Layer by Layer (LbL) Technique for fabrication of electrostatic Self assembled ultrathin films

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Abstract

Layer by Layer (LbL) technique is a unique way for fabricating ultrathin nanostructured electrostatic self assembled films of water soluble material with controlled layer structure and lattice parameters etc. LbL films have many technical applications in the field of molecular electronics and biotechnology. This paper reports the early development, technology and application of LbL films along with national and international status of this newly booming technique for the fabrication electrostatic Self Assembled ultrathin films.

Keywords: Layer by Layer (LbL) films, Polycation, Polyanion, Electrostatic interaction

Introduction

Ultrathin films in the recent years are technologically very important due to their vast applications in the field of molecular electronics and optical devices. For the last five decades molecular assemblies of supramolecular structure in nanometer scale were mainly achieved by Langmuir Blodgett (LB) technique. LB technique has certain restrictions on the type of materials and requires LB compatible materials i.e., amphiphilic molecules for film formation which are ideally suited but recently non amphiphilic molecules (without any hydrophobic chain) mixed with a long chain fatty acid (viz. Stearic acid or Arachidic acid) or with an inert polymer matrix (Polymethyl Methacrylate or polystyrene) are also observed to form stable LB films [1-4]. Now a days LB film of water soluble organic molecules are also reported but formation of LB films of water soluble material is a very complicated process and depends on the degree of interaction between the cationic surfactant and water soluble molecules and also requires a certain amount of time to reach the state of stability which might be a
problem towards the commercial application of the process. It is observed that interaction does not take place between all molecules at all conditions and requires certain microenvironment and other specific conditions for fabrication of stable film [5-6].

The most recent method along the direction of thin film fabrication of water soluble molecules is based on Layer by Layer Self adsorption process in which positively and negatively charged polycation and polyanion interact electro-statically to form mono and multilayered LbL films. Construction of functional and organized multilayered bio-molecule containing LbL film in predetermine ways is an important arena of research in biochemistry and biotechnology, which have potential application for fabrication of bio-molecular devices. The application of these bio-molecular devices is envisaged in such areas as bioelectronics, biosensors, biophysics, artificial bio membranes and bio-computing [7-8].

History

For more than 60 years multilayered organic films were fabricated dominatingly by Langmuir-Blodgett (LB) technique in which monolayers are formed on a water surface and then transferred onto a solid substrate [1-2]. Around 1960 Kuhn and his coworkers did pioneering work on synthetic Nanoscale Heterostructures of organic molecules [3].

In 1980, self assembled techniques based mainly on silane-SiO₂ and metal phosphate chemistry was developed as alternate LB films. These had some restriction on the choice of classes of organic substances and also the quality of films. Around early 1990’s G.Decher and his team focused a new route for Layer by Layer (LbL) Self assembly technique for the fabrication of thin films by electrostatic interaction. There after deposition of Heterostructures and device fabricating was reported. In the recent years deeper studies have been carried out on deposition processes and application of films fabricated by Layer by Layer self assembled technique. Now days there are few reports on the formation of Layer by Layer Self Assembled films of low molecular weight organic dye molecules [7].

Materials Required

Different process of fabrication has different types of constraints to several physical and chemical properties of the materials or the samples that can be used for the build up process. Materials that are compatible for the formation of LbL Self Assembled films are i) Polycations ii) Polyanions e.g. PAH (poly-allylehydrochloride), PAA poly(acrylic acid), PDDA poly( dimethylidiallyl ammonium chloride) etc. are Polycations and Amaranth, Rose Bengal, Congo red, Chicago sky blue etc. and all kinds of anionic dyes are polyanions. Moreover LbL films of organic dye molecules are reported and recently LbL films of protein and other biologically active molecules such as DNA RNA etc are also reported [7-8].
**Fabrication of LbL films**

The Layer by Layer technique of formation of thin film is employed for its simplicity in methodology. In this case polyanion and polycation deposition on a quartz surface take place due to strong electrostatic attraction occurs between charged surface (made by adsorption of polycation) and an oppositely charged molecule in the solution (polyanion). This phenomenon has long been known to be a factor in the adsorption of small organics and polyelectrolyte. But it is rarely observed in molecular layer formation.

