Dielectric Properties and Interfacial Phenomena of Metal/Insulator/Metal (MIM) Devices of Phosphatidic acid Langmuir-Blodgett Films

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ABSTRACT   The interfacial phenomena of metal/insulator (organic)/metal (MIM) devices of the phospholipid Langmuir-Blodgett (LB) films have been investigated. Two types of phospholipids with different length of alkyl chains i.e. 1,2-dimyristoyl-sn-glycero-3-phosphatidic acid (DMPA) and 1,2-dipalmitoyl-sn-glycero-3-phosphatidic acid (DPPA), were used in this study. The variations of capacitance and conductance of the MIM devices were examined as a function of number of LB layers as well as frequency. The results obtained from the measurements indicate that the phospholipid LB films sandwiched between two aluminium electrodes behave as a good insulator. The dielectric constants of 3.0 and 3.3 have been calculated for DMPA and DPPA monolayers respectively. The capacitance results also revealed that the devices consist of a native oxide layer of Al_2O_3 between the bottom aluminium electrode and the LB films. In this particular case, it has been evaluated that the oxide layer is about 25 Å. In general, the plots of conductance as a function of frequency of the MIM devices exhibit logarithmic variation.

ABSTRAK   Fenomena antaramuka dikaji bagi peranti logam/penebat/logam (LPL) filem fosfolipid Langmuir-Blodgett (LB). Dua jenis fosfolipid digunakan dalam kajian ini iaitu asid 1,2-dimiristoil-sn-glicero-3-fosfatidik (DMPA) dan asid 1,2-dipalmitoil-sn-glicero-3-fosfatidik (DPPA) dengan panjang rantai alkil yang berbeza.   Perubahan kapasitans dan konduktans bagi peranti LPL dikaji dengan mengubah bilangan lapisan LB dan juga frekuensi. Hasil-hasil pengukuran menunjukkan bahawa filem fosfolipid LB yang terapit diantara dua elektrod aluminum merupakan suatu penebat yang baik. Pemalar dielektrik bagi monolapisan DMPA ialah 3.0 manakala DPPA ialah 3.3. Keputusan ujian kapasitans menunjukkan bahawa peranti mengandungi satu lapisan oksida Al_2O_3 di antara elektrod aluminum bawah dan filem LB. Dalam kes tertentu, kajian mendapati lapisan oksida ini setebal 25 Å. Secara umumnya, graf konduktans melawan frekuensi bagi peranti LPL menunjukkan perubahan secara logaritma.

(Langmuir-Blodgett (LB); phospholipid; metal/insulator/metal (MIM); interfacial phenomena, dielectric constant)

INTRODUCTION

The Langmuir–Blodgett (LB) technique is an excellent method for preparing an ultrathin organic film fabricated layer by layer with a defined geometry. The LB technique is based on the property of amphiphilic molecules to form a compact monolayer film when spread at the air–water interface, subsequently subjected to compression and then transferred onto a solid substrate [1 - 3]. In the previous study, we have investigated the molecular orientation and phase transitions of phospholipids monolayer at the air/water interface by means of Maxwell-Displacement-Current (MDC) measurement coupled with Langmuir technique [4]. In this report, the fabrication of metal/insulator/metal (MIM) devices containing the phospholipid LB films is discussed.

Understanding of interfacial phenomena which occur at the electrode/film and film/film

interfaces provides an insight to improve fabrication method used in producing organic molecular devices [5, 6]. Beyond that, the understanding of interfacial phenomena and dielectric properties of metal/insulator/metal is also useful for future electrical insulation engineering. Besides, there is a huge demand of low-*k* (low dielectric constant) materials to be used as interlayer dielectrics for multilevel metallization of ultra large-scale integrated (ULSI) semiconductor devices. A low-*k* value is the most important requirement for interlayer dielectrics which lower the power consumption in ULSI devices.

In general, MIM sandwich structures are fabricated by transferring the floating Langmuir monolayers onto the metallised surface of a solid substrate. Subsequently the top metal electrode such as aluminium or gold has been used as the top contact. For example, Taylor and Mahboubian-Jones used a phospholipid material of dipalmitoyl phosphatidylethanolamine (DPPE) in the fabrication of MIM devices and then the frequency dependence of capacitance and conductance of the devices was studied [7]. Other researchers have used the thermally stimulated current (TSC) measurement to examine the dipolar polarization of the MIM devices containing dipalmitoyl phosphatidic acid (DPPA) monolayers [8].

