Electrical characterisation of stearic acid/eicosylamine alternate layer Langmuir–Blodgett films incorporating CdS nanoparticles

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Abstract

Electrical properties of stearic acid/eicosylamine alternate layer Langmuir–Blodgett (LB) film structure incorporating cadmium sulphide (CdS) nanoparticles are studied in the temperature range 300–400 K. The room temperature ohmic conductivity is found to be $3.87 \times 10^{-13}$ Sm$^{-1}$ for the as deposited LB film and $7.75 \times 10^{-12}$ Sm$^{-1}$ for the LB film containing CdS nanoparticles. At a relatively high field the electrode-limited Schottky effect is found to be responsible for conduction mechanism. The potential barrier height is calculated at several temperatures for the metal/LB film/metal system and the average temperature coefficient is found to be $0.0048$ eV K$^{-1}$ for the untreated LB film and $0.005$ eV K$^{-1}$ for the CdS containing LB film. Activation energies are found to be $0.46$ eV and $0.19$ eV for the untreated LB film and the LB film with CdS nanoparticles, respectively. The alternating current conductance for both samples shows typical power law dependence with a value of $\sim 0.9$ for the frequency dependence exponent.

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1. Introduction

Quantum size nanoparticles such as cadmium sulphide CdS [1–4], cadmium zinc sulphide Cd$_x$Zn$_{1-x}$S [5], and zinc sulphide ZnS [6,7] have been successfully formed within organic thin film multilayers using Langmuir–Blodgett (LB) thin film deposition technique for their potential applications in opto- and nanoelectronics.

The growth of CdS nanoparticles in Y-type mixed LB films using different concentration ratios of arachidic acid (AA) and octadecylamine (ODA) have been investigated using Atomic Force Microscopy (AFM) [8] and the size of particles was found to decrease with increasing the ratio of ODA material. Those results showed that CdS particles were not formed when ODA material was used as the sole component but CdS nanoparticles were formed within Y-type AA LB film structures. In a previous work we have observed similar results which showed that eicosylamine will not be affected by Cd$^{2+}$ during the LB film deposition, however, the chloride ions in the water subphase interacted with each eicosylamine head group (NH$_3^+$) [9]. It is well known that cadmium ions interact with carboxylic acid head groups (COO$^-$) and thus cadmium ions can easily accommodate in a multilayer LB film structure [10]. Fig. 1(a) shows the formation of alternate layers of stearic acid/eicosylamine LB film onto an aluminised glass substrate before exposure to H$_2$S gas.

When such multilayer assemblies were exposed to H$_2$S gas, cadmium ions reacted with sulphide ions to produce CdS nanoparticles in the film structure [11]. Fig. 1(b) shows the structure of LB films containing CdS nanoparticles with their size falling in the range 10 nm and 30 nm [12]. Similar structures were found for hybrid inorganic/organic thin films containing CdS quantum size nanoparticles [1,2,4,13].

Our previous work was concerned with the formation of CdS nanoparticles in the stearic acid/eicosylamine alternate layer multilayer using Surface Plasmon Resonance (SPR), AFM and Fourier Transform Infrared (FTIR) spectroscopy [12]. SPR measurements have shown a resonance shift of 0.458° for the
untreated stearic acid/eicosylamine alternate LB layer relative to the bare gold film while a resonance shift of 0.978° was observed for the H₂S treated alternate layer film. Using the SPR results the thickness of the film was found to have grown from 4.64 nm for the untreated film to 5.28 nm for the H₂S-treated film. The value of 0.46 was found for the volume fraction of the CdS nanoparticles and refractive index values of 1.31 and 1.75 were derived for the untreated and the treated films respectively. The grain heights in the CdS containing samples were approximately 17 nm as obtained from AFM results and the film roughness has increased as a result of nanoparticles formation in the multilayer structure. Using FTIR measurements, bands of IR spectra between 1700 cm⁻¹ and 1740 cm⁻¹ were found to be associated with C=O stretching, and some band intensities decreased when CdS nanoparticles were introduced into the multilayer structure. R’NH₃⁺ group is responsible for the bands observed between 1600 cm⁻¹ and 1550 cm⁻¹ and RCOO⁻ deformation usually produced IR bands between 1425 cm⁻¹ and 1400 cm⁻¹. Small changes occurred in the IR spectra when the LB films were exposed to the H₂S gas. The disappearance of the IR band at ~1545 cm⁻¹ and the increase in the intensity of IR band at ~1700 cm⁻¹ were similar to results previously obtained from composite conducting polymer LB films and was believed to be related to the formation of nanoparticles [14].

