Electrical characterisation of poly(methyl methacrylate)/arachidic acid Langmuir–Blodgett films

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Abstract

A series of poly(methyl methacrylate) (PMMA) molecules with different molecular weights and arachidic acid has been used to fabricate alternate layer Langmuir–Blodgett (LB) films onto aluminum coated glass substrates and electrical properties of these LB films have been investigated. The area per molecule for PMMA molecules was found to be approximately 2000 nm^2. I–V measurements showed that there is a polarity in the alternate layer LB films. Schottky barrier height values have been calculated using alternate layer type (AL-type) LB films.
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1. Introduction

Polymer materials are used in industry for their potential applications including light emitting diodes [1–3], gas sensing applications [4,5]. The thin film fabrication techniques have a wide range of alternatives such as spin coating, self assembly and Langmuir–Blodgett (LB) thin film technique. Among all techniques LB film fabrication is one of the most convenient method to produce well ordered and well defined molecular orientation with a few nanometres of thickness.

LB film fabrication technique requires a stable monolayer on the water surface. Although poly(methyl methacrylate) (PMMA) molecule forms a stable monolayer on the water subphase [6] but it is very difficult to produce a multilayer LB film because of their high molecular weight. It is well known that PMMA can be alternately deposited with fatty acid molecules using LB film fabrication technique [7–12].

In this work, alternate layer type LB film of PMMA with arachidic acid has been deposited onto aluminium substrate to fabricate a metal/LB film/metal device. The electrical properties of this LB device have been investigated.

2. Experimental part

Poly(methyl methacrylate) molecules with the different molecular weights have been synthesised using emulsifier-free emulsion polymerization method. The synthesis, physical and chemical properties of PMMA molecules has been reported in detail [13]. The polymerisation was carried out using potassium persulfate as the initiator. It is generally accepted that its use results in the incorporation onto the latex surface of charged sulfate and uncharged hydroxyl groups; the latter are produced either by hydrolysis of surface sulfate groups or by initiation by hydroxyl radical [14]. Fig. 1 shows the molecular structure of PMMA molecules with an end group of $SO_4^- K^+$. The surface
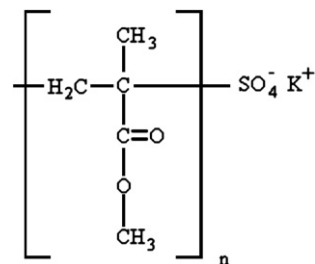

Fig. 1. Molecular structure of PMMA molecules.

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Table 1
Properties of PMMA molecules and alternate layer LB films

Materials	Molecular weight (kg/mol)	Number of alternate layers
P1	680	18
P2	810	14
P3	830	18

pressure–area (Π–A) isotherms and the deposition of mono-layers were carried out with a poly(tetrafluoroethylene) alter-nate layer LB trough system (NIMA 622) provided with a filter paper Wilhelmy balance, where the pH and ionic strength of the subphase were adjusted before the spreading of the polymer solution using NaOH or HCl solutions. The PMMA molecules were dissolved in chloroform at the concentration of 0.7 mg/ml. To take the isotherm graph, 30 μl of the PMMA solution was spread onto the water subphase with allowing 10 min for the solvent to evaporate and Π–A isotherms were performed with the compression speed of 30 cm^2/min at room temperature.

Al bottom electrode was thermally vacuum-evaporated on a glass substrate at a pressure of 10^{-7} Torr. Three different AL-Type LB films were transferred onto this aluminised glass substrate in ABABA sequence using three different PMMA molecules and arachidic acid alternately and this LB films were coded as P1-P3. Arachidic acid was deposited on the down-stroke and PMMA molecules were deposited on the upstroke. Transfer speed was 10 mm min^{-1} for both downstroke and upstroke. The constant surface pressure value of arachidic acid was 25 mN m^{-1} and PMMA molecules were 20 mN m^{-1} for P1 film and 15 mN m^{-1} for P2 and P3 films. Chemical properties of PMMA molecules and resulting number of layers of LB films are given in Table 1. After the formation of AL-type LB films top electrodes have been evaporated using a special mask which has 16 parallel, 1 mm × 15 mm sized opening interdigitated grids on it. The thicknesses of both top and bottom electrodes were approximately 10 nm and were controlled by the quartz crystal thickness monitor. Fig. 2 shows the metal/LB film/metal
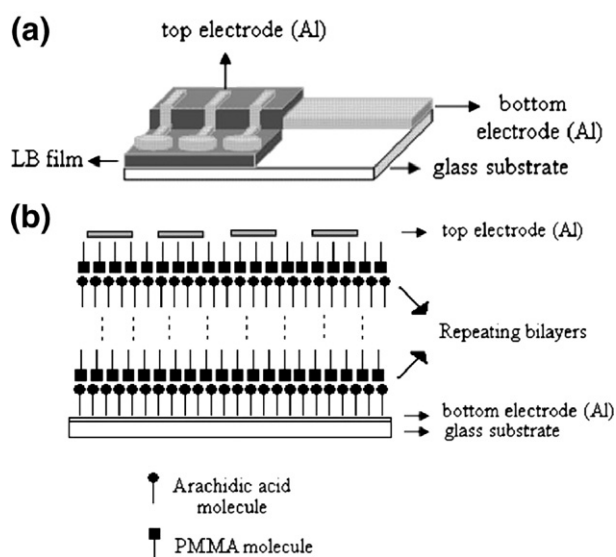

