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Electrical properties of a calix[4]acid/amine Langmuir–Blodgett thin film

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ABSTRACT

In this work the DC and AC characteristics for metal-LB film-metal structures deposited by a standard Langmuir–Blodgett film deposition technique are investigated. The conduction mechanism has been studied for a thin film structure in which a calix[4]arene substituted with carboxylic acid groups has been deposited alternately with a calix[4]arene molecule substituted with amine groups. This LB film structure shows a typical insulating behaviour for low voltage values and the Schottky effect becomes dominant when the voltage increases. The conductivity at low voltage values was found to be 1.34×10^{-13} S cm^{-1}. The height of the potential barrier was determined to be 1.65 eV for this alternate layer LB film system.

1. Introduction

Organic thin films find many applications in optoelectronic devices [1,2] and sensing applications such as in gas [3,4], heat [5] and biosensors [6]. However still very little is known about the electronic properties of the interfaces present in these systems. For the fabrication of any device, the physical and chemical properties of the device materials must be well characterised. In recent years, calix[*n*]arenes and their derivatives have been extensively studied for their possible application as sensors and electronic devices. These materials are often highly selective molecular receptors for various metal ions and organic compounds, making them suitable for separation and analysis applications [7]. The Langmuir–Blodgett (LB) thin film technique is an elegant method to fabricate symmetric or asymmetric organic molecular thin films. Conduction in LB film assemblies of fatty acids has been previously determined to occur by a combination of two mechanisms; electron tunnelling through each LB film bilayer and hopping conduction within the plane of carboxylic head groups [8].

The present article reports on the preparation of an Al/Al_2O_3/calix[4]acid/amine alternate layer LB film/Al system and the determination of the electrical properties of this structure. The DC and AC conduction mechanism has been studied for the calix[4]acid/amine LB film structure using I–V characteristics and C-F measurements. The details of these calculations will be given in this paper.

2. Experimental preparation

The chemical structures of the materials used in this work are shown in Fig. 1. Alternate layer LB films were prepared using a NIMA 622 type alternate layer LB trough. Both materials were dissolved in chloroform using a concentration of approximately 0.5 mg ml^{-1}. A Hamilton syringe was used to spread the solution onto the pure water surface and approximately 15 mins were allowed for the chloroform to evaporate. These monolayers were sequentially transferred onto an aluminised glass substrate by the alternate layer LB deposition technique at a surface pressure of 22.5 mN m^{-1}. Calix[4]acid was deposited on each upstroke with a deposition speed of 2 mm min^{-1} for the first three mixed monolayers and 10 mm min^{-1} for subsequent layers. Calix[4]amine monolayers were deposited on the downstroke of the substrate at a speed of 10 mm min^{-1}. 6 monolayers of calix[4]acid alternated with 5 monolayers of calix[4]amine were deposited onto the substrates which were aluminised (50 nm coating) glass microscope slides. An Edwards 306A evaporator was used to prepare aluminium vacuum-evaporated bottom and top electrodes in this work. The bottom electrode of 50 nm was evaporated directly from a tungsten filament onto the cleaned glass substrate using a rate between 3 and 6 Å/s. A shadow mask was used for making 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 for the first 5 nm. During the second stage, this rate was increased to 0.5–0.7 nm/s until 50 nm. The temperature and pressure were kept below 30 °C and 10^{-5} torr, respectively during the evaporation. In order to measure the electrical properties of the LB film sample, the chamber was evacuated to ∼4–6 Pa (10^{-2} torr) using an Edwards E2M5 two-stage rotary vacuum pump. The LB film was kept under vacuum with short-circuited electrodes overnight before testing to avoid any thermal current problems due to absorbed moisture and trapped charge collected from the air.

DC electrical measurements were performed using a Keithley 6517A electrometer controlled by a microprocessor. The measurements were performed in the range of ±4 V. An LCR meter (HP4284A) was used to provide AC conduction measurements over the frequency range 20 Hz to 1 MHz. Both measurements were performed at room temperature.

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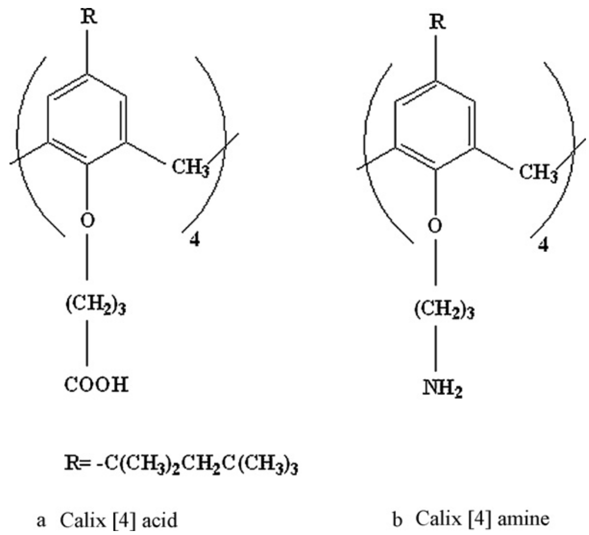

Fig. 1. The chemical structure of the materials used within this study.

