OVERVIEW ON STRUCTURAL PROPERTIES OF ULTRA THIN FILMS OF SOFT MATTER

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ABSTRACT:

In this article, a brief overview of the soft matter low dimensional systems has been presented. This article also describes brief history of thin films, peculiar properties of thin films and their applications approach. Further, general introduction about the periodic nanocrystalline growth of thin film and different approaches for the preparation of such nanocrystalline structure along with their applications has been discussed. It has evaluated the fundamental x concepts required to understand the physics of soft matter thin films and prospective methodologies which are appropriate to describe the theoretical orientation. Other issues covered included a brief discussion regarding an explanatively literature survey of relevant considerations. Each of the various aspects of literature survey has been structured to bring out the linkages between different systems discussed and also between the findings of survey.

Keywords: Ultra, Thin, Films, Nanocrystalline, Physics

INTRODUCTION:

The need of studies on the physical properties of thin films and multilayers of soft condensed matter. A detailed literature survey about the soft condensed matter thin film growth produced by the different methods, the effect of different parameters on the structural properties of thin films and the possibility of tuning and tailoring the desired properties has been done. It also contains a general introduction with a brief overview of relevant parts of existing work and concept required to interpret the experimental results. In the end, a brief overview of the work carried out and highlighting the motivation of the present work is discussed.

SOFT CONDENSED MATTER:

Soft matter comprises of materials such as polymer, colloids, surfactants and liquid crystals and their composites. They do not belong to any conventional class of materials, instead, they lie somewhere in between solids and liquids. Soft matter consists of units much larger than atoms but smaller than corresponding bulk; their typical length is 0.01 pm-100 pm. It represents a variety of physical states that are easily deformed by thermal stresses or thermal fluctuations, electric or magnetic fields. Such materials are important in a wide range of technological applications. Research topics in this diverse area ranges from innovative studies of the basic properties of condensed-matter systems to the nanofabrication and study of advanced electronic, nano-mechanical, optoelectronic and spintronic devices. They may appear as structural and packaging materials, foams and adhesives, detergents and cosmetics, paints, food additives, lubricants, sensor and digital electronics etc. Their universal presence in above mentioned applications has firmly established their versatility, integrity, and dependability. At the same time, their continuing expansion into new technologies and applications has inevitably revealed potential shortcomings and subtleness in their properties and behavior. In spite of the various forms of these materials, many of their properties have common physicochemical origins, such as a large number of internal degrees of freedom, weak interactions between structural elements, and a delicate balance between entropic and enthalpy contributions to the free energy [1-4]. Modern materials (especially those involving thin films) are increasingly produced in configurations in which the functionality and limitations of systems are determined by their surface or interfacial properties and by the structure and nature of atomic defects at these surfaces and interfaces. In the recent years, nanotechnology has shown great promise for providing breakthroughs in near future that is likely to change directions of technological advances in a wide range of applications.

LOW DIMENSIONAL SYSTEMS:

Low-dimensional systems have attracted increasing interest both in the fundamental and technological context. Low dimensional systems refer to those systems in which at least one of the three dimensions is exhibit nanometric size of the materials. Such reduction can however, be in one, two or all the three dimensions and accordingly have 2D (nanolayers), 1D (nano-wires) and 0D (nano-particles or nano-dots) structure, allow the carriers to move freely in two, one or zero dimensions respectively. Current research trend includes the fabrication of nanostructures in the form of thin films/multilayers, nano-wires, nano tubes, quantum dots etc. Low dimensional systems also referred as nano-materials (nanolayer) sometimes demonstrate completely different properties from bulk [5; 6]. The quantum confinement effect, large surface to volume ratio and interface energies of nano-materials are the probably reasons behind this. Among the various types of low dimensional systems, nanolayers on the substrate surface have received much attention due to their critical importance in different device applications such as integrated circuit (ICs), microelectronics, optoelectronics, digital sensors, biosensors etc. The wide use of nanolayer heterostructure in important engineering applications also has initiated extensive research on structure of nanolayer materials. The explosion in both academic and industrial interest in these materials over the past few decades arises from the remarkable variations in fundamental optical, electrical and magnetic properties that occur as a progress towards low dimensional system. These properties are strongly correlated with the structures of low dimensional systems. For example, high sheet resistance due to the rough surface morphologies of Ag and Au layers, have been found on electrically insulating substrates [7] which led to reduced device yield and poor optical quality, repeatability and reliability [8; 9]. Similarly bulk structure can be modified and even can be made smoother by incorporation of certain layer at the film-substrate interface [10; 11].