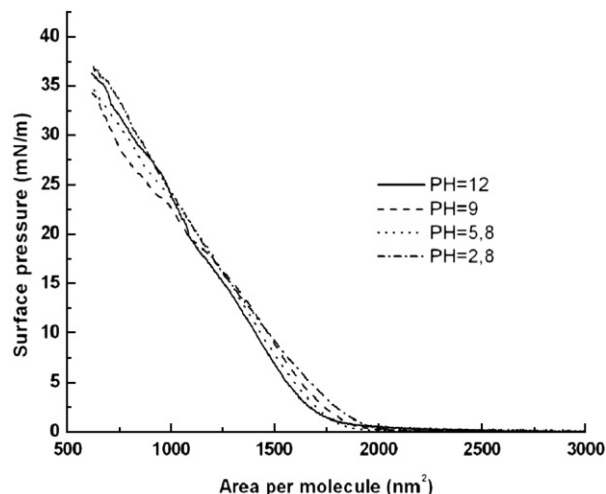Fig. 2. Metal/LB fim/metal device structure (a) 3 dimensional (b) 2 dimensional view.

Fig. 3. Isotherm graphs of P1 molecule at different water pH subphase.

device structure. The current–voltage (I–V) characteristics of these LB films were measured by using computer controlled HP 4192A impedance analyzer, Keithley 228A current source, Keithley 6514 voltmeter, and Keithley 485 ampermeter. The
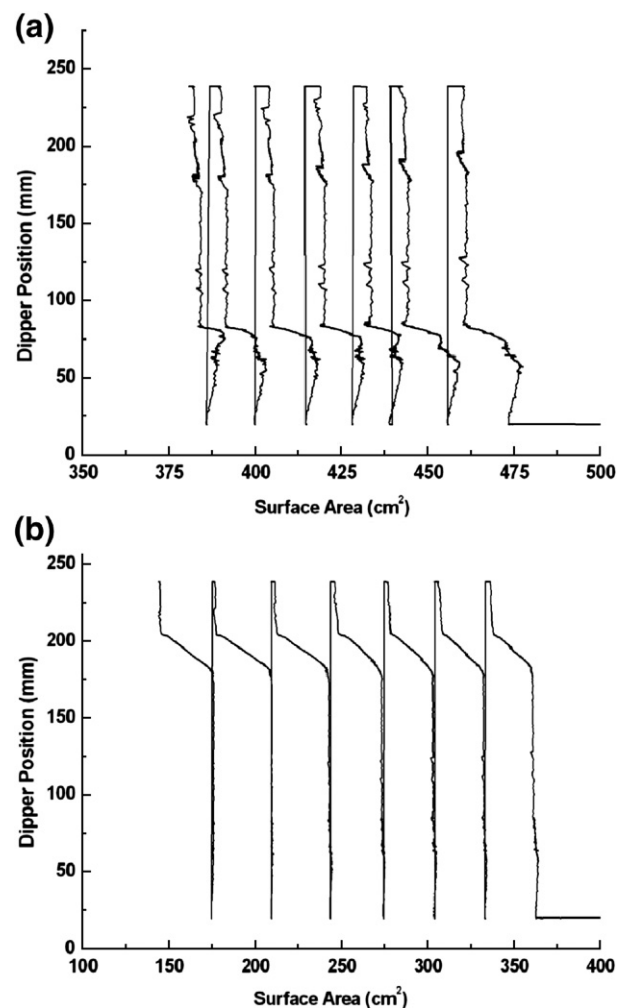

