Physica B 407 (2012) 4777–4782

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Structural and surface morphological studies of long chain fatty acid thin films deposited by Langmuir–Blodgett technique

Nayan Mani Das [a,*], Dhrubojyoti Roy [a], Mukul Gupta [b], P.S. Gupta [a]

[a] Department of Applied Physics, Indian School of Mines, Dhanbad 826004, India
[b] UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452017, India

ARTICLE INFO

Article history:
Received 25 July 2012
Received in revised form
24 August 2012
Accepted 26 August 2012
Available online 30 August 2012

Keywords:
LB thin films
Molecular orientation
Thickness
Surface roughness

ABSTRACT

In the present work we aim to study the structural and surface morphological characteristics of divalent cation (cadmium ion, Cd^{2+}) induced thin mono- to multilayer films of fatty acids such as arachidic acid and stearic acid prepared by the Langmuir–Blodgett (LB) technique. These ultra thin films of various numbers of layers were studied by X-ray diffraction (XRD), X-ray reflectivity (XRR) and Atomic Force Microscopy (AFM). In this specific Y-type deposition, it was found that as the individual layer thickness increases, the corresponding layer by layer interfacial electron density of the thin films decreases. Since the fatty acid chain tries to maintain its minimum value of cross-sectional area, tilting occurs with respect to its nearest neighbor. The tilt angle calculated for 9 layers of cadmium arachidate (CdA_2) and cadmium stearate ($CdSt_2$) are 18° and 19.5°, respectively. An asymmetric air gap of thickness ~3 Å was also seen between the tail parts of 2 molecular chains. The RMS roughness and average height factors calculated through AFM studies show non-uniform surface morphology of both CdA_2 and $CdSt_2$, although the calculated topographic variations were found to have more irregularity in case of $CdSt_2$ than in case of CdA_2.

1. Introduction:

LB films have shown wide application in devising sensors [1,2], molecular field-effect transistors [3], catalytic activity [4], synthesis of DNA–protein complexes [5], etc. Film deposition by this method is easy and cost-effective as compared to other processes like molecular beam epitaxy, sputtering technique, etc. In this method ordered orientation and molecular control over the layer by layer deposition of thin films of fatty acids of amphiphilic character can be achieved [6–10]. Fabrication of well ordered and efficient structures depends on proper handling of the molecular flexibility and complexity at the nanoscale region of the system. Defects [11] and instability [12,13] in metal–organic LB films, are treated as obstacles to the synthesis of films. The Pinhole defects [14] in such metal–organic LB films are infrequently observed. Reproducibility of the LB films is compromised due to presence of such defects. However by maintaining control over the subphase pH and further controlling the deposition parameters, reproducibility of the films can be achieved [15]. Parameters like compression pressure should be optimized and the rate of deposition is also controlled to get maximum interaction between the substrate and the hydrocarbon chain of film material. These features restrict overturning of the newly deposited layer [16]. Incorporation of a different divalent metal cation having different electro-negativity in the negatively charged head group of the organic acid also favors better deposition [17–19]. In many cases change of substrate can be found to be very effective [20].

In this report, detailed studies of the structural and surface morphological behavior of such cation induced fatty acids have been conducted. Since basic properties like the chain length, tilt angle, surface roughness, and height–height correlations are the most important parameters for the metal–organic LB films, one can take measures to handle these parameters to improve the film quality. The chain length and tilt angle are calculated from the out-of-plane X-ray diffraction (XRD) technique. In-plane XRD studies show a hexagonal structure for monolayers which steadily changes to an orthogonal structure for multilayer depositions [21]. A typical X-ray reflectivity study shows that an asymmetry (air gap) is associated with the individual bilayer structure. The RMS roughness measured through Atomic Force Microscopy (AFM) varies slower in case of CdA_2 than in $CdSt_2$. The roughness, calculated from the XRR studies for bilayer deposition is also complemented with the AFM study.

2. Experimental details

Thin films of CdA_2 and $CdSt_2$ were prepared using the Langmuir–Blodgett apparatus (Apex Instrument Co., India). Stearic acid and

* Corresponding author. Tel.: +91 9570104590; fax: +91 3262296563.
E-mail address: nayanmanidas3@gmail.com (N.M. Das).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.08.035

arachidic acid, purchased from Sigma-Aldrich were of high purity and used without further purification. Their solution of concentration 1 mg/ml in chloroform (analytical reagent, RANKEM, India) was spread in an aqueous subphase containing 5×10^{-4} M cadmium chloride (laboratory reagent, RANKEM, India). Deionised and ultra purified water (Millipore) having a resistivity of 18.2 MΩ cm, was used to prepare the subpahse. The subphase temperature was kept constant at 30 °C.

Initially, Teflon-made barriers were used for cleaning the subphase surface by wiping it. Any surface active foreign particulate and any other contaminants were removed from the interface using a suction pump. The subphase surface cleanliness was confirmed by keeping the surface pressure near about 0.0 mN/m by wiping the surface through the Teflon barrier several times. The subphase pH was controlled to 6.4 by adding a dilute solution of $NaHCO_3$. The monolayer was compressed with a constant barrier speed of 3 mm/min and the multilayer deposition was carried out at a surface pressure of 30 mN/m. The compressed monolayer was transferred by a vertical dipping method at a speed of 3 mm/min. Typically monolayers, 3 layers, 5 layers and 9 layers were transferred onto the glass plate. The deposition was of Y-type with an attachment of alternate hydrophilic and hydrophobic parts of the amphiphilic fatty acid within the bilayer. Before deposition over the glass substrate, they were made hydrophilic by cleaning with ethanol first and then keeping in an ultrasonic bath sonicator for 10 min in order to remove all foreign particulates from the glass plate substrate. The substrates were further made hydrophilic by placing inside a degreasing unit filled with iso-propanol. The sticking of a water layer over the glass substrate confirms hydrophilicity. After carrying out this process the substrates were directly put into the attaching clip of the LB apparatus for the vertical lifting and dipping process. The first layer was deposited by taking the monolayer over the substrate though an upward journey through the water subphase and then the substrate along with the film of monolayer was dried for 30 min. For deposition of the next layer the substrate was kept 3 min inside the water subphase and 5 min outside the water subphase. This time duration was followed for all subsequent layer depositions.