A vast amount of physical phenomena are inherent in systems having restricted dimensionality and are frequently studied to enhance the understanding of fundamental theories. The characterization of low-dimensional structure becomes important in understanding the underlying growth mechanism, which in turn helps in fabricating new desired structures, manifesting novel physical properties for device applications. The thesis work compiles to understand the growth, structure and stability of nano-layer on the substrate surface by studying the nanolayer/substrate interfacial structure and its physical behaviour.

THIN FILMS/NANO-LAYERS:

A thin film is a material created by the random/ordered nucleation and growth processes of individually condensing / reacting atomic / ionic / molecular species on a substrate of few nanometer thickness ranges. In thin film fabrication, the role of the structure and composition at the surfaces and interfaces of the materials plays crucial role that governs the performance of novel devices. Thin film can be bounded by either free surfaces which separate the film from the surrounding phases, as in the case of soap films, or by a free surface and a solid substrate. Many materials have been prepared in the form of thin films over a century because of their potential technical value and scientific curiosity in their properties. They show altered thermodynamics, modified chemical reactivity, modified electric, mechanical and optical properties and exhibit many other new properties. The majority of electronic devices are now confined to planar geometries; thus, thin films have played an ever-increasing role in manufacturing of modern electronic devices. Owing to the convenience for preparation, thin films are mostly used in industrial fields; however there remain many problems concerning the physical properties such as size and thermal stabilities. An emerging research trend is focused to probe and understand the thin film behaviour under different physical conditions. The reason behind these alterations is being understood and interpreted in terms of quantum size effects leading to a change in the bonding structure thereby affecting the overall properties. Because of the presence of an ‘intermediate length scale’ the properties of these materials can often be tuned and reproduced by precisely modulating a range of deposition parameters. Thus, one can say that if any of the dimensions of nanostructure or structural parameters are controlled, its properties can be tuned to desired values [12-14].

The films thickness that characterizes the degree of confinement and the substrate that controls the strength of substrate/film interface interactions are two most important parameters in thin films systems. Because of high surface-to-volume ratios, the study of surfaces and interfaces is crucial in the understanding of many technologically important processes as well as the underlying physics. The thin film geometry is appealing since it is straightforward to control the interactions at the free surface and film-substrate interface, and it is possible to produce films of uniform thickness and therefore uniform confinement, which can be varied continuously from nanometers to micrometers [13-17].

Thin films of a few nanometers thickness are the source of high expectations as being useful components in many practical and commercial applications such as sensors, detectors, displays and electronic circuit components, as coating component. The chemical, metallurgical and physical properties of such materials are strongly dependent on a number of deposition parameters and thickness. The ability to tailor numerous properties of thin-films required for an efficient application demands a good understanding of the material so produced with the help of a range of monitoring and analytical facilities. Also high sensitivity of film properties to deposition parameters can produce a multitude of undesired results.

Thus it becomes evident that though films are attractive, the materials and the deposition techniques need due care and understanding. By taking into the consideration the above discussion, the present thesis work mainly focuses on metal- organic Langmuir-Blodgett (LB) films, Polymer films and metal polymer nanocomposites. A brief description to all the three types of films is discussed below.

METAL ORGANIC LB FILMS:

Ultrathin organic films are currently gaining interest in many areas such as integrated optics, biosensors, chemical sensors, friction reducing coating, surface orientation layers and molecular electronics [17]. Most of the applications require well-defined and adhesive films, composed of molecules with tailor-made properties in unique spatial arrangements with respect to each other and also with substrates. Metal-organic films [18; 19] of well ordered structure and controlled thickness [20; 21] deposited by the LB technique [22; 23] are ideal source for testing physics of lowdimensional systems, viz electrical transport, magnetism, and melting [22; 24] specific growth mechanism arising from different types of observed in-plane correlations [25; 26]. Metal-organic LB films exhibit a high degree of orientation, molecular order and packing [19]. Long chain fatty acids and their divalent arachidate metal salts such as Cd^2+, Ni^2+, Mn^2+, Zn^2+ etc. have been the most extensively studied LB systems and their three-dimensional structure and molecular packing have been investigated using various characterizing techniques [19; 27]. These are the engrossing systems to study the behavior of organized twodimensional assembly of molecules in confined geometry [28]

These films have promising applications in the field of biosensor, catalysis and nanotechnology [29-36]. However, most of the proposed applications, arising from the unique physical properties of LB films strongly depend on their structure and hence control of the specific structure through proper understanding is important. To explore all the aspects and to have structure-property correlations, it is very important to know their structure, out-of plane fluctuations, in-plane correlations, etc. However, in most of the cases, the films made by the soft molecules have defects, imperfections [18; 37] and instability [38] but for the metal- organic LB films, defects can partially be removed by increasing pH [39; 40] or by dissolving different metal ions [18] in the water subphase.