Fig. 4. Deposition graphs of AL-type LB films (a) downstroke deposition of Arachidic Acid molecule (b) upstroke deposition of PMMA molecule.
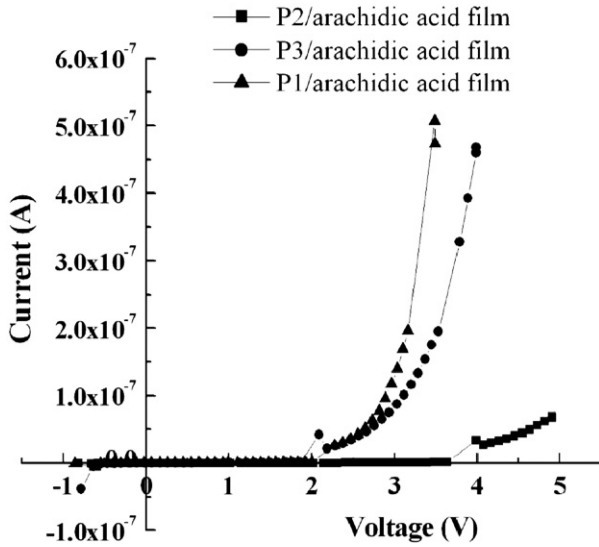
Fig. 5. I–V curves of the metal/LB film/metal devices.

Table 2
Barrier height values of LB films

Samples	Intercept of lnJ axis	Barrier height φ (eV)
P1	−17.67	1.09
P2	−15.37	1.03
P3	−14.46	1.01

voltage was applied initially from −0.5 to 0.5 V between the top and bottom electrode and the current was measured during the voltage applied. The voltage sweep was increased gradually from −0.5 to −0.8 V and from 0.5 to 4 V.

3. Results and discussion

To obtain LB film fabrication conditions, the surface pressure–area measurements have been performed for each PMMA material. Fig. 3 shows the isotherm graphs of P1 molecule at different water pH suphase. The isotherm graphs for P2 and P3 molecules were similar to the isotherm graph given in Fig. 3. It is found that the surface behaviour of PMMA molecules is independent from the pH value of the water subphase. The area per molecule for P1, P2 and P3 molecules have been calculated as 1750, 2300 and 2350 nm^2 respectively which is in good agreement with the literature [15].

The reduced surface area change of both arachidic acid and PMMA monolayers during the deposition onto aluminised glass
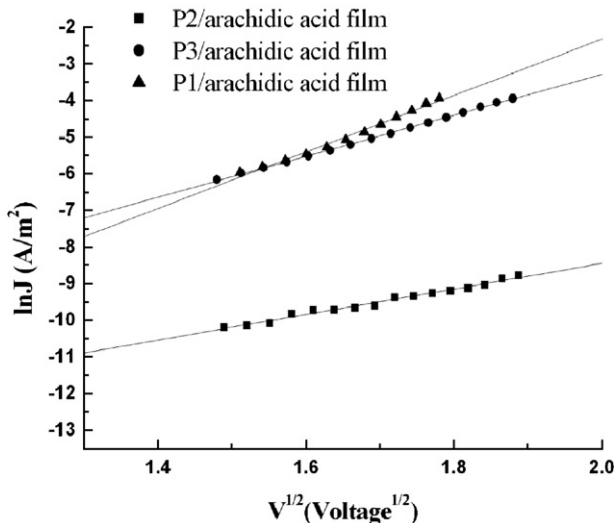
substrate for 7 bilayers are given in Fig. 4. It is found that the average reduction of the area for each bilayer was almost the same during the deposition process of monolayers onto aluminised glass substrate. The transfer ratio (τ) was found to be over 0.95 for arachidic acid and over 0.90 for PMMA molecules. These results indicate that uniform and reproducible LB deposition was achieved.

I–V result of the metal/LB film/metal device is given in Fig. 5. A high current was obtained at positive bias rather than a negative bias. This phenomenon may be explained by the thickness variation of Al$_2$O$_3$ oxide formed on the Al bottom electrode [16]. A detailed analysis of the shape of the I–V curves reveals that the conduction is ohmic between −0.8 V and 2 V region [17,18] where applied voltage between electrodes and current passing through the LB film is linearly proportional with each other.

