



Structural morphology study of Cd²⁺ induced Langmuir Blodgett multilayer films of arachidic acid



Dhrubojoyoti Roy*, Nayan Mani Das, P.S. Gupta

Department of Applied Physics, Indian School of Mines, Dhanbad 826004, India

ARTICLE INFO

Article history:

Received 27 September 2012

Received in revised form 30 January 2013

Accepted 31 January 2013

Available online 8 February 2013

Keywords:

LB film

CdAA monolayer

Layered crystalline growth

Alkyl chain tilt

Unidentate headgroup coordination

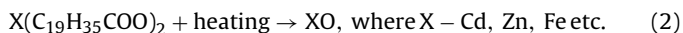
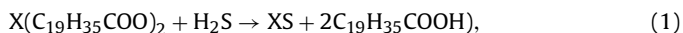
ABSTRACT

The organization and headgroup co-ordination of Cadmium Arachidate (CdAA) molecule in Langmuir–Blodgett (LB) multilayer films deposited on hydrophilic Glass (SiO₂) and Silicon (100) substrate at normal subphase pH (6.8) are studied. X-ray diffraction (XRD) and X-ray reflectivity (XRR) study reveals ordered layer by layer organization with uniform packing of CdAA molecules, and with a small tilt angle of alkyl chain of CdAA molecule equal to $6.8^\circ \pm 1.75^\circ$. Electron density profiles (EDPs) shows that the coverage of films remains almost constant with increase in bilayer thickness which indicate very little presence of pinhole defects. AFM study for 25 ML shows that coverage of the film remain intact upto 22nd ML and then decreases sharply due to presence of pinhole defects. Fourier transform infrared spectroscopy (FTIR) study is also consistent with XRD and XRR study of ordered deposition of CdAA molecule. FTIR and X-ray photoelectron spectroscopy (XPS) study indicates the formation of unidentate bridging metal-carboxylate coordination type headgroups consistent with one cadmium metal ion between two carboxylate (COO) groups in each headgroup structure.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Long-chain fatty acids have been extensively used as LB monolayers at the air–water interface [1–3]. They are amphiphilic molecules, where the hydrophilic groups attract the aqueous subphase and the hydrophobic groups point towards the air, thereby getting attached to the aqueous subphase. Due to this property of LB monolayers to array the amphiphilic molecules in a particular manner, it can successfully serve as a template for two-dimensional chemical reactions [4–6],



LB films are generated from LB monolayers deposited on a solid substrate layer upon layer, which have ordered molecular assemblies with planned structure. Through LB process, films of nanoparticles, nanowires and microparticles can also be synthesized [7–9]. It is a bottom-up assembly technique in nanotechnology and functional material application like chemical sensor, semiconductor light (CdS, CdTe), high temperature piezoelectric etc.

In recent years, the LB Technique for preparation of ultra- thin films of various organic, metallorganic and polymer compounds have generated interest among researchers of various fields due to their potential applicability in molecular electronics, non linear optics, conducting thin films, sensors and as a templates for growing functional nanomaterials like quantum dots [10–15]. LB process though economical and with better molecular-level-control compared with other sophisticated techniques like molecular beam epitaxy (MBE), sputtering or metal-organic chemical vapour deposition (MOCVD) could not find much appealing application because of low reproducibility owing to presence of pinhole type growth defects. Therefore to apply LB films in various devices and technology, it is very important to control the ordered molecular assembly in each monolayer such that coverage area of film remains almost same with successive monolayer deposition. This aspect has been included in the present study.

The LB system of long chain saturated fatty acids (stearic, arachidic, behenic) are studied mostly because of their strong amphiphilic property and to incorporate different divalent cations of transition metals having considerable electronegativity (e.g., Cd²⁺, Ca²⁺, Mn²⁺, Zn²⁺, Ba²⁺, etc.) into their headgroup structure in comparison to amines, esters and alcohols. The floating LB monolayer of the required fatty acid on the water surface, can react directly with the ions of given divalent metal, dissolved in the water subphase in submillimolar concentration, to yield a nearly purified form of the fatty acid salt that can be deposited as multilayers on a suitable substrate by the successive vertical dipping technique

* Corresponding author. Tel.: +91 8292190838; fax: +91 3262296563.

