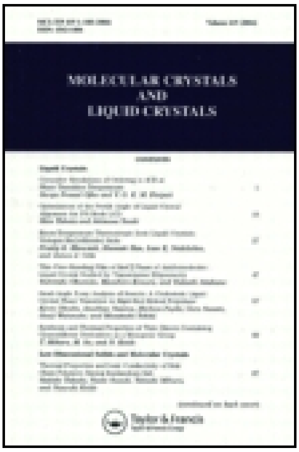

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Diffusion of Electron in Langmuir-Blodgett Ultra-Thin Films

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Abstract Diffusion of electron in polyimide LB films of Al / polyimide LB films / Au (MIM) structures is reported. Time dependences of the generated voltage in this MIM structures were proportional to the square root of time. Such a relation could be explained by the diffusion of electron from the Au electrode to the Al electrode through polyimide LB films. From the experimental results, the diffusion constant of electron was estimated as about 2.5×10^{-17}(cm^2/sec). Furthermore, the diffusion current calculated by the diffusion constant coincided with the current measured in the experiments. It is considered that the diffusion of electron is one of the main causes of the voltage generation in the MIM structures of polyimide LB films.

INTRODUCTION

It has been known for more than 20 years that dc voltage is generated in a Metal / Insulator / Metal (MIM) device in which LB insulation film was used. The dc voltage generated has been explained by assuming internal voltage[1], however, the reason for the generation of internal voltage is not clear. Kapil and coworkers[1] suggested that the voltage is generated by chemical reaction occuring in the LB films.

Recently we tried to measure the generated voltage in old samples of polyimide LB film made in 1986 ~ 1987 and in various LB films of MIM device. The result showed that almost the same magnitude of 0.1 ~ 0.2 volt measured at that time of fabrication was obtained.

It follows that the origin of voltage is not the chemical reaction, and hence we concluded that the voltage is generated due to some other reasons[2].

From the further research, it was found that the generated voltage depends on the thermal equilibrium[3] in MIM device which sandwiched polyimide LB film between Al and Au.

In addition, it was observed that the electrons on Au electrode were transferred through the LB film to Al electrode, which is opposite sense of the electric field. The origin electrons transfer without electric field is considered generally to be a diffusion process. In this paper, we will discuss mainly on the diffusion of electrons in the polyimide LB film.

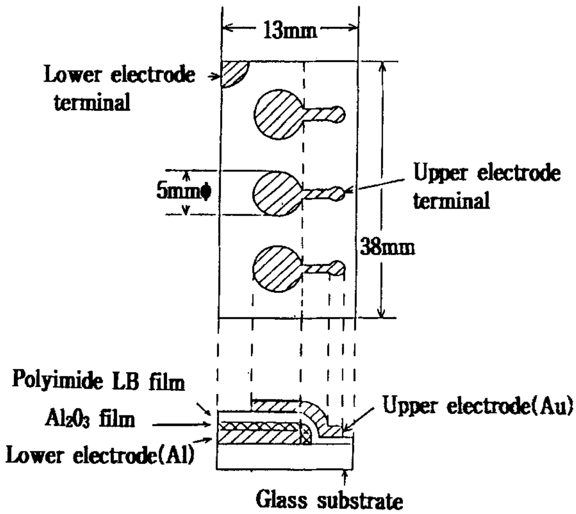

FIGURE 1 Schematic illustration of samples.

EXPERIMENTAL

Materials

The specimen used in this experiment is shown in Figure 1. For electrodes, Al and Au are deposited in vaccum on the glass substrate and on polyimide LB films respectively. LB film is composed of 7 layers and the thickness of monolayer of polyimide is 4.2 Å[4]. The structure of device is substrate / Al / Al_2O_3 / polyimide LB films (7 layers) / Au as shown in Figure 1. Here, Al_2O_3 is a natural oxidized film of the surface of Al electrode formed in the air and its thickness is about 30 Å. In this paper, we report the result performed one of the specimens made in 1986 and left in the air. However, results of the other specimens are almost the same as that of the specimen mainly experimented.

Measurement

The measurement was performed on the specimen with a circuit shown in Figure 2, which is kept in a glass container, and it was attempted in the surrounding of He, N_2, and Air respectively. If there is not any special notice the data means those measured in the air and in the room temperature. The voltage measured is the value of Au electrode VS. Al electrode. For the resistance, 10^8, 10^9, 10^{10} and 10^{11} (Ω) are used and a case where R is disconnected with switch S_2 open is expressed as R = ∞ . M is a voltmeter(Keithley 614 electrometer) and its input impedance is 5×10^{14}(Ω). S_1 is a short switch built in M (through 10 MΩ resistance).

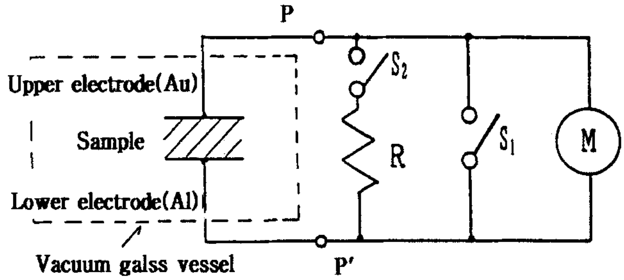

FIGURE 2 Circuit for the measurements.

