

Influence of Cd²⁺ ions on electrical properties of stearic acid Langmuir–Blodgett films

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ABSTRACT

Stearic acid incorporating cadmium ions prepared as an Langmuir–Blodgett (LB) thin films were grown onto aluminum coated glass substrate using different thicknesses to investigate the influence of cadmium ions on the electrical properties of the stearic acid. Electrical properties were investigated by measuring *C–V* and *I–V* curves at room temperature. The *I–V* curves show highly non-linear behavior with Schottky conduction mechanism in a high voltage regime for LB film samples. Barrier potential heights were calculated for the stearic acid LB films with and without cadmium ions. It was found that the Schottky barrier is lowered due to the presence of Cd²⁺ ions.

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1. Introduction

Langmuir–Blodgett (LB) film technique is simple and low-cost method to produce organic thin films. With this technique it is possible to control the thickness of the film in monolayer precision [1,2]. So far various organic films which have potential applications in pyroelectricity, chemical sensor and biosensor as well as optoelectronics have been grown successfully [3]. Nanoparticles of semiconductors and metals have been an extremely active area of research because of their interesting quantum confinement effect on both optical and electronic properties [4]. Nanostructured II–VI semiconductors, CdS and ZnS for example, have been studied very intensively in recent time due to their industrial implementation in nanoelectronic devices. CdS due to its low bandgap is one of the most extensively studied material among the II–VI compounds. A method for the formation of II–VI semiconductor nanoparticles within Langmuir–Blodgett films of fatty acids was proposed in 1980s [5]. This technique has now become very useful and promising for the formation of various nanostructures for opto- and nanoelectronic applications [6–9].

In order to understand the process of growing good quality of these nanoparticles in LB films it is essential understand the interaction between metal ions and organic films. The interaction between the Langmuir layers of fatty acids and metal ions has been studied since 1980s [10,11]. Pure G4–48PyP dendrimer (dendrimer molecule (G4) with 48 pyridylpropoxy end functional

group (48PyP)) and its complex with Fe²⁺ ions have also been investigated for the surface activity at the air–water interface and the electrical properties of the ultra-thin dendrimer LB films were investigated by studying the current–voltage characteristics of metal/LB films/metal structure. In electrical properties, there is a difference between pure G4–48PyP dendrimer LB film and its complex metal ions. G4–48PyP dendrimer LB film with metal ions had a larger current value than pure G4–48PyP dendrimer LB film. This has been generated by the metal ions' effect [12,13]. Pyroelectric activity in copolysiloxane/eicosylamine alternate layer LB films incorporating Cd²⁺ and Mn²⁺ ions is also investigated. Pyroelectric results show that cadmium ion incorporation leads to a significantly improved performance compared to the system without metal ions [14]. Pyroelectric results of non-centrosymmetric polysiloxane/eicosylamine alternate layer LB film show that dielectric constant value of LB films with ions are much higher than LB films without ions [15].

In this work, alternate layer of Y-type LB films of stearic acid and Cd²⁺ incorporated stearic acid films which are important to grow CdS nanoparticles have been deposited onto aluminium substrate in the form of a metal/LB film/metal device to investigate influence of Cd²⁺ ions on electrical and optical properties of stearic acid.

2. Experimental details

The chemical structure of the stearic acid (C₁₈H₃₆O₂) is dissolved in a 1:1 ratio of chloroform. The cadmium chloride was dissolved in the subphase and 0.5 mg ml⁻¹ concentration of stearic acid solution was used to produce LB film by spreading on the pure

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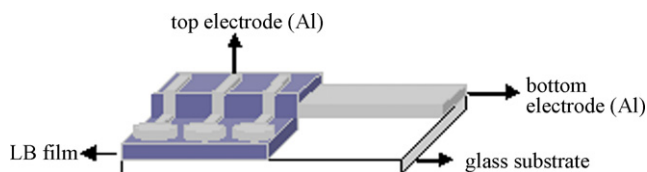


Fig. 1. The device structure of LB film for electrical measurements.

water surface. The pH value of the subphase is nominally maintained at 6. The deposition pressure of 22.5 mN/m is selected from the surface area (π -A) isotherm of the solutions to produce Y-type LB films in the thickness of the 5, 11 and 21 monolayer sets onto glass and aluminized glass substrate for optical and electrical measurements, respectively, by vertically dipping substrates into the solution. Transfer speed onto the substrate was 10 mm/min. The transfer ratio for stearic acid monolayer deposited onto the substrate was calculated over 95. After transferring the films on substrate, the time period of 15 min was allowed for the solvent to evaporate. The temperature of the water subphase was controlled by using Lauda Ecoline RE 204 model temperature control unit and all experimental data were taken at the room temperature.