3. Results and discussion

3.1. DC measurements

Fig. 2 shows the a schematic of the device structure incorporating the calix[4]acid/amine alternate layer LB film. Fig. 3 shows the variation of current as a function of voltage (*I–V*) for the Al/Al_2O_3/LB film/Al structure at room temperature. The *I–V* characteristics for these LB film samples display a non-linear behaviour for DC voltages in the range between −4 and +4 V. The *I–V* characteristic analysis was carried out by a method of decomposition within two regions and the *I–V* curves are linear in the range of 0–1.0 V. This Ohmic or linear part of the *I–V* curve yields a conductivity of $1.34 \times 10^{-13}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which is a typical value for insulators.

In order to identify the conduction mechanism through the calix[4]acid/amine alternate layer LB film structure, Poole-Frenkel or Schottky conduction mechanisms are used as models for 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 density *J* is described by the following equation [9]:

$$J = J_0 \exp\left(\frac{\beta_{PF} V^{1/2}}{kTd^{1/2}}\right) \tag{1}$$

where *V* is the applied voltage, β_{PF} is the Poole-Frenkel coefficient, J_0 is the low-field (0 V) current density, *T* is the absolute temperature, *k* is the Boltzmann's constant and *d* is the film thickness. β_{PF} is described by [10]:

$$\beta_{PF} = \left(\frac{e^3}{\pi \varepsilon_r \varepsilon_0}\right)^{1/2} \tag{2}$$

where *e* is the electronic charge, ε_0 is the free space permittivity and ε_r is the dielectric constant. The measurement of dielectric constant is complicated here because an aluminium substrate is used whose oxide layer possesses its own capacitance [11]. Fig. 4 shows a plot of the inverse measured capacitance against the number of calix [4] acid/amine LB film at 100 Hz. The dielectric constant of LB films can be determined using the graph of the reciprocal capacitance ($A\varepsilon_0/C$) as a function of film thickness. A straight line plot was obtained, using the intercept of this graph indicated that a small oxide effect occurs as it is expected and the dielectric constant for this LB film is determined to be 1.26 using the gradient of Fig. 4.

The Schottky effect corresponds to the injection of carriers from the electrodes over the potential barrier formed at the insulator–metal interface and it is described by [12].

$$J = AT^2 \exp\left(-\frac{\Phi_S}{kT}\right) \exp\left(\frac{\beta_S V^{1/2}}{kTd^{1/2}}\right) \tag{3}$$

where *A* is the Richardson constant, Φ_S is the Schottky barrier height at the injecting electrode interface and β_S is the Schottky coefficient given by [10].

$$\beta_S = \frac{1}{2}\beta_{PF} \tag{4}$$

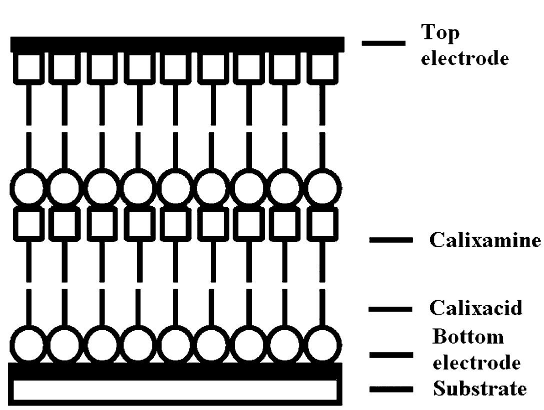

Fig. 2. Al/Al_2O_3/LB film/Al device structure.

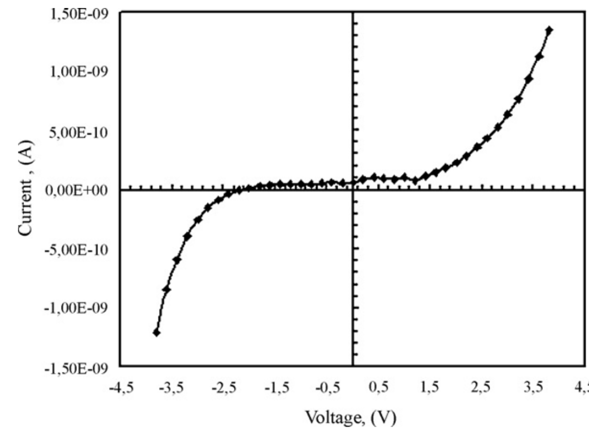

Fig. 3. *I–V* characteristics for calix[4]acid/amine alternate layer LB film sample.