Our present work is concerned with the investigation of the effects of incorporation of CdS nanoparticles on the electrical conduction mechanism in alternate layer LB films of stearic acid and eicosylamine molecules. Direct current (DC) and alternate current (AC) measurements have been performed at a range of temperatures between 300 and 400 K. All calculations associated with the electrical characterisation are discussed in details.

2. Experimental work

In this work, stearic acid CH₃(CH₂)₁⁶CO₂H and eicosylamine CH₃(CH₂)₁⁹NH₂ were used to fabricate a non-centrosymmetric alternate layer LB film structure. The substrates used for these LB multilayer assemblies were aluminised (50 nm coating) glass microscope slides. An Edwards 306 A evaporator was used to prepare aluminium vacuum-evaporated bottom and top electrodes. The bottom electrode of 50 nm was evaporated directly onto the cleaned glass substrates using a rate between 0.3 and 0.6 nm s⁻¹ from a tungsten filament. A shadow mask was used to deposit the top electrodes, which were evaporated onto the deposited LB films in two stages. In the first stage the evaporation rate of the top electrode was very slow at approximately 0.01–0.03 nm s⁻¹ for the first 5 nm. During the second stage, this rate was increased to 0.5–0.7 nm s⁻¹ until a thickness of 50 nm was obtained. The temperature and pressure were kept below 30 °C and 10⁻⁵ Torr respectively during the evaporation.

The cadmium chloride was dissolved in the water subphase to a concentration of approximately 0.5×10⁻⁴ M. Stearic acid and eicosylamine were separately dissolved in chloroform using a concentration of approximately 0.5 mg ml⁻¹ for each material. A NIMA 622 type alternate layer LB trough was used to prepare alternate layer LB films and solutions were spread onto the water surface using a microlitre syringe and approximately 15 min were allowed for the chloroform to evaporate. Monolayers at the water surface were sequentially transferred onto an aluminised glass substrate by the alternate layer LB deposition procedure. The deposition pressure of stearic acid was 28×10⁻³ N m⁻¹ and the withdrawal speed for the first monolayer was 2 mm min⁻¹ and for subsequent layers it was 10 mm min⁻¹. Eicosylamine monolayers were deposited during the downstroke of the substrate at a surface pressure of 22.5×10⁻³ N m⁻¹ and at a speed of 10 mm min⁻¹ for all layers. 16 monolayers of stearic acid and 15 monolayers of eicosylamine were deposited by this method, as shown in Fig. 1(a). After the fabrication of Al/Al₂O₃/LB film/Al structures, one of the as-deposited samples was placed in a chamber and was exposed to H₂S gas for more than 12 h to create CdS nanoparticles within the multilayer structure, as shown in Fig. 1(b).

Electrical measurements were carried out using a Keithley 6517 A electrometer and a Hewlett Packard 4284 impedance, capacitance, resistance (LCR) meter in a microprocessor.
controlled measuring system over the temperature range of 300–400 K using an Oxford cryostat. The samples were kept under vacuum before testing to avoid any thermal current problems due to absorbed moisture and trapped charge collected from the air.

3. Results and discussion

3.1. DC measurements

Fig. 2 presents a set of curves showing typical variation of current as a function of voltage ($I$–$V$) for the Al/Al$_2$O$_3$/LB film/Al structure at various temperatures in the range between 300 K and 400 K. The $I$–$V$ characteristics for a stearic acid/eicosylamine with and without CdS nanoparticle display a symmetrical and highly non-linear behaviour at the value of DC voltage between −4 and +4 V. Current increases for both samples as the temperature increases and the $I$–$V$ characteristic analysis is carried out by the method of decomposition within two regions. Fig. 3 shows that the $I$–$V$ curves are linear in the range of 0–1.8 V and this part yields conductivities of $7.75 \times 10^{-12}$ Sm$^{-1}$ at 300 K, and $1.93 \times 10^{-11}$ Sm$^{-1}$ at 400 K for the LB film with CdS nanoparticles, and $3.87 \times 10^{-13}$ Sm$^{-1}$ at 300 K and $1.74 \times 10^{-11}$ Sm$^{-1}$ at 400 K for the untreated LB film, which are characteristic of insulators. The conductivity increases with the temperature for both samples and the value for treated LB film is higher than that for the untreated LB film.