For electrical measurements the films grown on Al-coated substrate were placed into a thermal evaporator for top electrode fabrication right after the exposure. Top electrodes were fabricated under 8×10^{-7} mbar vacuum by evaporating aluminium through a mask which has 16 parallel; 1 mm \times 15 mm sized opening interdigitated grids on it. The final structure in the form of metal/LB films/metal configuration is shown in Fig. 1. Optical measurements were taken by Perkin Elmer Lambda-2 UV-vis spectrometer. For electrical measurements HP 4192A impedance analyzer, Keithley 228A current source, Keithley 6514 voltmeter, and Keithley 485 ampermeter were used. All the data were taken automatically by using GPIB interface card and labview data acquisition software.

3. Results and discussion

Film transfer from solution onto substrate and monolayer growth on the substrate was verified using UV-vis absorption spectra. Fig. 2 shows the UV-vis absorption spectra of the 11 and 21 monolayers thick LB film samples and the inset in Fig. 2 shows the chemical structure of stearic acid. When the number of layers is increased, the wavelength of the absorption peaks of the films remained unchanged, while the intensities of the peaks increase accordingly. The increase in absorption in 21 monolayer sample is due to the increase of thickness of the sample which has 10 monolayer more layers as opposed to 11 monolayer sample. It indicates that LB film monolayer deposited onto the substrate. From the Fig. 2

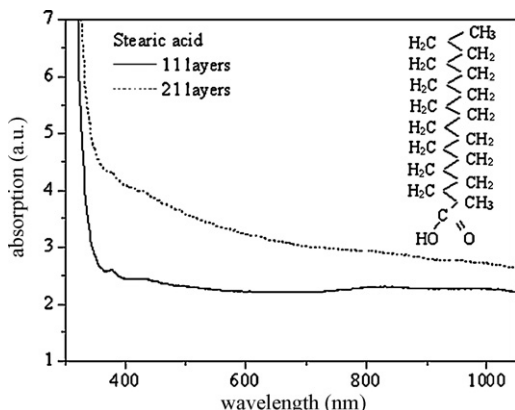


Fig. 2. UV absorption spectra for 11 and 21 multilayer LB films.

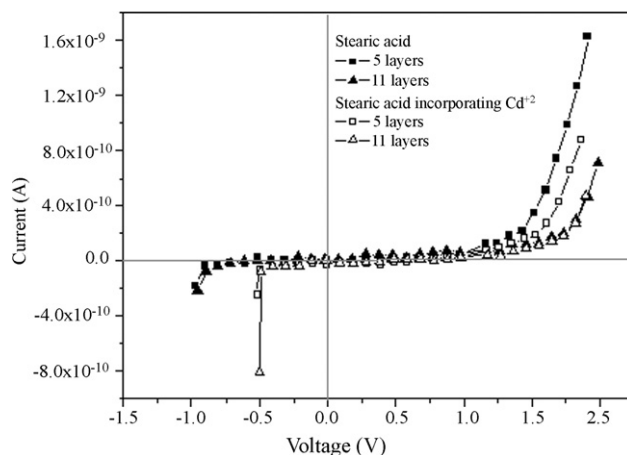


Fig. 3. Room temperature I - V graph of the films stearic acid and stearic acid incorporating Cd^{2+} films.

the absorption per monolayer is calculated as % 0.15 at 400 nm wavelength.

Electrical properties of the samples are investigated by measuring I - V characteristics. Fig. 3 shows the room temperature I - V graph of the 5 and 11 monolayer thick stearic acid and stearic acid incorporating Cd^{2+} films. All the samples show high non-linearity at high voltages. The films without Cd^{2+} ions have symmetric I - V curves and the breakdown voltage is around 1.7 V. Upon incorporation of Cd^{2+} ions, however, regardless of thickness the I - V curve of the films become asymmetric and the breakdown voltage changes from 1.7 V to approximately 0.5 V. As seen from the figure the breakdown voltage is very definite and it causes the current flow through the LB films drastically. At forward bias, there is no change in I - V curve of the 11 monolayer thick sample but there is slight change for the 5 monolayer samples.