MATERIALS AND EXPERIMENTAL DETAILS

Phosphatidic acids
Phosphatidic acid (PA) of 1,2-dimyristoyl-sn-glycero-3-phosphatidic acid (DMPA) sodium salt and 1,2-dipalmitoyl-sn-glycero-3-phosphatidic acid (DPPA) sodium salt were purchased from Genzyme Pharmaceutical, Switzerland. All the materials were used as received from the suppliers without further purification due to their highly pure contents (> 99.9%). The materials were stored in a refrigerator at the temperature of about 0 to 5 °C. The chemical structures of these PA are shown in Figure 1. At the neutral pH, PA lipids are in negatively charged form with one proton of phosphate group deprotonated.
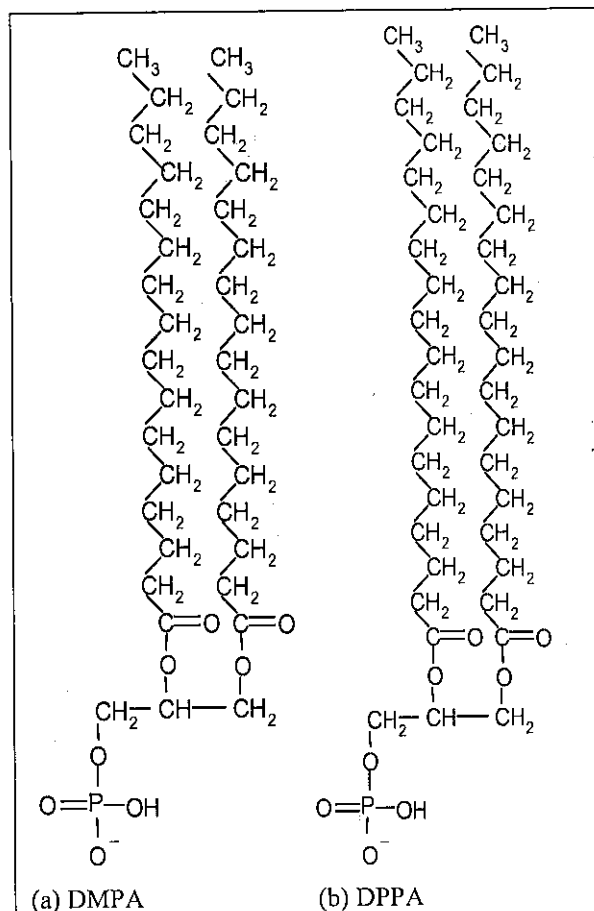

Figure 1. The chemical structures of phosphatidic acids, (a) DMPA and (b) DPPA

Deposition of phosphatidic acids Langmuir-Blodgett films
The phospholipid solution was spread using a Hamilton microsyringe onto the water surface to form a monolayer. After spreading, the monolayer was left approximately 2 hours to allow evaporation of the solvent and formation of stable monolayer [9]. This waiting time prior to deposition, was found to be crucial for obtaining good quality phospholipid LB films. The monolayer compression was initiated with a constant barrier speed of 20 mm/min. The surface pressure of 35 mN/m was kept steady during transfer via feedback loop mechanism. The vertical dipping was used with both the down-stroke and up-stroke dipping speed of 2 mm/min to deposit the phospholipid Langmuir-Blodgett films onto the aluminized glass substrates at 25 °C.

Aluminized coated glass slides behave as hydrophilic substrates due to the presence of native oxide layer onto the aluminium bottom

electrode. The cleaned aluminium coated glass slide substrates were placed at the dipper prior to solution spreading. Hence, the hydrophilic headgroup of the first monolayer was deposited onto an aluminized substrate during upward direction through the water surface. One layer was deposited on the substrates each time the substrates went through the film. All the LB films were transferred to solid substrate to form Y-type deposition.