E-mail addresses: dhrubojoyoti27@gmail.com, dhrubodhanbad@gmail.com (D. Roy).

[2]. At low pH, fatty acids do not dissociate because of their acidic property and hence the cations do not affect the monolayer on the water surface, nor can they get incorporated into the deposited LB film. However, at the intermediate pH range the relative fractions of free acid and their divalent metal salt are sensitive functions of pH [16]. The stability of the LB monolayer of these divalent metal fatty acid salt enhances greatly and its ease of deposition [17]. Hence, it led to better ordered organization of LB multilayers on solid substrates. This ordered organization is mainly attributed due to the formation of headgroup-headgroup interfaces, which are stabilized by the strong electrostatic interaction with divalent metal cations at the expense of the headgroup-substrate and headgroup-water interfaces [18,19].

The Cd^{2+} induced LB films of arachidic acid helps to improve the surface wetting properties (i.e. hydrophobic and hydrophilic property) of different substrate, which changes the surface energy of the substrate [20]. Also cadmium arachidic acid monolayer forms a suitable matrix for the epitaxial growth of cadmium sulfide and that it can be used to control the morphology, size, and orientation of the growing crystals [21,22]. In the present study, the growth and the interfacial molecular structures of Cd^{2+} induced LB films of arachidic acid deposited on hydrophilic glass (SiO_2) and silicon (100) substrates at pH 6.8 has been characterized by X-ray diffraction and X-ray reflection technique [23] which provide average information of the film along the growth direction and electron density profile (EDP) along the depth of the film. FTIR spectroscopy is useful to study the hydrocarbon tail packing and metal ion-headgroup conformational orders in the LB films. AFM study has been used for the morphological characteristics of the LB films. Study of chemical composition of surfaces and interfacial layer of LB film of CdAA has been done by XPS. XPS study to know the metal ion-headgroup conformational orders in the LB films has not been reported in literature and we have included this aspect in the present paper for the first time.

2. Experimental details

Cadmium chloride and sodium bicarbonate, the analytical grade chemicals obtained from Merck reagents are used without further purification. Arachidic acid ($\text{C}_{19}\text{H}_{39}\text{COOH}$) was obtained from Sigma Aldrich (purity 99.9%). Milli-Q filtered water (resistivity $18.2 \text{ M}\Omega \text{ cm}$) is used as subphase for deposition of LB films of different monolayers. Before deposition the Langmuir trough was cleaned with methanol and acetone thoroughly.

Multilayers film of CdAA having 3, 5, 9, 19 and 25 monolayers (ML) were deposited on Silicon (100) substrate and 3, 5, 9 and 25 monolayers (ML) film of CdAA were deposited over Glass (SiO_2) substrate using LB Technique. Cadmium metal ions were introduced by adding 0.5 mM cadmium chloride in a Langmuir trough (Apex Instruments Co.) containing Milli-Q water, pH (~ 6.8) was adjusted by sodium bicarbonate (NaHCO_3). The glass substrates were properly washed with soap solution and then kept in the ultrasonic bath sonicator for 10 min in order to remove all the foreign particulates. The substrates were then made hydrophilic by placing them inside the degreasing unit filled with iso-propanol. Similarly silicon substrates were made hydrophilic by treating with a solution containing ammonium hydroxide (Rankem, Analytical Reagent), hydrogen peroxide (Qualigens), and Milli-Q water ($\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ in ratio 2:1:1 by volume) for about 10–15 min at 80°C . Before spreading arachidic acid solution the substrate were dipped inside the subphase and then arachidic acid monolayers were spread from a 1 mg/ml chloroform (CHCl_3 , Rankem, Analytical Reagent) solution. The LB film deposition were done at monolayer pressure of 29 mN/m as measured from Wilhelmy plate, at temp of about 27°C at a 4 mm/min dipping speed for subsequent up-down

