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Non-centrosymmetric Z-type Langmuir-Blodgett (LB) films were prepared by transferring a calix[4] acid monolayer from a subphase of Millipore water (18 μl cm−1) onto aluminised glass substrates. Electrical measurements were performed at room temperature on LB films with a sandwich structure comprising a 50 nm thick thermally evaporated aluminium film. A pyroelectric figure of merit of 2.23 μC m−2K−1 is reported for this LB system. The low voltage value of conductivity is 1.82 × 10−12 Sm−1. The electrode–limited Schottky effect is responsible for the conduction mechanism at a relatively high field due to the dc bias and the barrier potential height is determined to be 1.72 eV. The ac conductance for both samples shows a typical power law dependence with a value of ≈0.86 for the exponent.

Keywords: Pyroelectric Effect, Conductivity, LB Films, Calixarene.

1. INTRODUCTION

Organic materials are particularly well suited for the fabrication of supramolecular polar systems because of their ease of processing. They have many applications in optoelectronics and sensing.1–3 The Langmuir-Blodgett (LB) thin film technique is a suitable method for the fabrication of a symmetric or asymmetric organic thin film device structure. Before the fabrication of a device, structural, electrical, optical and chemical properties of the device material must be known. In recent years, calix[n]arenes and their derivatives have been studied for their sensing applications such as gas sensing,4–6 chemical sensing7 and pyroelectric heat sensing.8 For the investigation of pyroelectric activity in calix[n]arene molecules, alternate layer calix[8]arene acid/amine LB films9,10 were studied because of their extreme thermal stability (the melting point of calixarenes is typically around 250 °C, compared with 50–70 °C for many other organic materials). Calix[8]arene was alternately deposited with a polysiloxane polymer to study the pyroelectric mechanism in alternate layer LB films.11 Conductivity in LB films has been described previously by a combination of two mechanisms: (i) electron tunneling through each LB film bilayer and (ii) hopping conduction within the plane of carboxylic head groups. Stearic acid and calix[8]arene LB films with CdS nanoparticles have been used to study electrical characterisation inside sandwich structures. The results showed an electron tunneling through multilayered LB films. The conductivity decreases when CdS nanoparticles are formed within the LB film multilayers because of the reduced layer-by-layer film order. AC measurements indicated a traditional insulating behaviour for both LB film system.12

For a pyroelectric device, it is well known that pyroelectric material should have a low dielectric constant in the temperature range of use, low dielectric loss and a high pyroelectric coefficient. However, there are other important physical properties that can require control, particularly electrical resistivity, conductivity etc. A pyroelectric device is required to generate charge in response to a change in the intensity of radiation incident on its surface. Very
slow temperature changes can also give rise to a gradual build up of charge that can eventually cause the input of the following electronics to saturate. Therefore it is very important to know all electrical properties of a pyroelectric device for an easy control of the device during its operation. Poultier et al. studied the pyroelectric and dielectric properties of organo-metallic LB films measuring conductance as a function of frequency to investigate a Universal Dielectric Model based on hopping of charge carriers.

In this work calix[4] acid is used to produce a Z-type LB film structure for the investigation of the pyroelectric, dc and ac electrical properties using two electrodes technique at room temperature. The pyroelectric figure of merit for this LB film has also been determined using a quasi-static measurement system. Dc and ac conduction mechanisms are investigated using I–V and C–F measurements. The details of these calculations will be given in this paper.

2. EXPERIMENTAL WORK

Figure 1 shows the chemical structure of the calix[4] acid which was dissolved in chloroform with a concentration of 0.5 mg ml$^{-1}$. Z-type LB films were prepared using a NIMA 622 type alternate layer LB trough. The solution was spread onto the water surface using a microlitre syringe and approximately 15 minutes were allowed for the chloroform to evaporate. The II-A isotherm graph of calix[4] acid was recorded as a function of surface area at pH 6.0 and the compression speed for the monolayer was controlled at 1000 mm min$^{-1}$. Isotherm graph given in Figure 2 was repeated several times at room temperature using Lauda Ecoline RE 204 model temperature control unit and the results were found to be reproducible. The surface pressure starts rising at an area around 1.1 nm$^2$ and gradually increases upon compression until the surface pressure rises to nearly 36 mN m$^{-1}$ when collapse of the monolayer occurs.

The monolayer at the water surface was transferred onto an aluminised glass substrate for which the aluminium was thermally evaporated using an Edwards E306A evaporation system with a rate of 1 nm s$^{-1}$ under vacuum of 10$^{-4}$ Pa to fabricate 50 nm thick aluminium top and bottom contacts. The thickness of the aluminium contact was monitored using the conventional quartz crystal method. The device structure and non-centrosymmetric Z-type LB film structure are shown in Figure 3. The deposition pressure was 22.5 mN m$^{-1}$ and 15 monolayers have been deposited. The deposition speed for the first three monolayers was 2 mm min$^{-1}$ and it was 10 mm min$^{-1}$ for subsequent layers. In order to measure the pyroelectric, dc and ac 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. The pyroelectric measurement itself is a quasi-static technique in which a Peltier heating device is used to create a temperature gradient on the pyroelectric LB sample with heating and cooling temperature ramps. The pyroelectric current, $i_p$, was measured using a Keithley 614 electrometer and a Jenway 7900 thermometer was connected to one channel of a Scientific Instrument 312 chart recorder. Electrical measurements are carried out using a Keithley 6517 A electrometer and a Hewlett Packard 4284 LCR meter in a microprocessor controlled measuring system. DC measurements were performed in the range of ±4 V and AC measurements are taken from 10 to $10^6$ Hz.