The first information on monolayer deposition is given by transfer ratio (the decrease area in the area occupied by the monolayer on the water surface divided by the coated area of the solid substrate). The transfer ratio of DPPA deposition is shown in Figure 2. Almost similar results were

observed for DMPA LB films (results are not shown here). The transfer ratios for the up-stroke (shown by the upward arrow: ↑) direction are always higher in comparison with those in the down-stroke (shown by the downward arrow: ↓) direction. The deposition process of DPPA retains transfer ratios above 0.8 up to 9-monolayers. The reproducibility of DPPA multilayers up to 9-monolayers will be discussed together with the FTIR spectra results. Unfortunately, after depositing more than 11-monolayers of the DPPA molecules, some of the molecules were not transferred onto the substrates which are indicated by the low transfer ratio recorded that is about 0.6 during both down-stroke and up-stroke depositions.
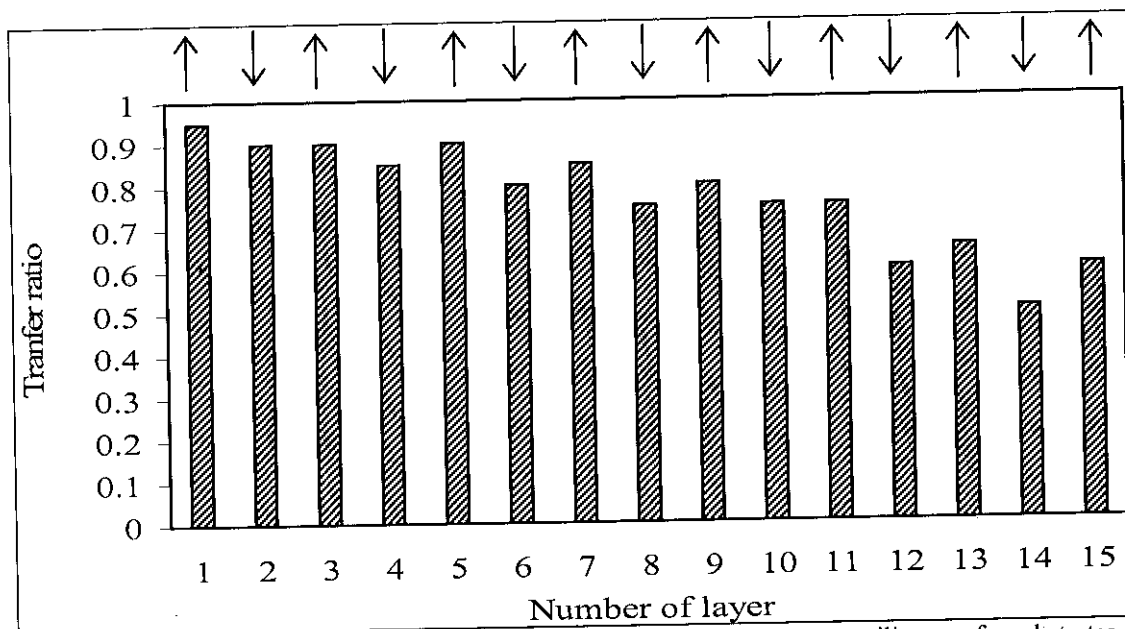

Figure 2. The transfer ratio of the LB deposition of DPPA monolayers onto silicon wafer substrates. The arrows indicate the directions of the substrate movement during deposition process.

Fabrication of the Bottom and Top Metal Electrodes of MIM devices

The cleaned microscope glass slides were carefully arranged onto a shadow mask to define pattern and then placed into an Edwards Auto-306 Evaporator. The bottom and top electrodes were performed via thermal evaporation at a pressure of about 10^{-6} mbar. Aluminium wire was placed in a tungsten filament and subsequently thermally evaporated through a contact mask. The thickness of the evaporated aluminum was about 500 Å thick. A thickness monitor which was attached to the evaporator was used to control the evaporation rate and the aluminium thickness during the thermal evaporation.