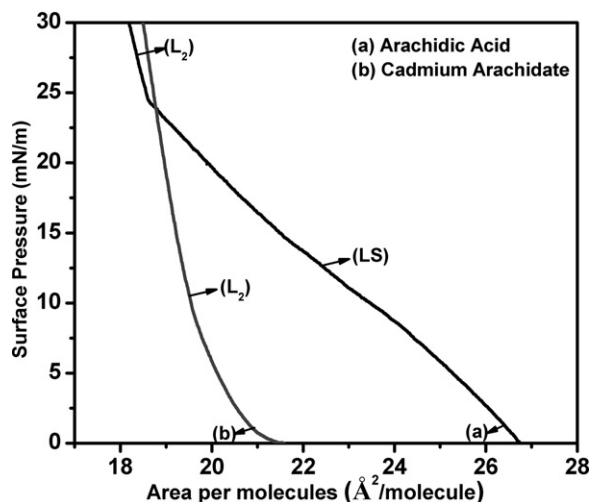


Fig. 1. Pressure vs. Area isotherm of arachidic acid (a) before and (b) after incorporation of Cd^{2+} ions.

strokes of substrate through the air–water interface. Drying time for first up stroke was kept 20 min and then for each subsequent upstroke i.e. above subphase was kept 10 min and similarly for downstroke i.e. below subphase was 5 min. The arachidic acid LB film showed good reproducibility.

Stability of LB monolayer increases greatly in presence of minute amount of di- or tri- valent metal ions over a pH range. The transition metal ions have very high ion-specific contribution to their interactions with fatty acids in LB monolayer because of their favourable physical and chemical properties [24], and the effect is reflected in π -A isotherm (Fig. 1). Arachidic acid monolayer isotherm shows that arachidic acid molecule passes through two phases i.e. liquid-condensed (LS) and condensed phase (L_2) whereas CdAA monolayer isotherm grow with a single phase i.e. in the condensed phase (L_2). There is complete disappearance of the liquid-condensed phase (LS) as the cadmium metal ions (Cd^{2+}) lead to condensation of the arachidic acid monolayers and without surface pressure two-dimensional crystals form. The area per molecule for CdAA was found out to be 18.5 \AA^2 whereas that of arachidic acid is 18.2 \AA^2 at the deposition monolayer pressure of 29 mN/m .

For required structural study of the films X-ray diffraction studies were performed using Bruker D8 Advance X-ray diffractometer which uses $\text{Cu-K}\alpha$ radiation ($\lambda = 1.543 \text{ \AA}$) and a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). FTIR Study was performed in absorbance mode using PerkinElmer D850 Instrument in the region 450 cm^{-1} – 3500 cm^{-1} on silicon (100) substrate. XRR study was performed using Bruker D8 Discover Diffractometer using $\text{Cu-K}\alpha$ wavelength for measuring film thickness and electron density profile. Atomic force microscopy (Digital Instruments Nanoscope-IV, with Si_3N_4 $100 \mu\text{m}$ cantilever, 0.56 N/m force constant) study was done to observe the morphological and structural details in contact mode. For chemical analysis of the LB film XPS measurements were performed with Omnicron Multiprobe spectrometer fitted with an EA 125 hemispherical analyser and a monochromatized $\text{Al K}\alpha$ (1486.6 eV) source. All data were collected at pass energy 40 eV with analyzer angular acceptance $\pm 1^\circ$.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD measurements of 3 ML, 5 ML and 9 ML LB film of CdAA shown in Fig. 2 depicts that with increase in the monolayer number,

Download English Version:

<https://daneshyari.com/en/article/5363137>

Download Persian Version:

<https://daneshyari.com/article/5363137>

[Daneshyari.com](https://daneshyari.com)