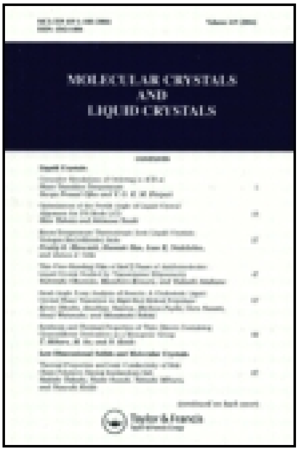

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Anisotropic DC Electrical Conductivity and AC Response in C_{22}-Quinolium (TCNQ) LB Films at Room Temperature

Tae-Wan Kim [a] , Seung-Kyu Park [b] , Dou-Yol Kang [b] , Eon-Sik Hong [c] & Chul Park [d]

[a] Dept. of Physics, Hong Ik Univeristy, Mapoku, Seoul, KOREA

[b] Dept. of Electrical and Control Engineering, Hong Ik Univeristy, Mapoku, Seoul, KOREA

[c] Dept. of Electronic and Computer Engineering, Hong Ik Univeristy, Jochiwon, Chungchungbukdo, KOREA

[d] Goldstar Central Research Lab, Umyundong, Seochoku, Seoul, KOREA

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ANISOTROPIC DC ELECTRICAL CONDUCTIVITY AND AC RESPONSE IN C_{22}-QUINOLIUM (TCNQ) LB FILMS AT ROOM TEMPERATURE

TAE-WAN KIM
Dept. of Physics, Hong Ik Univeristy, Mapoku, Seoul, KOREA
SEUNG-KYU PARK, DOU-YOL KANG
Dept. of Electrical and Control Engineering, Hong Ik Univeristy, Mapoku, Seoul, KOREA
EON-SIK HONG
Dept. of Electronic and Computer Engineering, Hong Ik Univeristy, Jochiwon, Chungchungbukdo, KOREA
CHUL PARK
Goldstar Central Research Lab, Umyundong, Seochoku, Seoul, KOREA

Abstract Ultra-thin organic films of C_{22}-Quinolium (TCNQ) were deposited onto ordinary microscope slide-glass substrates with a Langmuir-Blodgett technique. Surface pressure(π) - area(A) isotherms were studied to find optimum conditions of deposition by varying the environments. Several tools were employed to confirm the deposition such as the electrical capacitance and the direct thickness measurement. Electrical conductivities were studied in two different directions of the film. It has turned out that this film is highly anisotropic. The obtained conductivities are $\sim 1 \times 10^{-7}$ S/cm along the film surface direction, and $\sim 1 \times 10^{-14}$ S/cm in the perpendicular direction. We have also studied ac response by applying a step voltage (1 Hz, 1 V) to the film. From this study, we were able to correlate the electrical capacitance to the number of film layers.

INTRODUCTION

There is a growing concern on the Langmuir-Blodgett (LB) ultra-thin film, since it has a lot of potential application to the molecular electronic devices, biosensors and etc.[1] Langmuir studied a motion of organic monolayer floating on the liquid subphase in 1917.[2] Later Langmuir and Blodgett developed a technique of transferring monolayer from the subphase to the solid substrate,[3] which is now called "LB method". In addition to the LB method, there are several ways of making ultra-thin films such as PVD (physical vapor deposition), and CVD (chemical vapor deposition) method. Among these methods, the LB method has some advantages. By depositing monolayer, which is formed in air-water interface, to the solid substrate, we can make an Å(10^{-10})-order thick film as well as giving functionality to the molecules more easily.

The behavior of the organic molecules on the subphase can be studied with a surface pressure(π) - area(A) isotherm. Here, A is the effective area occupied by one molelcule on the expanded subphase. Since the molelcule is amphiphilic, hydrophilic part (head group) is attached to the water subphase and hydrophobic part (tail group) tends to be away from the subphase. When these molecules are compressed with a barrier, there occurs an interaction between the molecules. These interactions can be observed indirectly with a surface pressure measurement. This π-A isotherm gives an information on a limiting area of the molecule and deposition conditions of the LB films.

The LB films are classified into three categories (X, Y, and Z type) depending on the arrangement of the molecules on the substrate. Physical properties are expected to be different in each type. A status of deposited film can be identified with X-ray diffraction, electron diffraction, SEM (Scanning Electron Microscope), ellipsometry and etc.[4] These methods, however, need some special care in measuring the Å-order ultra-thin film.