LB films of DMPA and DPPA were deposited onto the aluminized solid substrates with thickness variation of 5, 7, 9, 11, 13 and 15 monolayers. Subsequently, the top aluminium electrode was thermally evaporated to a thickness of approximately 500 Å. A very slow evaporation rate of 0.1 – 0.3 Å/s was applied for the first 50 Å of aluminium coated on the LB films and the temperature inside the evaporator chamber was controlled such that it was always below 40 °C. Higher evaporation rates will lead to short circuits, due to penetration of electrode through the ultra thin LB films. The final devices consist of the LB films sandwiched between similar

metal electrodes to form aluminium/LB films/aluminium as metal/insulator/metal (MIM) configuration. The MIM device construction is shown in Figure 3.
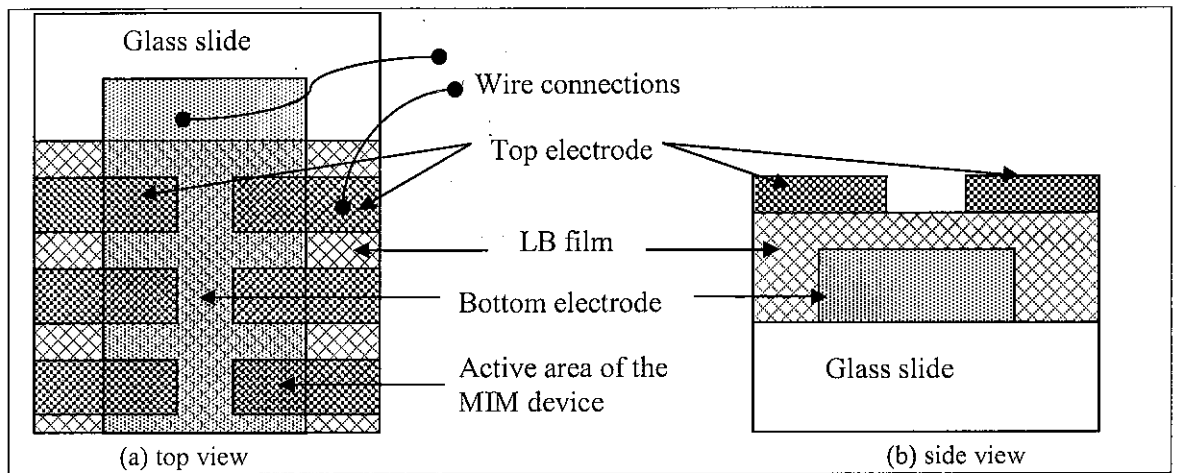

Figure 3. A schematic diagram of the metal/insulator/metal (MIM) devices, which LB film is sandwiched between the bottom and top electrodes of aluminium, (a) top view (b) side view

RESULTS

Capacitance and conductance characterizations

The expected molecular arrangement in the MIM devices of phosphatidic acid LB film is shown in Figure 4(a), while the equivalent circuit is given in Figure 4(b). The polar head group of the first monolayer is attached to the aluminium substrate, which has a thin coating of natural oxide. It will be shown later that the thickness of this oxide layer is approximately 30 Å. The orientation of the phospholipid molecules in subsequent monolayers alternates so that the upper electrode contact is adjacent to the hydrophobic alkyl chains of the molecules.
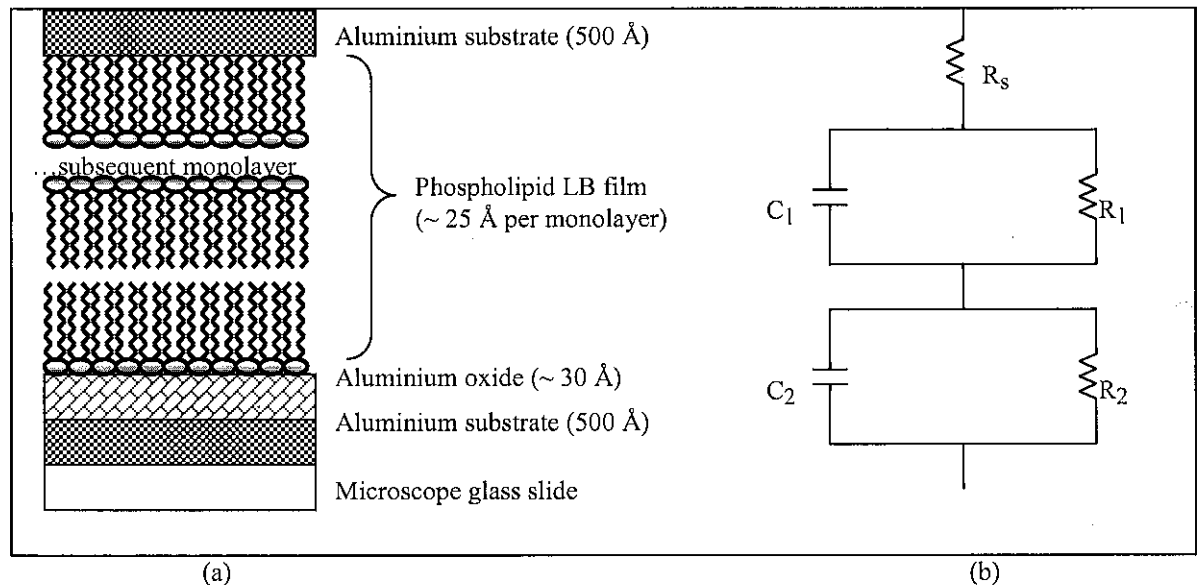