### 3. RESULTS AND DISCUSSION

#### 3.1. Pyroelectric Figure of Merit

If a pyroelectric material between two metal electrodes experiences a temperature gradient, a pyroelectric current, $I$, flows as a function of temperature gradient. This current is given below:

$$ I = \Gamma A \frac{dT}{dt} $$

where $dT/dt$ is the rate of temperature change, $A$ is the area of overlap of the two electrodes and $\Gamma$ is the pyroelectric coefficient (the rate of change of polarisation with respect to temperature).

The pyroelectric coefficient for 15 monolayers of Z-type calix[4] acid LB film is calculated to be 0.50 μC m$^{-2}$ K$^{-1}$ at room temperature using Eq. 1. Figure 4 shows capacitance and dielectric loss measurements as a function of frequency for 15 monolayers of Z-type calix LB film at room temperature. Capacitance results for the sample indicate a reduction with increasing frequency and dielectric loss increases as a respect of increasing frequency. There is no evidence of any Debye type dipolar relaxation for Z-type calix LB film. Using the definition of a parallel plate capacitance, the capacitance of the LB film is expressed by:

$$ C_{LB} = \frac{\varepsilon_0 e A}{Nd} $$

where $\varepsilon$ is the dielectric constant, $A$ is the overlap area of LB film, $N$ is the number of LB film layers and $d$ is the monolayer thickness.

Calix[4] acid/calix[4]amine alternate layer LB film assemblies used to investigate the effect of oxide layer and the relationship between reciprocal capacitance versus the number of transferred monolayers. Results indicated that a small oxide effect occurs as it is expected and a linear relationship between $1/C$ and $N$, which means the transfer process of the LB film is reproducible. The molecular thickness of the calix[8] arene acid molecule is calculated to be 1.5 nm using Corey-Pauling-Koltun (CPK) models. Using this value, the dielectric constant for our LB film is calculated to be 2.32. The Figure of Merit (FOM) is one of the most important parameters for the design of pyroelectric detectors and is described for an LB films by:

$$ \text{FOM} = \frac{\Gamma}{\sqrt{\varepsilon \tan \delta}} $$

where $\Gamma$ is the pyroelectric coefficient of LB film, $\varepsilon$ and $\tan \delta$ are the dielectric constant and dielectric loss, respectively. Values of the figure of merit (FOM) at 100 Hz are found to be 2.23 μC m$^{-2}$ K$^{-1}$ using Eq. 3 and Figure 4.

#### 3.2. DC Analysis

The I–V characteristic for the Z-type calix[4] acid LB film is shown in Figure 5. The experimental results show that the I–V characteristics are symmetrical and highly non-linear. The I–V characteristic analysis was carried out by a method of decomposition within two regions. Each of these regions corresponds to a specific carrier conduction mechanism. The Ohmic or linear part of the I–V curve between 0–2 V yields a conductivity of $1.82 \times 10^{-13}$ S m$^{-1}$, which is representative of a characteristic insulating medium.

Poole-Frenkel or Schottky conduction mechanisms can be considered when inspecting the current as a function of voltage in the range of 2–4 V. Figure 6 gives the $\ln(I)$ as a function of $V^{1/2}$. The Poole-Frenkel conduction mechanism is associated with the excitation of carriers out of traps in a material. The current for the Poole-Frenkel effect is described by:

$$ I = I_o \exp \left( \frac{\beta \sqrt{V}}{kTd^{1/2}} \right) $$

**Fig. 4.** Capacitance and dielectric loss as a function of frequency.

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where \( V \) is the applied voltage and \( \beta_{\text{F}} \) is the Poole-Frenkel coefficient, \( I_0 \) is the low field current at zero voltage, \( T \) is the absolute temperature, \( k \) is the Boltzmann’s constant and \( d \) is the film thickness. \( \beta_{\text{F}} \) is the Poole-Frenkel field-lowering coefficients, which is given by:\(^{18}\)

\[
\beta_{\text{F}} = \left( \frac{e}{\pi \varepsilon_r \varepsilon_0} \right)^{1/2} eV m^{1/2} V^{-1/2}
\]