Electrical conduction mechanism in the LB film is still uncertain. As far as the conductivity is concerned, the LB film shows a wide range of conductivity. There may be even a possibility of superconducting phase.[5] We have studied dc electrical conductivity and ac response in the Al/Al_2O_3/LB film/Al structure.

In this paper we have, at first, emphasized how we can make a better film of C_{22}-Quinolium (TCNQ) through the π-A isotherm study. Since the π-A isotherm depends not only on the kinds and chemical properties of compounds but on the surroundings (such as the temperature, pH, ...), we have tried to optimize the deposition conditions. To understand the physical properties of the deposited

LB film, electrical and mechanical measurements are applied. Especially, electrical conductivities and ac response of the LB films were extensively studied.

EXPERIMENTAL DETAILS

Substrate Preparation

The nature and surface quality of the substrate are very important in manufacturing the desired LB films. The ordinary optical microscope slide glass (76 mm x 26 mm x 1 mm) was used as the substrate. It was ultrasonically cleaned 3 times (30 minutes at each time) in acetone, and then more than 2 times (20 minutes at each time) in purified water (18 MΩ · cm). Ultrasonic cleaning was done in Branson 2200. Purified water was obtained by flowing the distilled water through the Elgastat Spectrum water purification system. Furthermore, to make the surface of the substrate to be water-loving, the substrate was dipped in the solution of H_2SO_4 saturated with $K_2Cr_2O_7$ for more than 24 hours. It was ultrasonically cleaned again in purified water more than 5 times, and then dried completely in a vacuum chamber.

Aluminum(Al) electrodes were deposited by vacuum evaporation at a pressure of 10^{-5} Torr to characterize the electrical properties. A structure of the electrode is shown in Figure 1. Mask was designed for a distance between the electrodes and a width of electrode to be 1 mm and 3 mm, respectively. To measure the

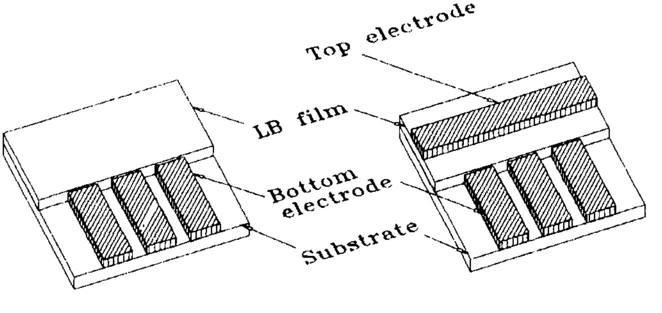

FIGURE 1 Schematic structure of the electrodes.

conductivity along the horizontal direction, bottom electrodes were only deposited as is shown in Figure 1a. Since the top and bottom electrodes are needed to characterize along the vertical direction, electrodes were made like in Figure 1b.

Thin Film Preparation

We have used a Kuhn type LB apparatus manufactured by Kyowa Co. (Model: HBM-H). Precautions were taken to minimize vibration and contamination of the trough and the substrates. Purified water was used as the subphase and the value of pH was 5.6. Approximately 200 μl of solution was spreaded onto the expanded area of LB trough (45 cm x 14 cm). After waiting for 20 ~ 30 minutes for the solvent ($CHCl_3$) to evaporate, the floating film was then compressed with a barrier at a rate of approximately 20 mm/min.

As was introduced in the beginning, it is important to understand the relation between the surface pressure π and the effective area A of the molecule for a better construction of the thin film. After studying the π-A isotherm, 45 mN/m was selected as the proper surface pressure of the LB film manufacture. The substrate was dipped to the subphase at a rate of 5 mm/min using a vertical dipping method. During each deposition, transfer ratio was measured for X, Y, and Z type.

Measurements

Electrical and mechanical measurements were performed to characterize the deposited films. All electrical measurements were carried out in air surroundings at room temperature. Direct thickness measurement was done using Dektek 3030.

For the dc experiments a voltage source was a Yokogawa 2861 regulated voltage supply and the current was measured by means of a Keithley Model 617 programmable electrometer. And then, electrical conductivity was calculated from the current-voltage (I-V) characteristics. For the ac response measurements, ac signal (1 Hz, 1V step voltage) from the function generator was applied across the film and then the transient current flow was detected using the HP oscilloscope.