Figure 4. (a) The molecular arrangement of the MIM device of the phospholipid LB film on aluminized microscope slide; (b) the equivalent circuit for modelling the MIM devices: C_1 and R_1, the capacitance and resistance of the phospholipid; C_2 and R_2, the capacitance and resistance of the aluminium oxide layer and R_s is a series resistance associated with electrode contacts.

The data of capacitance per unit area, C and the number of deposited monolayers, N (multilayers) can be used to estimate the average capacitance of a single monolayer, C_m. DMPA reveals a vallue of $C_m \approx 1.14$ whilst DPPA has $C_m \approx 0.93$ μF cm^{-2}. The capacitance of bilayer lipid membranes (BLM) were quoted to be in the range of 0.3-0.4 μF cm^{-2} giving a capacitance per monolayer, C_m of 0.6-0.8 μF cm^{-2} [10]. A rather higher value was obtained for distearoylphosphatidylcholine (DSPC) with C_m of 1.16 μF cm^{-2} [11]. The values of C_m of DMPA and DPPA obtained in this study are reasonable as compared to those phospholipids reported in the literatures [10, 11].

A useful relationship is commonly used between reciprocal of capacitance, $1/C$ against the number of monolayer, N :

$$\frac{1}{C} = \frac{1}{\varepsilon_o}\left(\frac{d_{ox}}{\varepsilon_{ox}} + \frac{Nd}{\varepsilon}\right) \qquad (1)$$

where ε_o is the relative permittivity of free space, d is the thickness of an LB monolayer with dielectric constant of ε [12]. The thickness and relative permittivity of the natural aluminium oxide layer are d_{ox} and ε_{ox} respectively. The reciprocal of capacitance per unit area of phospholipids MIM structure as a function of film thickness at 10 kHz is shown in Fig. 5. The measurements were performed at 10 kHz because the capacitance becomes independent at this moderate frequency (will be shown later in Figure 7). The data in this figure is presented in the form of reciprocal capacitance $(1/C)$ versus number of monolayers (N). Each point has been obtained from many individual readings of eight contacts and statistically averaged to give a weighted mean value of the capacitance for each thickness. The error bars reflect the spread of capacitance values obtained from measurements on eight contacts.
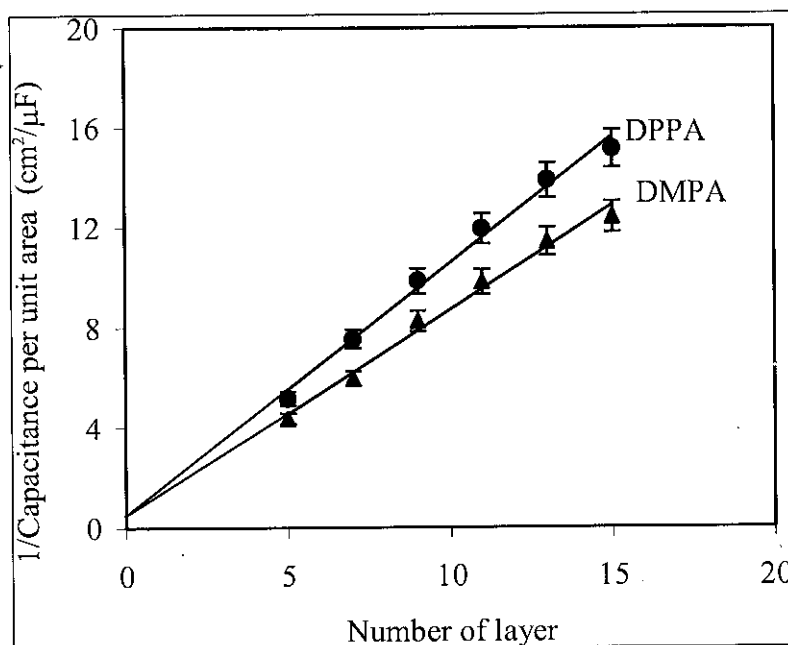