In order to identify the conduction mechanism through the stearic acid/eicosylamine LB film multilayer, Poole–Frenkel or Schottky conduction mechanisms are used to investigate the experimentally measured dependence of current on voltage. The Poole–Frenkel effect is associated with the excitation of carriers out of traps in the insulating film and the current is described by [15]:

$$I = I_0 \exp\left(\frac{\beta_{PF} V^{1/2}}{kT d^{1/2}}\right)$$

where $V$ is the applied voltage, $\beta_{PF}$ is the Poole–Frenkel coefficient, $I_0$ is the current at zero voltage, $T$ is the absolute temperature, $k$ is the Boltzmann’s constant and $d$ is the film thickness. $\beta_{PF}$ is given by [16]:

$$\beta_{PF} = \left(\frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{1/2}$$

where $e$ is the electronic charge, $\varepsilon_0$ is the dielectric constant of LB films and $\varepsilon_r$ is the free space permittivity.

On the other hand, the Schottky effect corresponds to the injection of carriers from the electrodes over the potential barrier formed at the insulator–metal interface, and the relationship between current and applied voltage can be described by [16]:

$$I = A S T^2 \exp\left(\frac{\Phi_S}{kT}\right) \exp\left(\frac{\beta_S V^{1/2}}{kT d^{1/2}}\right)$$

where $A$ is the Richardson constant, $S$ is the electrode area, $\Phi_S$ is the Schottky barrier height at the injecting electrode interface, and $\beta_S$ is the Schottky coefficient given by [17]:

$$\beta_S = \frac{1}{2} \beta_{PF}$$

The theoretical values of $\beta_{PF}$ and $\beta_S$ are calculated from Eqs. (2) and (4). In our previous work, the bilayer thickness for the LB films was found to be 4.65 nm without CdS and 5.28 nm with CdS nanoparticles, respectively [12].
value of $\beta$ can be calculated from the gradient of the ln$V$ versus $V^{1/2}$ plots, and the slope is given by [18]:

$$m = \frac{\beta}{kTd^{1/2}}$$  \hspace{1cm} (5)

The calculated $\beta$ values for alternate layer stearic acid/eicosylamine LB film structure are given in Table 1. When experimental and theoretical values of $\beta$ are compared, the experimentally obtained coefficient $\beta$ is found to be closer to $\beta_S$ than $\beta_P$. This result suggests that carriers are transported through the LB film by the Schottky effect. Conduction mechanism is therefore described by Schottky theory and is characterised by the Richardson–Schottky formula [19].

$$I = AST^2 \exp \left(-\frac{\Phi_S}{kT}\right) \exp \left[\frac{1}{kT} \left(\frac{e^3V}{4\pi\varepsilon_0\varepsilon d}\right)^{1/2}\right]$$  \hspace{1cm} (6)

where $\Phi_S$ and $A$ are as described by Eq. (3). $A$ is described by Richardson–Dushman expression given by [19]:

$$A = \frac{4\pi m_e e k^2}{h^3}$$  \hspace{1cm} (7)

where $h$ is the Planck’s constant and $m_e$ is the carrier effective mass described by [20]

$$m_e = \left[\frac{\hbar^2(e\varepsilon_0\varepsilon d)^{3/4}}{1.76\pi^2kT}\right]^{1/2}$$  \hspace{1cm} (8)

$E^*_{k}$ is the electric field intensity that is corresponding to the transition in conduction mechanism points [15]. Using Eq. (8), the carrier effective mass values are calculated for the different temperature values and are summarised in Table 1.

To determine the barrier height ($\Phi_S$), of alternate layer LB films, the value of $I_0$ must be known. This value can be found from the intercept of the current axis at zero voltage in the graph of ln$V$ against $V^{1/2}$. $I_0$ values obtained at different temperatures are listed in Table 1. The potential barrier can be described as [21]:

$$\Phi_S = \left[kT\ln\left(\frac{A^2}{\alpha d^2}\right)\right] / e$$  \hspace{1cm} (9)

Barrier potential values calculated using Eq. (9) for a range of temperatures are given in Fig. 4. The graph shows a monotonic increase of $\Phi_S$ with temperature for both samples. The average temperature coefficient, $\alpha$, is found to be about 0.0048 eV K$^{-1}$ for the LB film without CdS and about 0.005 eV K$^{-1}$ for the LB film with CdS nanoparticles from the linear regression fit to derived data.