These kinds of experiments on the LB film, measuring the electrical capacitance by applying the step voltage and the direct thickness measurements mechanically, are thought to be the first trial attempted in our laboratory.

EXPERIMENTAL RESULTS AND DISCUSSION

π-A isotherm

Since the π-A isotherm depends on the environments, it was studied by varying the temperature and pH of the subphase, barrier moving speed, and the spreading amount of solution.

Temperature of the subphase was varied in the range of 12.5 ~ 50 ℃. Figure 2a shows the π-A isotherm measured at three different temperatures, 12.5 ℃, 25 ℃, and 50 ℃. Since the observed π-A isotherms are similar to each other in 12.5 ~ 35 ℃, the ones obtained at 12.5 ℃ and 25 ℃ are only depicted in the figure. If we see the data taken at 25 ℃, the surface pressure increases monotonically as the area is compressed. This region is called a gas phase. And then there is a little drop in the surface pressure near 30 mN/m. This region might be a liquid, or partly a solid phase. As the monolayer on the subphase is further compressed, the surface pressure increases more rapidly and then drops suddenly near 50 mN/m. This sudden drop is possibly due to

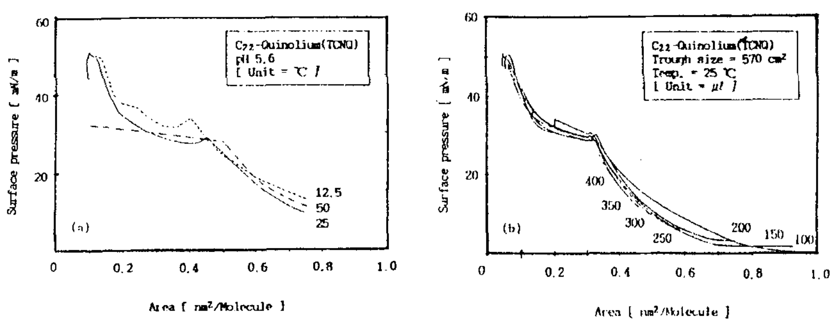

FIGURE 2 π-A isotherms depending on the (a) temperature, and (b) spreading amount of solution.

the collapse of the monolayer after a formation of the solid phase.

The π-A isotherms in 40 ~ 50 ℃ are more or less different from the previous results. The behavior below 30 mN/m is similar to the previous ones. However, the increase of surface pressure is very low even though the monolayer is compressed further. This implies that as the temperature of the subphase increases, the gas and the liquid phase of the monolayer still remain but the solid phase does not. Thus, the proper temperature for a deposition of the LB film in C_{22}-Quinolium (TCNQ) is near 25 ℃.

Figure 2b shows the π-A isotherms depending on the spreading amounts of solution in the range of 100 ~ 400 μl. We can see the increase of initial surface pressure as the spreading amount increases. In 100 ~ 150 μl solution, the surface pressure does not reach the solid phase. It seems to be due to the small amount of solution compared to the size of trough. Thus a proper amount of spreading solution is around 200 μl (2.11×10^{14} molecules/cm^2).

In addition, π-A isotherms were also studied by varying the pH (1.4 ~ 8.4) of the subphase, and the barrier moving speed (10 ~ 50 mm/min). The optimized deposition conditions are summarized in Table 1.

TABLE 1 The optimized deposition conditions of C_{22}-Quinolium (TCNQ) from the study of π-A isotherm.

VARIABLE	VALUE
Temperature	25 ℃
Spreading amount of solution	2.11×10^{14} molecules/cm^2
pH	5.6
Barrier moving speed	20 mm/min
Surface pressure	45 mN/m

Film Deposition

Transfer ratio was measured during a deposition of the film to the substrate. Figure 3 shows the transfer ratio for X, Y, and Z type up to 10 layers. In general, the transfer ratio of the Z type is nearly constant irrespective of the number of layers. This indicates that the monolayer on the subphase is well transferred to the substrate. The transfer ratio of the first layer is about 20 % higher than the average value, which may be due to the roughness of the substrate. In X-type film, the transfer ratio of the first layer is about 0.5. And as the number of layer increases, it decreases down to 0.1 and stays almost constant. Thus, the X-type film is unable to make. In Y-type film, the transfer ratio repeats between that of X and Z type. From these measurements, the Z-type LB film is a good candidate in C_{22}-Quinolium (TCNQ).