The principle of this technique is the charge reversal of the film layer during each dip which makes the surface alternate charge reversal. The film is deposited on glass/gold or quartz substrate by dipping the slide into a beaker containing polycation, manually or by automated device, and there by making the substrate positively charged (i.e. the slide positive ) and then multilayered films are formed by the adsorption of polyanion and polycation successively (shown in figure )

**Elaborate discussion of the method comprises of the following steps:**

First of all, electrolyte deposition baths are prepared with about $10^{-3}$ M (based on the repeat units of Polyanion and Polycation) aqueous solution using triple distilled de-ionized (18.2 MΩ) Millipore water. Then fluorescence grade quartz slide which is washed extensively is dipped in a beaker containing polycation solution making the slide a positively charged surface. The slide is dried completely and then rinsed into a water bath which causes a wash away of excessive ions from the surface of the slide. The film is dried and is then dipped into a beaker containing a solution of negatively charged polyelectrolyte. The film is again washed and dried. Repetition of the above mentioned procedure puts in the architecture of building charge transferred layer by layer Multilayered organic and inorganic ultra thin films.

Dipping a cleaned quartz substrate into a solution of positively charged polyelectrolyte (polyanion) results in adsorption of first layer. A washing step is needed to remove supernatant material. Now the surface potential is positive and a polyanion is adsorbed and thus one bilayers is formed. Again, a washing step.

**Characterization of the LbL films**

The characteristics of the Layer by layer self assembled films largely depends on the parameters like pH of temperature, Time of dipping, dissolution of the materials.
Ultrathin films fabricated by Layer by Layer technique are mainly characterized by UV-Vis absorption spectroscopy, Fluorescence Spectroscopy, X-Ray diffraction (XRD), Raman Spectroscopy, IR spectroscopy. Other than that harmonic generation, Electron and neutron diffraction, Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Electron Spin Resonance (ESR), Raman Spectroscopy, Optical harmonic generation, Infra Red Spectroscopy, Piezoelectric, AES, SIMS, ESCA, Surface potential, Scanning transmission microscopy (STM), Brewster angle microscopy (BAM), Transmission electron microscopy (TEM) etc.

**National and International Status**

**International status**
In 1927 Irving Langmuir and Katherine Blodgett developed an elegant technique for the fabrication of ultrathin films and the process later known to the world as LB technique paved the way for the development of fabrication of ultrathin films. However the technique has not been successful in the commercial sector although the scientific results related to LB films have been quite exciting but there was never a commercial breakthrough. These problems associated with the practical application of Langmuir-Blodgett technique have been solved G. Decher and his worker by a pioneering the development of Layer by Layer Electrostatic self assembled technique for the fabrication of Ultrathin Films.

Other works on self assembled monolayers at that time was done Ralph G.Nuzzo, PhD. [9]. In 1992 Dr. Harry Finklea reported about the electronic transfer kinetics of organized monolayers then in 1997 two famous papers of G.Decher and Julius Rebek. Jr PhD. reported the pioneer work of their group which envisioned the development of the foresaid technology [10-11].

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 univerist of Leicester is working on a new technique for growing nanoordered 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.

**National status**
Work on self assembled monolayer boomed all around the world since 1990. 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 then that Department of mechanical Engineering IISc, Raman Research
Layer by Layer (LbL) Technique for fabrication

Institute, Bangalore, Institute of Technology and Science, Indore, Institute of Physics, Bhubaneswar, 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, Tripura are caring out significant research activities in this field.

Conclusion
The assembly of multilayers by LbL (Layer by Layer) technique is a unique novel approach for the fabrication of ultrathin films on solid substrate. This technique has high flexibility over the selection of materials from small organic molecules, polymers, proteins, ceramic, colloids to bio active molecules. The organization of different molecular units in ordered Nanoscale range has potential towards device fabrication. As the films fabricated by LbL (Layer by Layer) process show dynamic change in photophysical properties from bulk or solution so future development of this technique will provide an envisioned up growth towards the understanding of anisotropy and other photophysical characteristics of electro-statically organized self assembled molecular assemblies, which could lead to remarkable progress in the arena of device fabrication as well as also fundamental research.

References


