the deposition process needs to be chosen as well as the characterization methods for spectroscopic behavior, adsorption kinetics of the bio-active molecules, aggregation behavior, any new properties (J aggregation, H aggregation, eximer formation etc.), homogeneity measurements, durability, reproducibility and functionality tests. There are many technological applications of thin films, e.g. lubricants [119], electronic
components [120-121], paper protection, food and food packaging [122-123], solar cells [124], smart windows [125], thermal barriers [126], and in the field of bio-medical application for the enormous application of the study of thin film in life science the present work was carried out. The organic thin films deposited mainly onto non-organic substrates such as glasses, silicon wafer, mica substrate etc. The main objectives of this work are:

1. To fabricate and characterize Langmuir and Langmuir-Blodgett (LB) films on solid surface (quartz/silicon wafer) prepared by transferring the Langmuir monolayer from the water surface. Variation of composition of the mixture on the LB films will also be analyzed. Therefore, the spectroscopic and aggregating properties of nonamphiphilic molecules, when mixed with long chain fatty acid viz. Arachidic acid (AA) and a polymer such as Poly methyl methacrylate (PMMA) are investigated. A comparative study has also been investigated when the nonamphiphilic molecule mixed with two different matrices.

2. To investigate the successful incorporation and detailed spectroscopic studies of an anionic dye into LbL films along with the poly cation, poly (allyl amine) hydrochloride (PAH), and also investigate the spectroscopic behaviour of organic molecules in ultra thin films.

3. This study is focused on the monolayer characteristics and miscibility behaviour of non amphiphilic substance when it is mixed with two different matrices viz behenic acid (BA) and poly methyl methacrylate (PMMA) at the air–water interface. Two different matrices are used due to their different dielectric constant, which gives different polar environments for the subject molecules. Another reason for using two matrices is that they have different inner spacing which may create the conformational change of the subject molecule. And also studied the condition under which certain new properties (J aggregates, H aggregates, eximer etc) of the organic bioactive molecules appeared.

4. Generally amphiphilic molecule (water insoluble) can form a stable Langmuir film at the air–water interface but present study is focused on a water soluble dye, and fatty
acid to know about the mixing behaviour and to characterize the complex film form in the Langmuir and Langmuir-Blodgett films. This study is done in order to reveal the adsorption behavior and organization of dye molecule on the complex monolayer film at the air-water interface.

5. Present work also carried out to investigate the monolayer characteristics of liquid crystals molecules mixed with arachidic acid (AA) at air–water interface and in LB films. The current investigation has been done to understand the stability of the films. The spectroscopic behavior of the bio-liquid crystal molecules in solution and in films also studied.
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