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Role of substrate in melting behavior of Langmuir–Blodgett films

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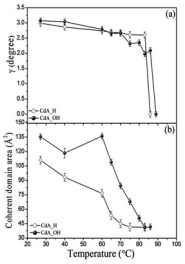
HIGHLIGHTS

- The CdA LB films deposited on —H and —OH terminated Si surfaces have been investigated using X-ray reflectivity and in-plane EDXRD techniques.
- CdA-OH film is found to be more stable against temperature as compared to CdA-H film.
- The transition temperature from distorted hexagonal to hexatic like phase as well as melting temperature are lower in the case of CdA-H film.

GRAPHICAL ABSTRACT



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ABSTRACT

Grazing incidence energy-dispersive X-ray diffraction (GID) studies of Langmuir–Blodgett (LB) films have been performed to study the role of substrate in controlling structural transformation in LB films. Thirteen monolayered LB film of cadmium arachidate (CdA) were deposited on two different chemically treated (—OH and —H terminated) Si(1 0 0) substrates. In both the CdA-H and CdA-OH LB multilayers, with increasing temperature the distorted hexagonal lattice structure transform to hexaticlike phase, followed by melting transition. However, there is a significant difference in the structural evolution of the two multilayers with temperature. In CdA-H multilayer the size of the coherent domains shows a continuous decrease right from the room temperature onwards while in CdA-OH multilayer it remain almost unchanged till 65 °C. In CdA-H multilayer both the transition to hexaticlike phase as well as melting transition take place at significantly lower temperatures as compared to CdA-OH multilayer. This difference can be attributed to possible higher level of defects and imperfections in the CdA-H multilayers, as a result of post-deposition configurational evolution.

1. Introduction

Well ordered metal–organic films [1,2] of controlled thickness [3,4] can be prepared by Langmuir–Blodgett technique [5,6]. Such LB films are ideal for studying the basic physics of low-dimensional systems. Characterization of low-dimensional structure becomes important to understand the underlying growth mechanism. This understanding helps us in fabricating new desired structures, which manifest novel physical properties for device applications [7,8]. Low dimensional systems sometimes demonstrate completely different properties from bulk [9,10]. Confinement effect, large surface to volume ratio and interface energies of nanomaterials is the probable reasons behind this. Substrate surface condition also plays crucial role in the growth and stability of nanolayer on it [11,12]. A promptly implemented method to improve the film quality is to alter the surface energy of the substrate to boost a better film growth. The surface and interface energies influence the structural properties significantly, because large surface is available

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to react [12–15]. As the LB film contains amphiphilic molecules, having both hydrophobic and hydrophilic parts, its structure can be improved by changing the surface nature of the substrate. The modification of surface can be easily done by passivation of the substrate surface. This basically modifies the surface nature, in term of free energy or polarity and accordingly, hydro nature of the surface can be tuned. Some studies on LB film shows that different types of layered structures can be grown [1,16–19]. In addition, marked dependence of the morphologies and the qualitative dynamics on the surface composition has been observed in blends of polystyrene and poly(methyl methacrylate) spun cast on Si, Au and Co surfaces [20]. Higher interfacial interaction resulted in an increase in the glass transition temperature of poly(methyl methacrylate) on Si and Al surfaces [21]. Apart from that thermal stability of low dimensional system has become one of the critical issue for future development and applications of this new materials family. However, the transition temperature as well as melting temperature depends significantly on the type of layer [22]. These results can be understood in terms substrate induced perturbation at the interface.

Low dimensional systems offer the possibility of exploring phase transitions in the crossover region between two and three dimensions. KTHNY theory predicts two-step melting in thin films, from crystal to a hexatic phase and then from hexatic to a liquid phase [23–27]. Melting of LB films as a function of film thickness has been extensively studied in the literature [7,28–32]. In literature distorted hexagonal lattice structure of Cd arachidate multilayer has been reported [7,32–34]. Existence of a hexaticlike phase has been clearly evidenced in such studies. Further, existence of an intermediate smectic or nematic phase inserted between solid and hexatic phases in a system with a distorted hexagonal symmetry, as predicted by theory, has also been observed [7,35]. Even in thick films of cadmium arachidate, low dimensionality effects have been observed in the surface region [33], while CdA LB film of same thickness confined between two metallic layers shows a lack of additional smectic phase [34]. Before melting transition the distorted hexagonal lattice structure of CdA LB film transform to hexaticlike phase with increasing temperature [32–34]. This hexatic like phase is specified by a tilting of chains in vertical direction and a decrease in the in plane distortion. In the present work, we have used Cd arachidate multilayer prepared using LB technique on two different chemically treated Si(1 0 0) substrates in order to study the effect of interfacial interaction energy on its melting behavior. In-plane energy dispersive X-ray diffraction [36] has been used to extract temperature dependent structural information, which is essential for understanding physics of low dimensional system.