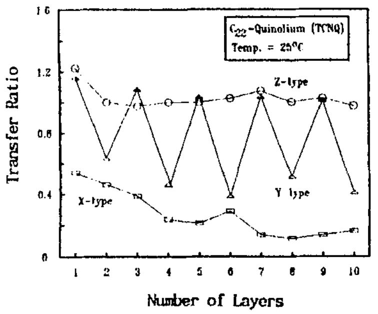

FIGURE 3 Transfer ratio as a function of number of layers.

Conductivity

Current-voltage (I-V) characteristics were measured by employing the conventional two-probe method. Figure 4 shows the I-V characteristics measured alon the film surface direction. The I-V characetristics shows an ohmic behavior in the working voltage range. We see the increase of current as the number of deposited layer increases under a constant bias voltage. However, in the I-V characteristics along the vertical direction, the current decreases as the number of layer increases. The nonohmic behavior can be seen in the 5 layer film. The interpretation on this nonohmic behavior is quite controvertial. We think that as the bias voltage increases, Shottky, Child, and Pool-Frenkel effect start to dominate the conduction mechanism. For the thicker film, nonohmic behavior occurs at higher voltage.

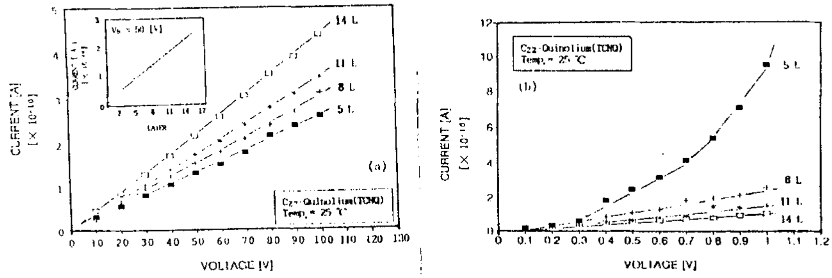

FIGURE 4 Current-voltage characteristics along (a) the horizontal, and (b) the vertical direction.

Figure 5 shows the conductivity as a function of the number of layers obtained from the I-V characteristics. The conductivity along the horizontal direction is around 10^{-7} S/cm, and that of vertical direction is about 10^{-14} S/cm. The higher conductivity in the horizontal direction might be a contribution from TCNQ, while the lower conductivity in the vertical directioon is due to the nonconducting alkyl chains. These values of conductivity are similar to the ones of C_{22}-Pyridinium (TCNQ) reported earlier in our laboratory.[6]

<u>Capacitance</u>

The capacitance of the C_{22}-Quinolium (TCNQ) films were determined as a function of the number of deposited layers N in the vertical

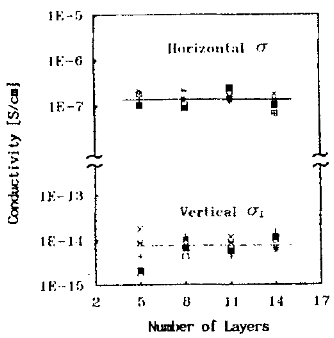

FIGURE 5 Electrical conductivity along the horizontal and the vertical direction.

direction. Since the aluminum electrode was used, a simple structure of the LB film is Al/Al_2O_3/LB film/Al. An equivalent capacitance in this configuration can be thought of series combination of naturally oxidized capacitance C_{ox} and the capacitance of LB film C_{LB}. That is,

$$\frac{1}{C_T} = \frac{1}{A}\left(\frac{d_{ox}}{\varepsilon_{ox}} + \frac{Nd_{LB}}{\varepsilon_{LB}}\right) \tag{1}$$

Here, A is the area of the electrode, ε_{ox}, d_{ox}, ε_{LB}, and d_{LB} refer the dielectric constant and the thickness of the oxide layer and the LB film, respectively. And N is the number of deposited LB layers. This equation shows clearly that the slope of a straight line plot of $1/C_T$ versus N gives the dielectric thickness d_{LB}/ε_{LB} of each monolayer while the intercept yields similar information about the interfacial layer.