The dependence of the DC electrical conductivity versus inverse temperature is studied in the temperature range 300–400 K. The thermal activation energy is calculated using the relation:

$$\sigma_0 = \sigma_0 \exp \left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (10)

where $E_a$ is the activation energy of the electrical conduction and $\sigma_0$ is a parameter depending on the LB film material. Fig. 5
shows a plot of ln (σ\(_{dc}\)) for the alternate multilayer LB film as a function of inverse temperature.

Values of activation energy can be obtained from its slope and are found to be around 0.46 eV for the untreated stearic acid/eicosylamine LB film and 0.19 eV for stearic acid/eicosylamine LB film containing CdS nanoparticles. The latter may be associated with conduction through nanoparticles grains, in which case electrons may have to overcome a lower potential barrier due to grain boundaries. This is thought to be feasible as CdS grains as large as 30 nm are grown within the stearic acid/eicosylamine alternate layer LB film [12].

3.2. AC measurements

An electrical equivalent circuit for the Al/Al\(_2\)O\(_3\)/LB film/Al sandwich structure is given in Fig. 6. In this diagram \(R_{S1}\) and \(R_{S2}\) are the resistance of the bottom and top aluminium electrodes, \(R_{Ox}\) and \(C_{Ox}\) are the resistance and capacitance of the oxide layer, and \(R_{LB}\) and \(C_{LB}\) are the resistance and capacitance of the LB film multilayer.

Capacitance and conductance measurements as a function of frequency for the alternate layer LB film with and without CdS nanoparticles at several temperatures are shown in Fig. 7. Capacitance results for both LB film samples indicate a reduction with increasing frequency but there is no evidence of any Debye type dipolar relaxation.

The frequency dependence of AC conductivity, \(\sigma(\omega)\), for an LB film sample has two contributions and can be expressed in the form:

\[\sigma(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega)\]  

where \(\sigma_{dc}\) is the DC conductivity at zero-frequency and \(\sigma_{ac}(\omega)\) is the frequency-dependent component of the conductivity. When the electrode effects can be neglected, insulating LB films show a power law dependence of conductance on frequency as described by [15]:

\[\sigma_{ac}(\omega) \propto \omega^n\]  

with the index value \(n\) lying in the range between 0 and 1 and is given by [22]:

\[n = 1 - \frac{6k_BT}{\Phi_S + k_BT\ln(\omega\tau_0)}\]  

where \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\Phi_S\) and \(\tau_0\) are the effective hopping barrier height and the effective relaxation time, respectively. Using Eq. (13) and the experimental data for our samples, \(n\) values are given in Fig. 8 as a function of temperature between 300 and 400 K. As shown in Fig. 8, \(n\) values are almost constant over the studied temperature range, and its value is about 0.87 for the as-deposited alternate LB layers, but slightly lower (~0.865) for the LB film with the CdS nanoparticles. These results are indicative of high frequency electron transport by hopping, as suggested by Geddes and co-workers [15].

4. Conclusion

Multilayered Langmuir–Blodgett films with and without CdS nanoparticles are prepared by alternately transferring 16 layers of stearic acid and 15 of eicosylamine molecules from the subphase of Millipore water 18 MΩ cm\(^{-1}\) on aluminised glass substrate for the study of their electrical properties. The \(I–V\) characteristic shows a symmetrical and highly non-linear behaviour between ±4 V. The low voltage values of conductivity
at the room temperature are found $3.87 \times 10^{-13}$ Sm$^{-1}$ for the freshly prepared LB film and $7.75 \times 10^{-12}$ Sm$^{-1}$ for the CdS-containing LB film respectively. At high applied voltages the electrode-limited Schottky effect is responsible for electron transport through the LB films. The average temperature coefficients using the barrier height values are determined as 0.0048 eV K$^{-1}$ for the untreated LB film, and 0.005 eV K$^{-1}$ for the LB film with CdS nanoparticles. Activation energies for electron conduction are 0.46 eV for LB film without CdS and 0.19 eV for CdS-containing LB film. The AC conductance for both samples shows typical power law dependence on frequency, with a value of $\sim 0.9$ for the frequency exponent.

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