In order to explain conduction process through LB films and the effect of the Cd^{2+} ions on conductivity $\ln J$ versus $V^{1/2}$ has been replotted in Fig. 4 for all the samples in the voltage range corresponding to the exponentially increasing current regime. As seen from Fig. 4 the relation between $\ln J$ and $V^{1/2}$ shows rather linear dependence. The linear dependence suggests that conduction is governed by either Poole-Frankel or Schottky mechanism [16]. It is difficult at this point to determine theoretically which mechanism is responsible for conduction process. However, we can make basic assumptions and extract some physically acceptable information. If we assume, conduction is governed by Schottky conduction

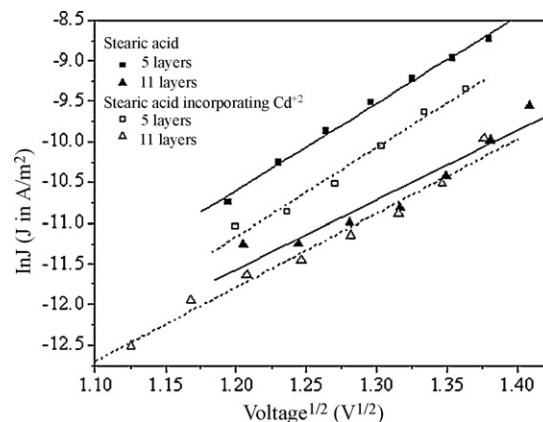


Fig. 4. Plot of $\ln J$ vs. $V^{1/2}$ for different layers stearic acid and stearic acid incorporating Cd^{2+} .

Table 1
Calculation details for barrier height energy.

Molecules	Number of layers	$\ln J(V=0)$	Schottky barrier height ϕ (eV)
Stearic acid	5	-24.56	1.26
	11	-24.61	1.26
Stearic acid incorporating Cd ²⁺	5	-25.79	1.29
	11	-24.45	1.26

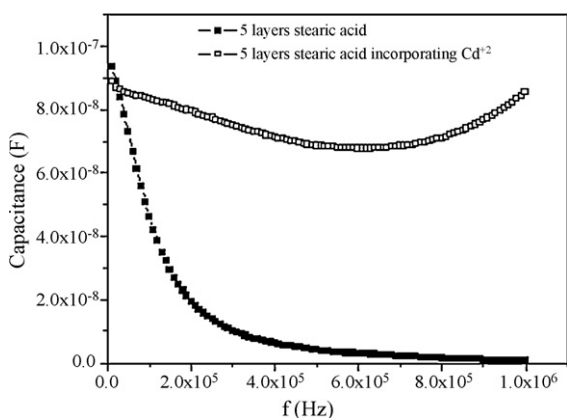


Fig. 5. C - f graph of 5 layer stearic acid and stearic acid incorporating Cd²⁺.

mechanism, which is given by [17]:

$$I_{\text{Schottky}} = AST^2 \exp\left(\frac{-e\phi}{kT} + \beta V^{1/2}\right) \quad (1)$$

where A is the Richardson constant, S is the metal contact area, T is absolute temperature, e is the electronic charge, k is the Boltzmann's constant, ϕ is the potential barrier, V is the applied voltage, and β is the Poole–Frankel field-lowering coefficients given by:

$$\beta_{\text{PF}} = \frac{e}{kT} \left(\frac{e}{\pi\epsilon_0\epsilon_r d}\right)^{1/2} \quad (2)$$

here ϵ_r is the dielectric constant of the films, ϵ_0 is the permittivity of free space, and d is the film thickness.

The intercept of the linear curve with the $\ln J$ axis at $V=0$ can be expressed in terms of barrier height (ϕ) and temperature using Eq. (1):

$$\ln J = \ln(AT^2) - \left(\frac{e}{kT}\right)\phi \quad (3)$$

The calculated barrier heights of the 5 and 11 monolayer thick samples with and without Cd²⁺ incorporation are summarized in Table 1. The samples incorporating Cd²⁺ ions have slightly different barrier height than the stearic acid samples regardless of thickness.