The films were subjected to X-ray diffraction studies for structural analysis using a Bruker D8 Advance X-Ray Diffractometer which uses Cu-K_α radiation ($\lambda=1.543$ Å) and a fast counting detector based on the Silicon strip technology (Bruker LynxEye detector). The thickness of the thin film and the electron density profile were calculated by X-ray reflectivity measurements using the Bruker D8 Discover Diffractometer with Cu-K_α wavelength. The atomic force microscopy (Digital Instruments Nanoscope-IV, with Si_3N_4 100 μm cantilever, 0.58 N/m force constant) study was done to see the height–height correlation and the structural details of the different sample parameters in contact mode. We used standard silicon nitride (Si_3N_4) pyramidal tips mounted on triangular cantilevers. The scan area was set to 1 μm × 1 μm. The scan rate was kept constant at 10.48 Hz to obtain stable images. The images presented here have been flattened with a simple polynomial function to remove the curvature that results from the movement of the tube piezoelectric scanner.

3. Results and discussion

3.1. XRD studies

Results of XRD studies of CdA_2 and $CdSt_2$ are shown in Fig. 1 for different numbers of layers. Bragg's reflection peaks were

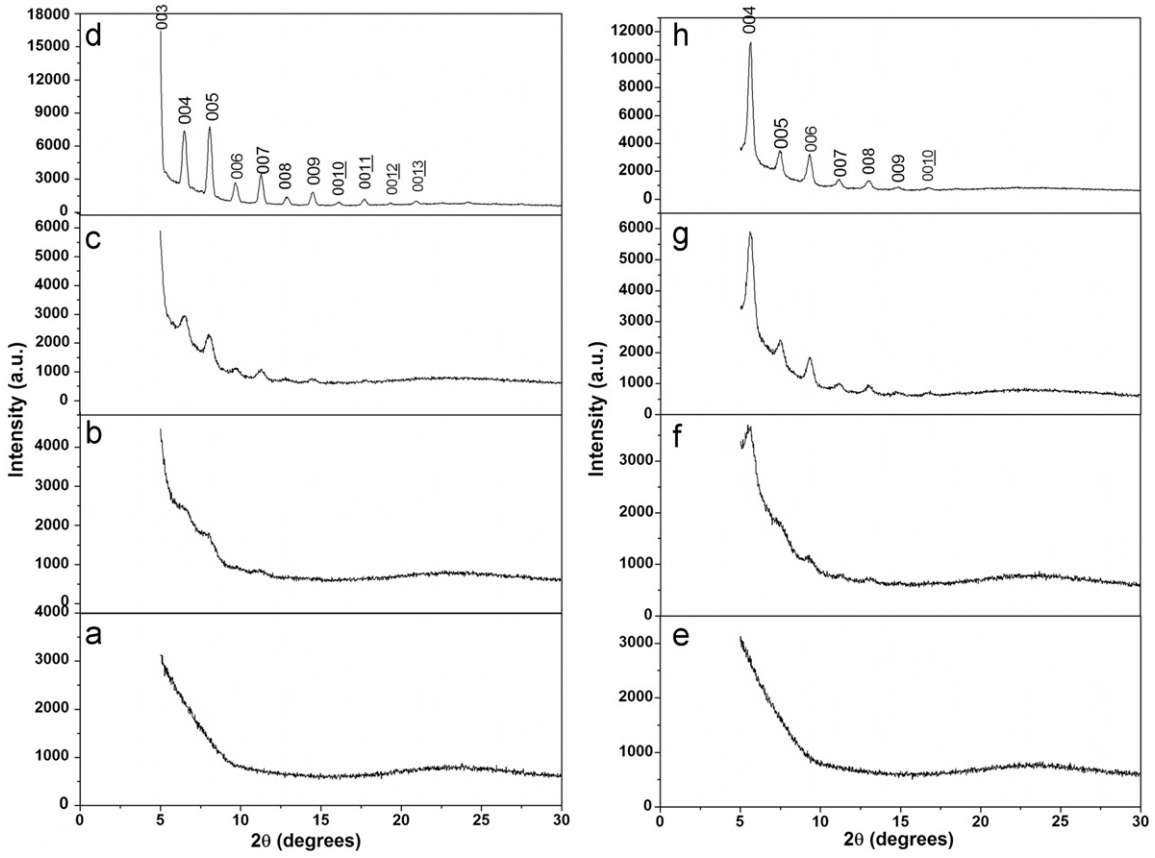

Fig. 1. Out-of-plane X-ray diffraction patterns of various layers of CdA_2 and $CdSt_2$: (a) monolayer, (b) 3 layers, (c) 5 layers, and (d) 9 layers of CdA_2 and the corresponding (e) monolayer, (f) 3 layers, (g) 5 layers, and (h) 9 layers of $CdSt_2$.