Figure 5. Reciprocal capacitance, $1/C$ (at 10 kHz) as a function of number of monolayers N for two types of phospholipids: DMPA and DPPA in the MIM structures

From Equation (1), it is clearly shown that the gradient of a straight line plot of $1/C$ against N gives the dielectric thickness (metric thickness per dielectric constant (permittivity)) of the monolayer material. The variation in capacitance with the thickness of LB film provides a good indication that the monolayers of phospholipids were deposited in a reproducible manner. The intercept of the graph is equal to the dielectric thickness of the interfacial metal oxide, which in this case is the aluminium oxide, Al_2O_3.

Using the thickness value obtained from the previous analysis, the dielectric constants, ε are

calculated to be about 3.3 ± 0.5 for DMPA and 3.0 ± 0.5 for DPPA. These results of low-*k* dielectric constant materials indicate that phospholipid thin films have a potential application as a passivation dielectric layer for thin-film transistor (TFT) arrays [13]. Analysis of capacitance results in this work shows that the dielectric constants of phospholipids are relatively higher to the published data for fatty acid and fatty acid salts. Robert *et al.* [12] reported the dielectric constant of cadmium arachidate and cadmium stearate as 2.45 and 2.52 respectively. A higher dielectric constant of tricosenoic acid was stated by Alekna *et al.* [14].

From the intercept of DMPA plot, the average interfacial oxide, d_{ox} layer on the aluminium substrates is estimated to be 26 ± 4 Å, by having assigned the relative dielectric constant of aluminium oxide as 8 [15, 16]. Table 1 shows the calculated values of capacitance per lipid monolayer, dielectric constant of phospholipid as well as the thickness of the aluminium oxide

layer. The d_{ox} quoted in this analysis may not correctly reflect the properties of the interfacial oxide layer. This is because Equation (1) ignores the possibility of the first monolayer may differ physically from the rest of deposited layer. In other words, the interfacial oxide layer might penetrate into the first lipid monolayer. The measurement of a simple capacitor based on purely aluminium oxide, Al_2O_3 layer has always shown higher values than those given by the intercept of the 1/C against *N* graph [12]. Metal-insulator-metal junctions have been studied using a silver/ LB film/magnesium structure. With careful preparation and choice of electrode configuration, it is possible to fabricate LB material sandwiched between the two metal electrodes without the presence of an oxide layer [17]. The graph of inverse capacitance against number of monolayers which produces a straight line passing through the origin indicates that the insulating properties come from the LB film and not due to any metal oxide barriers.

Table 1. The estimated values of lipid and oxide layer thicknesses and the dielectric constant of lipids

PARAMETER	DMPA	DPPA
Phospholipid monolayer thickness, *d* (Å)	24.5	27.0
Calculated capacitance per monolayer ($\mu F\ cm^{-2}$)	1.14 ± 0.08	0.93 ± 0.06
Calculated dielectric permittivity of phospholipid, ε	3.3 ± 0.5	3.0 ± 0.5
Calculated thickness of the aluminium oxide layer, d_{ox} (Å)	26 ± 4	32 ± 3

The change in conductance, *G* (1/resistance, 1/*R*) with frequency of MIM devices containing DPPA LB films, is shown in Figure 6. The displayed data were obtained from the same samples used for the capacitance measurements. The variation of conductance is seen to be logarithmic dependent on the number of deposited monolayers. In some cases the distinction is up to three orders of magnitude higher between two different thicknesses of LB films. Clearly, there is a dependence on monolayer thickness.