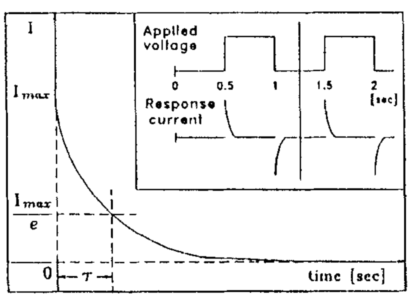

FIGURE 6 Current flowing across the circuit when the step voltage is applied.

Figure 6 shows a current flow through the film as a function time when the step voltage (1 Hz, 1 V) is applied. The inset in the figure shows a current response over the several periods. In this response, we can measure the time constant τ, which is related to the capacitance C_T.

Figure 7 is a plot of $1/C_T$ versus N. It shows an excellent agreement to the expression (1). From Figure 7, the dielectric constant of the LB film and the thickness of the oxide layer were obtained. They are $\varepsilon_{LB} \cong 5$ and $d_{ox} \cong 50$ Å. These values are close to the reported values by several authors.[7]

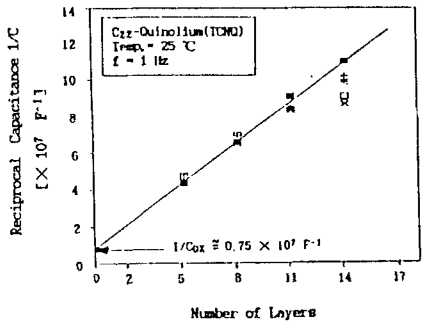

FIGURE 7 Reciprocal capacitance versus the number of layers.

Mechanical measurement

Figure 8 is a morphology of the film surface observed by Dektek 3030. Figure 8a shows the morphology scanned from the substrate to the 11 layer deposited LB film. The lower one in the figure is the morphology of the glass substrate only, which has a roughness of about 46 Å. The roughness of the substrate was measured to be around 50 ~ 90 Å depending on the positions. The lower one in Figure 8b shows the morphology of the electrode scanned from one electrode to the next on the glass substrate. Similarly, we have scanned the electrodes on top of the LB film, which is the upper one in Figure 8b. Here, the thickness of the evaporated Al electrodes is about 350 ~ 500 Å and the roughness is similar to that of the glass substrate. Generally, the thickness of the Al electrode was observed to be 350 ~ 1500 Å depending on the different runs.

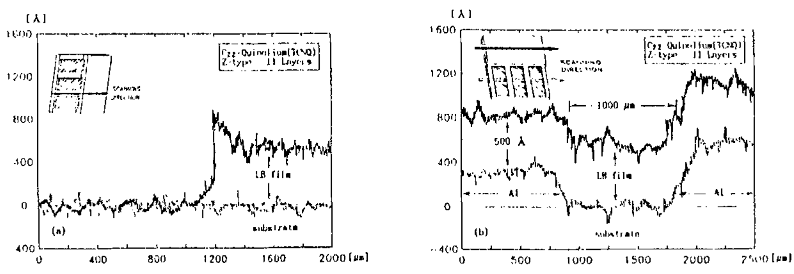

Figure 8 Scanned shape of the surface of substrate and 11 layers of the LB film with Z-type formation.

Since the height of one molecule of C_{22}-Quinolium (TCNQ) is expected to be around 49 Å, 11 layers of LB film may have a thickness of about 539 Å. From the above measurement, the thickness was observed to be about 500 Å, which is close to the expected one. A more detailed experiments are going on in our laboratory.

CONCLUSIONS

We have mostly studied the deposition conditions, and the electrical properties of the C_{22}-Quinolium (TCNQ) LB film. The following conclusions were able to be drawn.

(1) From the π-A study, the optimized deposition conditions were determined.

(2) In C_{22}-Quinolium (TCNQ) LB film, Z-type formation is preferred.

(3) Deposition of the film was confirmed by the electrical and mechanical methods. By applying an ac voltage, we were able to correlate the reciprocal capacitance to the number of deposited layers. The information on the roughness and the thicness of the electrode and the LB film were obtained by mechanical measurements.

(4) This film shows highly anisotropic characteristics in the electrical conductivity. The conductivity in the film surface direction is about 10^{-7} S/cm and that of vertical direction is around 10^{-14} S/cm.

Besides, the nonohmic behavior the I-V characteristics were observed. This requires some more detailed experiments.

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