To explain conduction process through LB films, conductivity lnJ versus $V^{1/2}$ behaviour is replotted in Fig. 6. The relation between lnJ and $V^{1/2}$ shows a linear dependence between 2–4 V and it suggests that the conduction mechanism is governed by either Poole–Frenkel or Schottky mechanism [19,20] given by [21].

$$I_{\text{Poole–Frenkel}} = I_0 \exp\left(\frac{\beta_{\text{PF}} V^{1/2}}{kT d^{1/2}}\right) \tag{1}$$

$$I_{\text{Schottky}} = A.S.T^2 \exp\left(\frac{-e\varphi}{kT} + \beta_{\text{S}} V^{1/2}\right) \tag{2}$$

Where V is the applied voltage, T is the absolute temperature, e is the electronic charge, k is the Boltzmann constant, d is the

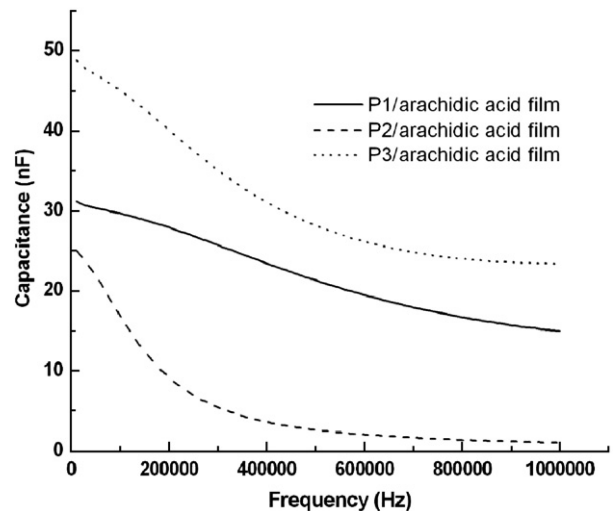Fig. 6. Relationship between ln J and V$^{1/2}$ for the applied voltage.

Fig. 7. Variation of capacitance as a function of frequency.

thickness of the film, A is the Richardson constant, S is the metal contact area, φ is the potential barrier. β_{PF} and β_S are Poole–Frenkel and Schottky coefficients, respectively. Poole–Frenkel field-lowering coefficient (β_{PF}) is given by [21]:

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

where ε_r is the dielectric constant of the films, ε_0 is the permittivity of free space and d is the film thickness. Schottky coefficient is $1/2\ \beta_{PF}$. If we assume that the conduction mechanism obeys the Schottky conduction mechanism, the intercept of the linear curve with the lnJ axis at $V=0$ can be expressed in terms of barrier height (φ) using Eq. (2):

$$\ln J = \ln\left(AT^2\right) - \left(\frac{e}{kT}\right)\varphi \qquad (4)$$

Using the value of Richardson constant for free electron and the intercept values from Fig. 6, the barrier heights of each LB film were calculated and given in Table 2. Geddes et al. have calculated the barrier height of 22-tricosenoic acid LB films grown with various thicknesses on different substrates and fabricated in an M/I/M structure using a similar approach [22].

The dielectric properties of PMMA/arachidic acid LB films were investigated by measuring the variation of the capacitance as a function of frequency for metal/LB film/metal structures at room temperature (Fig. 7). The value of the capacitance gradually decreases with the increasing frequency and then it became almost constant at the high frequency values. The most reasonable explanation of the observed decrease in ε_f with increasing frequency may lie in disorientation of amphiphilic molecules and the resulting reduction in the polarisability of LB films [23].

Neglecting the thickness difference between three different films and considering our system as a plane capacitor $C=(\varepsilon_f\varepsilon_0 A)/(d_f)$ we can conclude that the dielectric permittivity or dielectric constant (ε_f) of AL-type LB films of P3 has the highest value. Exact evaluation of dielectric constant ε_f was difficult without knowing exactly the film thickness. That is why in this paper, we were limited to discuss the value of ε_r.

4. Conclusion

In this paper, optimum condition of the LB film fabrication of PMMA molecules has been reported. It is found that transferring monolayers of PMMA molecules from water surface on solid substrates have been successfully made using arachidic acid molecules in alternate layer LB film structure.

Using isotherm graphs, it is found that the surface behaviour is independent of the pH value of the water subphase. The area per molecule for PMMA molecules was calculated around 2000 nm^2. Electrical measurements of metal/LB film/metal structures of these alternate layer LB films showed that there is a polarity in the film. The dependence of the current versus an applied voltage was characterised as ohmic in the low voltage region and square root dependence in the high voltage region. Capacitance dependence of these films as a function of frequency showed that the highest capacitance value was obtained in P3/arachidic acid LB film structure. Further studies will be on the investigating the conduction mechanisms in detail.

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