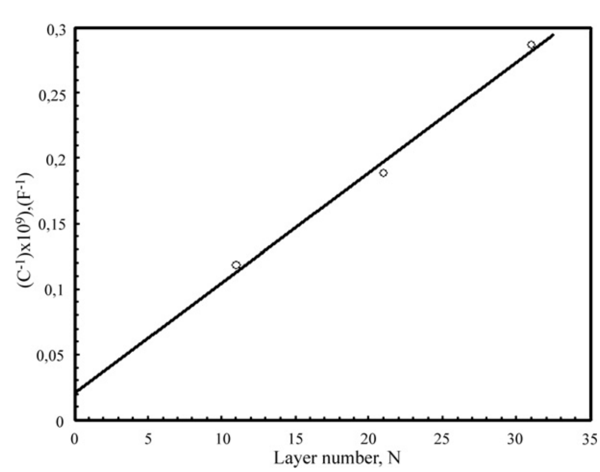

Fig. 4. Reciprocal capacitance of LB film versus number of layer.

Table 1
A comparison of potential barrier heights for LB fims.

Material	σ (Ω^{-1} cm^{-1})	ϕ (eV)	d (Å)	Reference
Fatty acid (barium stearate)	2.7×10^{-16}	2.53	25.8	[18]
Fatty acid (barium arachidate)	8.7×10^{-17}	2.26	28.0	[18]
Carotenoic acid	1.95×10^{-14}	1.70	28.0	[18]
22-tricosenoic acid		1.10	30.0	[9]
Calix[4]acid/amine alternate layer LB film	1.34×10^{-13}	1.65	16.5 (11 layer)	

The theoretical values of β_{PF} and β_S are calculated from Eqs. (2) and (4). Using this value, the theoretical Poole-Frenkel and Schottky coefficients are found to be $\beta_{PF} = 6.76 \times 10^{-5}$ eV $m^{1/2}$ $V^{-1/2}$ and $\beta_S = 3.38 \times 10^{-5}$ eV $m^{1/2}$ $V^{-1/2}$, respectively.

Fig. 5 shows the linear dependence of ln$J$ as a function of $V^{1/2}$ in the voltage range of 1–4 V. The experimental value of β can be calculated from the gradient of the ln$J$ versus $V^{1/2}$ plots, and the slope is given by [13].

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

The monolayer thickness for the similar calix[8]arene acid and amine compounds reported previously has been calculated as 1.5 nm using Corey–Pauling–Koltun (CPK) models [14]. In this paper, the bilayer thickness of a calix[4]acid/amine alternate layer LB film is assumed to be approximately 3 nm. From Eq. (5) and Fig. 5 the value of β is found to be 1.07×10^{-5} eV $m^{1/2}$ $V^{-1/2}$. This calculated β value for calix[4]acid/amine alternate layer LB film structure is found to be closer to β_S than β_{PF}. This result suggests that carriers are transported through the LB film by the Schottky effect which is described by the Richardson–Schottky formula as given in Eq. (3). The Richardson constant is obtained from the Richardson–Dushmann expression [15].

$$A = \frac{4\pi m_e e k^2}{h^3} \quad (6)$$

where h is the Planck constant and m_e is the carrier effective mass described by [16].

$$m_e = \left[\frac{h(e\varepsilon_r\varepsilon_0)^{1/4}}{1.76\pi^2 kT}\right]^2 E_k^{3/2} \quad (7)$$

$E_k^{3/2}$ is the electric field intensity that is corresponding to the transition in conduction mechanism points at 1.2 V [9]. Using Eq. (8), the carrier effective mass is found to be 4.291×10^{-31} kg$(0.47m_0)$ for the calix[4]acid/amine alternate layer LB film.

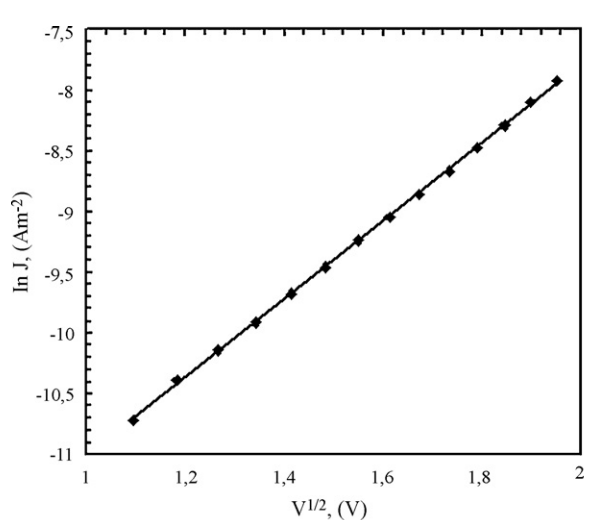

Fig. 5. A plot of ln$J$ as a function of $V^{1/2}$.