The conductance decreases or the resistance increases dramatically with more layers deposited. The MIM devices of both DMPA and DPPA phospholipids have devices resistances in the range of 10^9 to 10^{12} Ωcm^{-2}. These very high resistances indicate that there are no metallic filamentary pathways through the phospholipid ultra-thin LB films. If the short-circuit pathways or pin-holes occur, the MIM resistance would be

typically in the order of ohms, which is the case of the MIM with monolayers of a single monolayers up to 4-monolayers. In order to verify the pin-hole phenomena as well as the surface roughness, the observations on the surface morphology by Atomic Force Microscopy (AFM) of the MIM devices can be carried out. However, the AFM images are not reported here and will be reported elsewhere.

The frequency dependence of the capacitance of the MIM devices is shown in Figure 7 over a large range of frequency between 10 to 10^5 Hz. There is a slight decrease in capacitance with increasing frequency especially in the region of 1000 Hz. The dependence of the conductance of the MIM devices on frequency is shown in Figure 8. The conductance shows a logarithmic dependence on frequency for frequency higher than 100 Hz. At low frequency range (lower than 100 Hz) the conductance flattens-off.
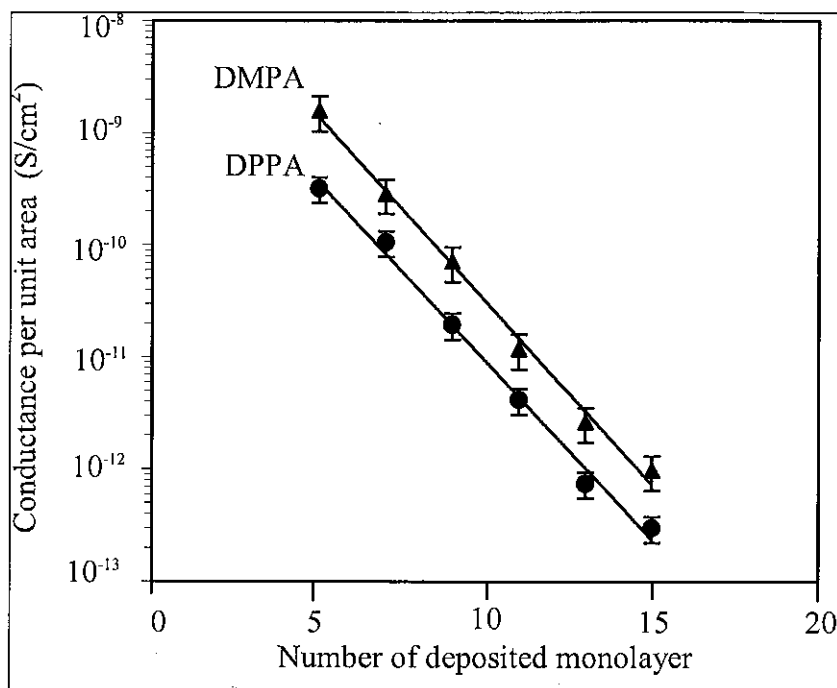
Figure 6. Graph of conductance, G ($1/R$) (at 10 kHz) as a function of number of monolayers N for two types of phospholipids: DMPA and DPPA in the MIM structures
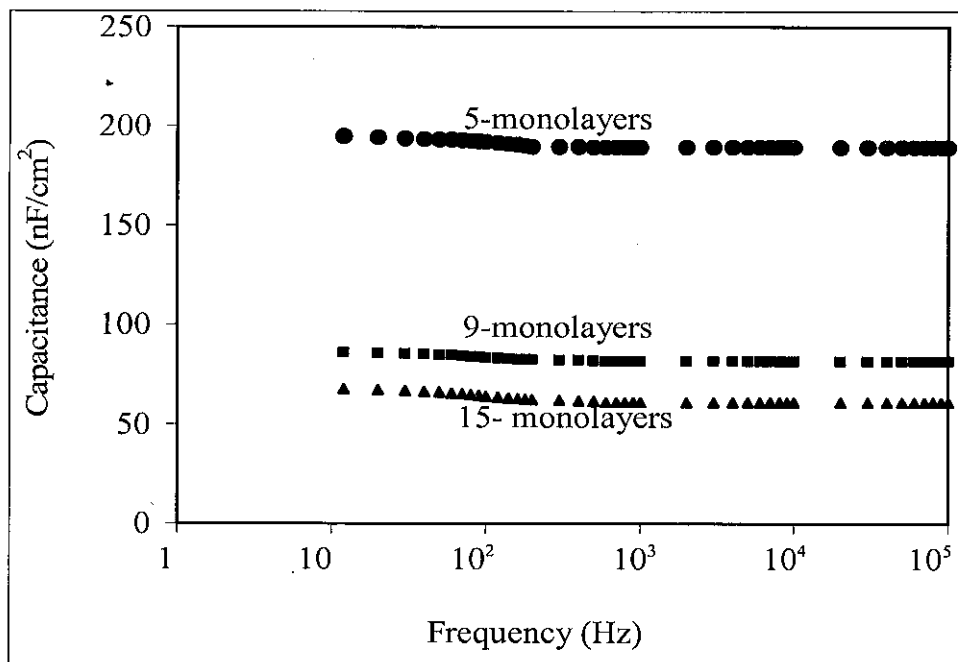