Earlier Dutta et al. [41] have shown that high pH (>8.5) monolayer phase of CdA has more condensed and lower energy lattice structure than that of normal pH (~7) phase. By using imaging technique, Schwartz et al. [20] have shown that the defects in LB film can be removed substantially by increasing pH from 7 to 8.5. Similarly, Kundu et al. [42] have shown that the metal ion incorporation into the head of LB film can be increased by increasing pH, which is mainly responsible for the structural quality of the film. Moreover, Schwartz et al. [43] also have shown that the Langmuir monolayer is more ordered in presence of Pd, Cd ions rather than Ba. This effect was explained by varying degree of ionic and covalent bonding. Different substrates have also been used to understand the substrate effects in controlling LB structure [18-21; 38; 44]. Zasadzinski et al. [45] have also shown that for a particular pH, the morphology of LB film strongly depends on the different types of substrate surfaces. They have compared the structure of CdA at pH ~5.5 on Si and mica substrates. They have observed that LB film was uniform i.e. hole free on Si substrate whereas on mica, holes of 10-100 nm in diameter were present. This difference in film quality was described in term of less extensive hydration of the mica at pH ~ 5.5. Although a lot of research has been carried out in this field yet quite a number of issues are still untouched. The interest is not only from the viewpoint of understanding nano-structured organic systems but is also prompted by the possibility of using these multilayer systems as precursors to develop oxides for nano- structured device. In the present work, melting behaviour of CdA LB film under depth selective consideration and different chemical treatment effect on their in-plane structure has been carried out.

POLYMER FILMS:

Polymer thin films play an increasingly important role in a wide range of technological applications including antireflection coatings, adhesives, nano-lithography, opto-electronics, and sensors etc. [46- 49]. These applications require polymers to meet diverse performance criteria that range from electronic and optical performance to adhesive and mechanical performance. The major advantage of using polymer thin films over non-polymeric materials in some technologies is that polymers are inexpensive and easy to fabricate. As applications of polymers become smaller and thinner, the behavior of polymer chains in these confined geometries needs to be understood. Many aspects need to be probed such as the effect of molecular weight, thermal degradation, and the adhesion properties. Polymers undergo severe low-dimensionality effects when they are confined to ultrathin films since most of the structural and dynamical processes involving polymer molecules are correlated to length scales of the order of nanometers [50-52]. For example, Jaime Martin observed that the PCDTBT polymer confined to the thin film in absence of any substrate (free-standing thin film) showed a 30% lower Young modulus than bulk and 45% lower than that of a thin film of the same thickness (40 nm) deposited onto glass. This softening was considered to be a real low-dimensionality effect taking place in the nano-confined polymer material [53]. Lovejeet Singh et al. have shown decrease in glass transition temperature (Tg) for polymer film having thickness lower than the critical thickness. This critical thickness is found to be approximately 10 times the radius of gyration of polymer [54].

In past, numerous groups comprehensively studied the effects of surface interactions as well as surface morphology on the melting point of polymer films as a function of thickness. It was shown that the nature of the substrate significantly influences thermal behaviour of the polymer film. It has been observed that larger interfacial interaction energy results in an increase in the melting temperature, which has been attributed to a decrease in the overall free energy upon melting [55]. In addition, even the glass transition temperature in films of stereoregular poly (methyl methacrylate) has been found to be affected significantly by the substrate used [56]. Studies on spin-casted films of poly (methyl methacrylate) on Si and Al surfaces show that a higher interfacial interaction results in an increase in the glass transition temperature. This suggests that the structure of nanolayer is strongly dependent on the nature of the underlying substrate surface on which it is grown. It means that the nanolayer-substrate interface plays significant role in growth and stability of the overlayer.

Polymers generally have lower dielectric constants than ceramics or metals. Their incorporation into integrated circuits has been limited above all by low thermal stability and inability to form high quality thin films. Thus a better fundamental understanding of the physical properties of ultrathin polymer films would be useful in a variety of fields.