Φ_S is the Schottky barrier height which can be described by [17].

$$\Phi_S = \frac{[kT \ln(AT^2/J_0 S^2)]}{e} \quad (8)$$

The value of J_0 can be determined from the intercept of the current density axis at zero voltage in the graph of ln$J$ against $V^{1/2}$ (S is the electrode area). Using Eq. (9), Φ_S value is calculated to be 1.65 eV for the calix[4]acid/amine alternate layer LB film and a comparison of electrical properties of this LB film compared to LB films of other materials is given in Table 1.

3.2. AC measurements

The frequency dependence of the conductance of an LB film, $G(\omega)$, consists of two contributions and can be expressed in a form:

$$G(\omega) = G_{dc}(0) + G_{ac}(\omega) \quad (9)$$

where G_{dc} is the dc conductance at zero-frequency and G_{ac} is the frequency-dependent component of the conductance. When the electrode effects can be minimized, insulating LB film samples show a power law relationship between AC conductance and frequency described by [9].

$$G_{ac}(\omega) \propto \omega^n \quad (10)$$

with an index value n lying between 0 and 1 and is given by the equation [19].

$$n = 1 - \frac{6k_B T}{\Phi_S + k_B T \ln(\omega\tau_0)} \quad (11)$$

where k_B is the Boltzmann's constant, Φ_S and τ_0 are the barrier height and the relaxation time respectively. T is the temperature.

The results presented in Fig. 6 shows the dependence of the AC conductance and capacitance as a function of frequency. Using the experimental data in Fig. 6 for our sample the power value n is determined to be 0.85 ± 0.02 at 20 Hz and 0.88 ± 0.02 at 1 MHz. Earlier work shows similar behaviour for fatty acid LB films, the power value n was found to be 0.87 ± 0.02 over a frequency range 10^2–10^4 Hz [20]. Fig. 7 shows a plot of the capacitance and dielectric

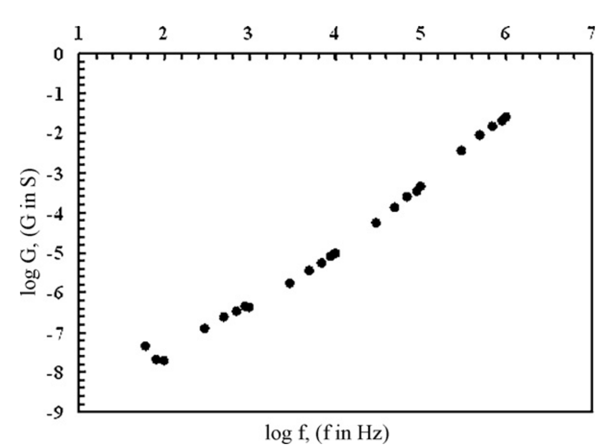

Fig. 6. The conductance as a function of frequency.

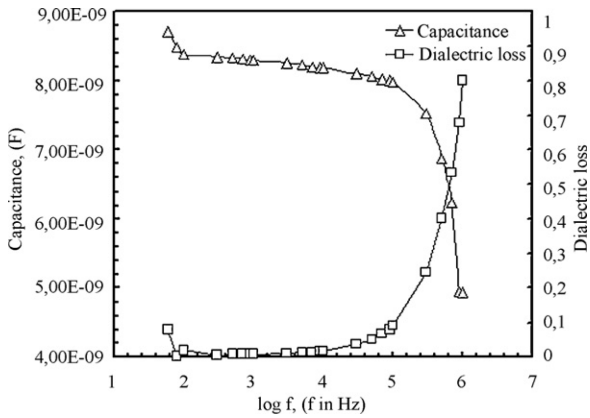

Fig. 7. A plot of the capacitance and tan δ against frequency at room temperature.

loss against frequency at room temperature. Our results indicate a traditional insulating behaviour for this alternate layer LB film system and there is no evidence of any Debye type dipolar relaxation [21,22].

4. Conclusion

Alternate layer LB films were fabricated by alternately transferring 6 layers of calix[4]acid and 5 layers of calix[4]amine molecules onto aluminised glass substrates for the study of DC and AC electrical properties at the room temperature. The *I–V* characteristic of this LB sample was determined in the range of −4 V and +4 V and it showed a highly non-linear behaviour. At the low voltage values, a linear or Ohmic regime dominates with the conductivity value being 1.34×10^{-13} S cm^{-1}. At the high voltages the Schottky effect prevails for electron transport through the LB films. The carrier effective mass and the potential barrier height are determined as $0.46m_0$ and 1.65 eV, respectively. The AC conductance for calix[4]acid/amine alternate layer LB film is proportional to the frequency raised to the power *n*, where $n = 0.85 \pm 0.02$ at 20 Hz and 0.88 ± 0.02 at 1 MHz.

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