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

The Schottky effect corresponds to the injection of carriers from the electrodes over the potential barrier formed at the insulator-metal interface and current in the Schottky effect is described by:\(^{19}\)

\[
I = A T^2 \exp \left( \frac{-\Phi_S}{kT} \right) \exp \left( \frac{\beta_S V^{1/2}}{kT \sqrt{d}} \right)
\]

where \( V \) is applied voltage and \( \beta_S \) is the Schottky coefficient, \( A \) is the Richardson constant, \( S \) is the electrode area, \( T \) is the absolute temperature, \( \Phi_S \) is the Schottky barrier height at the injecting electrode interface, \( k \) is the Boltzmann’s constant, \( d \) is the film thickness and \( I_0 \) is the low field current density. \( \beta_S \) is the Schottky coefficient and is given by:\(^{19}\)

\[
\beta_S = \frac{1}{2} \left( \frac{e}{\pi \varepsilon_r \varepsilon_0} \right)^{1/2} eV m^{1/2} V^{-1/2}
\]

where \( e \) is the electronic charge, \( \varepsilon_r \) is the dielectric constant of LB films and \( \varepsilon_0 \) is the free space permittivity. The theoretical value of \( \beta_{\text{F}} \) and \( \beta_S \) is found to be 4.98 \times 10^{-5} eV m^{1/2} V^{-1/2} and 2.49 \times 10^{-5} eV m^{1/2} V^{-1/2} using Eq. 2 and Eq. 4. The experimental value of \( \beta \) is calculated 2.50 \times 10^{-5} eV m^{1/2} V^{-1/2} using the gradient of the \( \frac{\Delta V}{\Delta I} \) given in Figure 6. The experimental \( \beta \) value for Z-type calix LB film is very close to theoretical \( \beta \) value. This result suggests that carriers are transported through the LB film by the Schottky mechanism.

Chaibane et al.\(^{20}\) have studied metal-calixarene-semiconductor thin films prepared the vacuum deposition technique. They found that at high voltages (>0.5 V), space charge injection across the calixarene films became dominant and the conduction mechanism obeyed the Schottky effect.

The Richardson-Schottky law for a conduction mechanism is described by:\(^{21}\)

\[
I = A T^2 \exp \left( -\frac{\Phi_S}{kT} \right) \exp \left[ \frac{1}{kT} \left( \frac{eV}{\pi \varepsilon_r \varepsilon_0} \right)^{1/2} \right]
\]

where \( A \) is the Richardson constant, \( \Phi_S \) is the Schottky barrier height is described as:\(^{22}\)

\[
\Phi_S = \frac{kT \ln \left( \frac{\beta_S V^{1/2}}{kT \sqrt{d}} \right)}{e}
\]

From this Equation, the potential barrier height is found to be 1.72 eV.

### 3.3. AC Analysis

Figure 7 shows the capacitance and conductance data as a function of frequency for the Z-type calix LB film at room temperature. The AC conductivity, \( \sigma(\omega) \), for an LB film sample has two contributions and can be described by:

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

where \( \sigma_{dc} \) is the dc conductivity at zero-frequency and \( \sigma_{ac} \) is the frequency-dependent component of the conductivity. If the electrode effects are minimized, the sample shows a power law relationship between conductance and frequency described:\(^{23}\)

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

\( n \) value is lying between 0 and 1 and is given by:\(^{24}\)

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

where \( k_B \) is the Boltzmann constant, \( \Phi_S \) and \( \tau_0 \) are the effective hopping barrier height and the effective relation.
The value of the figure of merit (FOM) is obtained has been prepared using the LB film deposition procedure. Z-type calix[4] acid alternate layer LB film assemblies have been prepared using the LB film deposition procedure. Z-type calix[4] acid multilayer LB film assemblies have prepared using the LB film deposition procedure.

4. SUMMARY

Z-type calix[4] acid multilayer LB film assemblies have been prepared using the LB film deposition procedure. Z-type calix[4] acid alternate layer LB film assemblies have been prepared using the LB film deposition procedure. A value of the figure of merit (FOM) is obtained as a function of temperature. Using our experimental data and Figure 7, the value of $n$ is calculated to be 0.861 at 100 Hz at room temperature.

Fig. 7. Capacitance and conductance against frequency.

time and $T$ is the temperature. Using our experimental data and Figure 7, the value of $n$ is calculated to be 0.861 at 100 Hz at room temperature.

4. SUMMARY

Z-type calix[4] acid multilayer LB film assemblies have been prepared using the LB film deposition procedure. Z-type calix[4] acid alternate layer LB film assemblies have been prepared using the LB film deposition procedure. A value of the figure of merit (FOM) is obtained as $2.23 \times 10^{-12} \text{K}^{-1}$ which is higher than certain other alternate layer LB film materials. Organic LB film materials show a promising result for the pyroelectric heat sensor applications. The I–V characteristic shows a symmetrical and highly non-linear behaviour between ±4 V. The low voltage value of conductivity for this Z-type LB film obtains $1.82 \times 10^{-12} \text{S m}^{-1}$. At high voltage, the electrode–limited Schottky effect is responsible for conduction mechanism. The potential barrier height is found to be 1.72 eV using dc measurements. The ac conductance for both samples reveals a typical power law dependence with a value of $0.86$ for the exponent and the n value has a small decrease as a function of temperature.

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References and Notes


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