METAL POLYMER NANOCOMPOSITE:

Composite materials have gained sustained research interest due to their combinatorial properties and diversity of applications which cannot be achieved with metals, semiconductors or polymers alone [57-63]. Recently, the combination of metal nanoparticles in polymer matrices has attracted great technological relevance from both technological and fundamental aspects, as their fine control and design lead to the fabrication of materials with novel electronic, magnetic or catalytic properties [64]. These materials are of current interest because of their multifunctionality, ease of process-ability, potential for large-scale manufacturing, significantly lighter than metals, ease of synthesis [65-67]. The size of the nano-clusters in the nanocomposites determines their electronic, thermal and optical properties [68].

This small size offers some level of controllable performance in nanocomposites that is different from the expectations developed in the macro-world. Their fine control and design lead to the fabrication of materials with novel electronic, magnetic or catalytic properties [64]. As the technological properties of these materials depend on the structure and ordering of the embedded metal nanoparticles; a detailed understanding of the dynamic processes involved is desirable. Uniform dispersion of metal nanostructure in polymer matrix has been extensively studied by a large number of research groups for wide variety of applications.

By carefully choosing the metal content, one can selectively manipulate specific physical properties including impact strength [69], magnetic [70-72], electronic [73; 74], and optical properties [75-78], and conductivity. For example, considerable enhancement in dielectric constant of PVDF/Ni composites has been observed at the percolation threshold and was attributed to increased adhesiveness between the filler and the polymer leading to better homogeneity [79]. An increase in dielectric permittivity of the nanostructured material was found with increasing nanoparticles concentration in the polymer matrix [80]. Also some groups studied the optical behaviour of metal-polymer nanocomposites. As an example, Balamurugan et al. [81] noted red shift in the SPR peak of Au with increasing the particle size. Gao et al. [82] and Gole , Murphy [83] and Carotenuto et al [84] found that the Plasmon absorption maxima of nanoclusters decrease with increase in the thickness of the coating. Athawale et al [73] and Sadik et al [74] state that incorporation of metal nanoclusters into conducting polymer matrices resulted in enhancement in the electrical conductivity. They found that the conductivity increase with decrease in the particle size and increase in the nanoclusters content. Additionally, Xia et al. [85], Aymonier et al. [86], and Hsu et al. [87] demonstrated that the thermal stability of nanocomposites increases with increase in metal nanocluster content. The increment in thermal stability is due to the increase in metal-nanocluster interfacial area.

Another group studied the thermally driven assembly of gold nanoparticles (NP) in PS-d-PMMA block co-polymer. [88] This study showed that Au NPs were randomly dispersed in PS or PMMA domains in the as-cast bulk films. After annealing majority of the Au NPs were found either in PS domains or at the interfaces between PS and PMMA domains. It means that annealing cleaves the PMMA from the Au NPs, creating a PS functionalized nanoparticle exterior. The Au NPs then migrated to PS phase to reduce interfacial energy and a swelling of the polymer domains were observed when a significant number of functionalized Au nanoparticles were localized within a single domain [88]. The diffusion of gold nanoparticles in polymer matrix has been studied with effect of low energy irradiation. The blue shift in the plasmon absorption peak revealed that the size of nanoparticles could be tailored by varying the electron fluence [89]. Since the properties of the nanoparticles strongly depend on their size, distribution and shape, the determination of their exact morphology is important in order to understand and control their physical properties.

CONCLUSION:

Metal organic LB films are an ideal source for testing physics of low-dimensional systems.

The natural monolayer orientation and precise control over thickness provides strong reason for their utilization. The structural transition in metal organic LB films depends on the thickness and surface/interface energy. By taking into consideration the low dimensionality effects in melting behavior of cadmium arachidate (CdA) multilayers have been studied in two parts: a) effect of surface chemical treatment b) effect of confinement between two metallic layers.

Polymer thin films have become an important part of our everyday life and are ubiquitous in countless industrial and biomedical applications. It is important to optimize the preparation conditions to achieve good quality polymer films in nanometre thickness range. We have used two different techniques namely Langmuir-Blodgett and spin coating technique to achieve good quality polymer films of various thicknesses in nanometre range. In the present ultra-thin films of PMMA LB films and PLLA films (by spin coating) has been prepared and studied.

Metal-polymer nanocomposite has gained great interest in technological and fundamental aspects, as their fine control and design lead to the fabrication of materials with novel electronic, magnetic or catalytic properties. The thermal evolution of gold nanoparticle in PTFE matrix has been studied by Small angle x-ray scattering (SAXS) and Wide angle x- ray scattering (WAXS) technique. The optical properties of the nanocomposites were also studied by using UV-Vis. spectroscopy.

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