2. Experimental details

We have deposited 13 monolayered (ML) CdA LB films on silicon (1 0 0) substrates, chemically treated according to the wet passivation. A LB trough model KSV 2000 was used. Arachidate acid (purity >99.9%) was dissolved in chloroform (HPCL grade) at a concentration of 1 g/L for use as the spreading solution. 70 μL of solution in chloroform was spread on the subphase surface. The subphase was prepared with $CdCl_2$ (purity >99.8%) dissolved in Milli-Q water (resistivity >18 MΩ cm) to a concentration of 0.9966 g/L and adjusted to pH 6.7 using $NaHCO_3$ (purity >99.9%) [34].

Prior to the deposition, Si(1 0 0) substrates were chemically treated in two different ways. Different treatments provide differently terminated surfaces. In first case, substrate was kept in a basic piranha solution of ammonium hydroxide NH_4OH (30%), hydrogen peroxide H_2O_2 (30%), and Milli-Q water (∼18 MΩcm) [H_2O:NH_4OH:H_2O_2 = 2:1:1], for 10–15 min at 100 °C. This results in —OH termination of the surface making it hydrophilic in nature [37]. Another set of Si substrates were kept in a solution of hydrogen fluoride HF (10%) for 3 min at room temperature. HF solution removes the native oxide layer at the surface and results in passivation of silicon dangling bonds with hydrogen atoms. This —H terminated surface has hydrophobic nature [37]. As observed in some earlier studies, on exposure to ambient atmosphere, such surfaces exhibit formation of native oxide at a time scale of a few days [19]. 13 monolayers of CdA were deposited on these two sets of substrates, and are designated as CdA-OH and CdA-H respectively. LB deposition was performed at a surface pressure of 30 mN m^{-1} with a dipping rate of 3 mm min^{-1} at 20 °C. The films were prepared by the vertical deposition mode and allowed to dry in air for 5 min after each upstroke. Layers were characterized by X-ray specular reflectivity (XRR) measurements using Bruker AXS make D8-Discover diffractometer at Cu Kα wavelength.

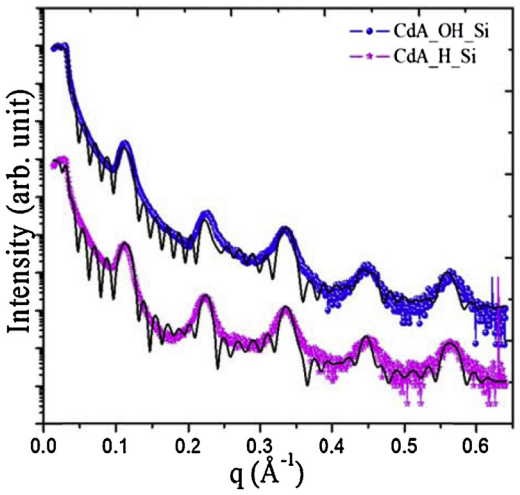

Fig. 1. X-ray reflectivity of CdA LB films deposited on different chemically treated Si substrates.

GID measurements have been performed at EDXRD beam line BL-11, of INDUS-II synchrotron radiation source, RRCAT, Indore [38]. Diffracted radiation is energy analyzed at fixed 2θ (=18°) angle using high resolution HPGe detector mounted on detector arm. The diffraction scans were performed at the fixed grazing angle of θ = 0.2°. An exposure time of 300 s was used for taking one diffraction pattern. A miniature furnace was used for controlled heating of the sample, which was kept in ambient atmosphere. The sample temperature was maintained with an accuracy of ±0.5 °C. In order to avoid any influence of radiation damage during the measurements, the sample was shifted across the beam by 2 mm after each scan so that a fresh area of the film was exposed to the X-rays.

3. Results and discussion

Fig. 1 shows the X-ray reflectivity pattern of the CdA LB films deposited on different chemically treated Si surfaces, along with the best fit. The reflectivity data were analyzed using Parratt's formalism [39]. Both the reflectivity patterns show the presence of well-defined Bragg peaks corresponding to the bilayer periodicity of 5.54 nm in case of CdA-OH and 5.52 nm in case of CdA-H multilayer. Visibility of more than 5th orders of Bragg peaks in reflectivity pattern suggests good quality of multilayers. However, overall reflectivity patterns of the two films exhibit subtle differences, which could be fitted by considering structural models which take into account the hydrophilic and hydrophobic nature of the Si—OH and Si—H surfaces. Langmuir–Blodgett films are