In Fig. 5, the dielectric properties of stearic acid incorporating Cd²⁺ LB films were plotted by measuring the variation of the capacitance as a function of frequency for metal/LB film/metal structures at room temperature. The value of the capacitance of stearic acid incorporating Cd²⁺ samples exhibits small decrease with the increasing frequency and then it increases for higher frequencies while the capacitance of stearic acid show steady decrease even at higher frequencies. If we assume, stearic acid

and stearic acid incorporating Cd²⁺ LB films have the same thickness which is nearly equal to a chain-length of a stearic acid molecule, i.e., 2.5 nm [18] and considering the system as a plane capacitor $C = (\epsilon_r\epsilon_0A)/(d_f)$ we can conclude that stearic acid incorporating Cd²⁺ LB film's dielectric constant (ϵ_r) is higher value than stearic acid film's. Stearic acid incorporating Cd²⁺'s dielectric constant has been calculated 4.62 (stearic acid incorporating Cd²⁺ monolayer thickness is 2.51 nm/layer [5]). Another work carried on metal–insulator–semiconductor structures fabricated using 40-layers-thick LB film of stearic acid incorporating CdS nanoparticles on hydrophobic n-type silicon (n-Si) substrate and the dielectric constant of the CdS embedded stearic acid LB film is found to be 5.1 [19].

4. Conclusion

In this paper, stearic acid thin films were grown in various layer thickness on both glass and aluminized substrates with LB technique. After the growth some of the films were doped with CdCl₂ solution. The thickness of the samples which have different layers was verified using UV–vis spectra. By assuming Schottky conduction mechanism the average LB film/barrier height was found to be as 1.29 eV for stearic acid incorporating Cd²⁺ samples and 1.26 eV for stearic acid samples, respectively. It is found that Cd²⁺ incorporation influences the breakdown voltage, barrier height and dielectric constant of stearic acid LB films.

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References

- [1] W. Jones, Organic Molecular Solids, CRC Press, New York, 1997.
- [2] M.C. Petty, Langmuir–Blodgett Films, Cambridge University Press, Cambridge, 1996.
- [3] N. Watanabe, H. Ohnuki, M. Izumi, T. Imakubo, Colloid Surf. A 284–285 (2006) 640.
- [4] E. Hanamura, Phys. Rev. B 37 (1988) 1273.
- [5] A.V. Nabok, Iwantono, A.K. Hassan, A.K. Ray, T. Wilkop, Mater. Sci. Eng. C 22 (2002) 355.
- [6] V. Erokhin, P. Facci, S. Carrara, C. Nikollini, Thin Solid Films 284–285 (1996) 891.
- [7] P. Facci, V. Erokhin, S. Carrara, C. Nikollini, Proc. Natl. Acad. Sci. U.S.A. 93 (1996) 10556.
- [8] H. Weller, Chem. Int. Ed. 37 (1998) 1658.
- [9] H. Sari, T. Uzunoglu, R. Capan, N. Serin, T. Serin, C. Tarimci, A.K. Hassan, H. Namli, O. Turhan, J. Nanosci. Nanotechnol. 7 (2007) 2654.
- [10] I.R. Peterson, G.J. Russell, Thin Solid Films 134 (1985) 143.
- [11] M.R. Buhaenko, M.J. Grundy, M.R. Richardson, S.J. Roser, Thin Solid Films 159 (1998) 253.
- [12] S.B. Jung, S.Y. Yoo, C. Kim, Y.S. Kwon, Synth. Met. 135–136 (2003) 75.
- [13] S.B. Jung, C. Kim, Y.S. Kwon, Thin Solid Films 438–439 (2003) 27.
- [14] R. Capan, T. Richardson, D. Lacey, Thin Solid Films 327–329 (1998) 369.
- [15] R. Capan, Mater. Lett. 61 (2007) 1231.
- [16] N.J. Geddes, J.R. Sambles, W.G. Parker, N.R. Couch, D.J. Jarvis, J. Phys. D 23 (1990) 95.
- [17] S.M. Sze, Physics of Semiconductor Devices, Wiley-Interscience, New York, 1981.
- [18] K. Kobayashi, Y. Tomita, K. Matsuhisa, Y. Doi, Appl. Surf. Sci. 244 (2005) 389.
- [19] S. Malik, A.K. Ray, A.K. Hassan, A.V. Nabok, IEEE Trans. Nanotechnol. 2 (2003) 149.