Figure 7. Capacitance against frequency characteristics for the MIM devices of DPPA films
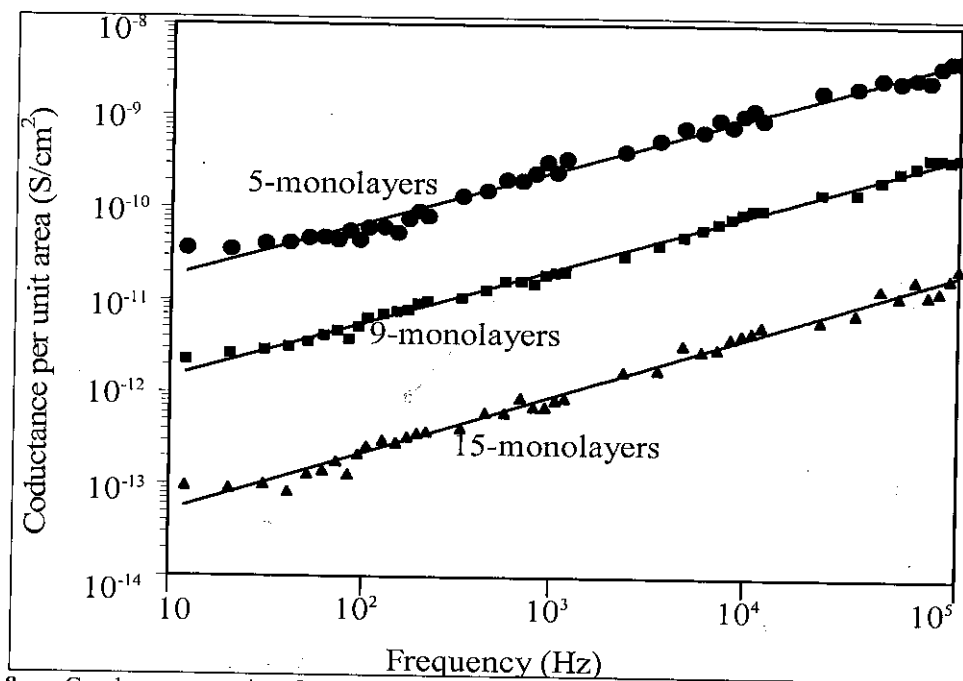
Figure 8. Conductance against frequency characteristics for the MIM devices of DPPA films

Many insulating films of dielectric materials show the power relationship:

$$G(\omega) \propto \omega^{n} \tag{2}$$

with *n* lying between 0 and 1 [18]. The results presented in Figure 7, give the dependence of the conductance on frequency approximately $G(\omega) \propto \omega^{0.6}$ are in good agreement with the reported values of the exponent for the MIM devices of fatty acid [12, 16].

SUMMARY

The MIM structures of aluminium/phosphatidic acid/aluminium (Al/PA/Al) devices exhibit a good insulator films with dielectric constant of 3.3 ± 0.5 and 3.0 ± 0.5 for DMPA and DPPA respectively. The capacitance measurements on the MIM devices indicate that the native aluminium oxide has been formed between aluminium coated surface and the deposited LB films. The formation of this oxide layer takes place during deposition process of LB films. The variation of capacitance of the Al/PA/Al devices is almost independent on frequency. On the other hand, these MIM devices show logarithmic reliance of conductance on frequency.

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