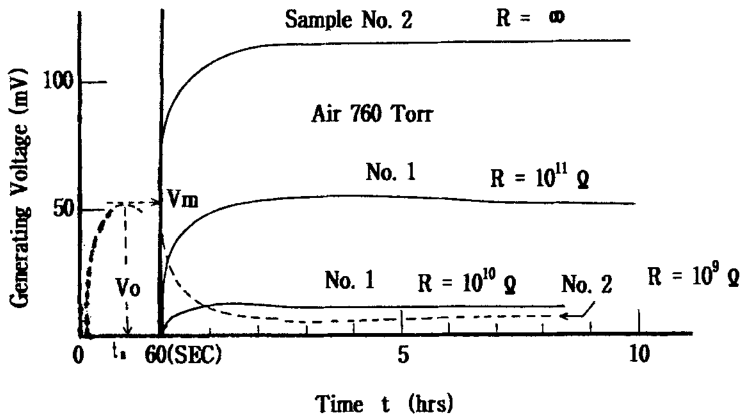

FIGURE 3 Time dependences of the generated voltage on various samples

RESULTS AND DISCUSSION

Movement of electron carrier

The relation between generated voltage and passing time is measured by closing switch S_2 and connecting a resistance and opening short switch S_1 of the circuit in Figure 2. In Figure 3, the generated voltage is shown as the resistance and specimens are changed. The generated voltage reaches the maximum V_m and starts to decreases, and after about 10 hrs. pass, it converges to a constant value V_0. V_m , V_0 and the time t_m to reach the maximum V are different depending on the specimen and resistance, however, the characteristic shown in Figure 3 is verified in every specimen. But, V_m is not measured for the case where a resistance is not connected (R = ∞).

The fact that constant voltage V_0 exist infers that conduction current through Al/ LB film / Au / R / Al. At this time, the electron is first considered as carrier from the results of Figure 4 and it is possible to presume that the electron move through LB film.

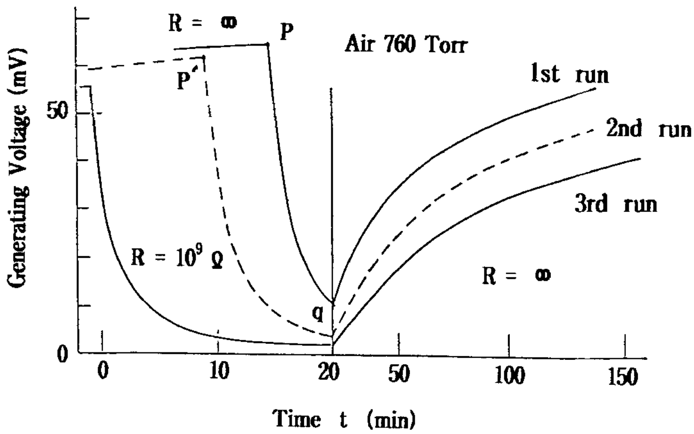

FIGURE 4 Generated voltage measured successively in various resistance

First, a resistance is disconnected by opening switch S_2 (R = ∞), and then, the relation of generated voltage - time is measured following opening switch S_1. As the generated voltage increases to a P point, resistance R = 10^9 (Ω) is connected by closing switch S_2 in Figure 2. The generated voltage decreases quickly, however, as it reaches q point, it increases again by opening switch S_2 and disconnecting R. The measurement was performed even at the time of switch on - off shown in Figure 4 and attention was paid to avoid noise disturbance.

For the case previously described, while the voltage is generated up to P point, the electric current does not flow since the resistance is not connected in the external circuit. Therefore, the charge in the electrode is changing. In other words, the electrons move from Au electrode to Al electrode through LB film opposite to electric field since the positive voltage of Au electrode increases up to P point. Between p-q the electrons move from Al electrode to Au electrode through the external resistance R by electric field. The direction of this movement of electrons up to P point is the same as electron behavior. After q point, the voltage increases again, however, the electrons move opposite to electric field from Au electrode to Al electrode through the LB films, since the external circuit is open. (R = ∞)

The results described above are shown in Figure 4 as 1st run. After the measurement of 1st run is finished, the same measurements of P' point where the magnitude of voltage is close to P point are performed and the results are shown as 2nd run and 3rd run. From the results of Figure 4, it is known that the electrons move from Au electrode to Al electrode through LB film.

Diffusion of electron

Figure 5 shows the characteristic of log(volt) - log(time) and linear slope of 1/2 between V-T is observed. This same linearity and slope of 1/2 can be obtained from repeated measurement and in the surrounding of air and N_2. The increase shown in Figure 5 is considered to occur due to the movement of electrons from

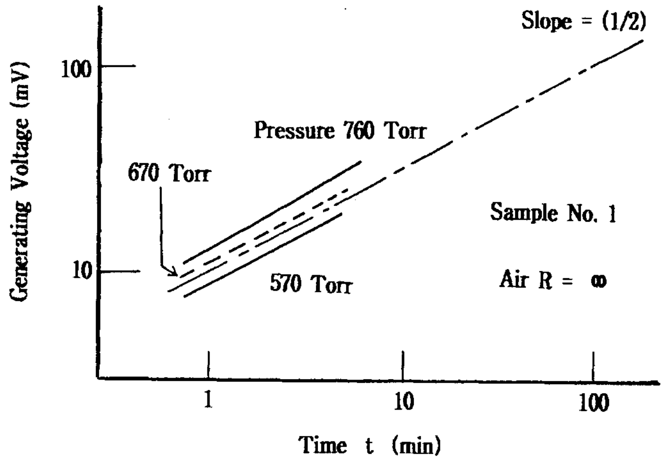

FIGURE 5 The relationship of generated voltage versus time.

Au electrode to Al electrode through LB film since external resistance is not connected. However, the inference that the characteristics of electron in LB film can be explained as following.

The 1-dimensional concentration distribution of material C(x,t) for the case that x=0 and material M diffuses to semi-infinity circle ($X \geq 0$) is expressed as following;

$$C(x,t) = \{ M / (\pi D t)^{1/2} \} \exp(-X^2 / 4Dt) \quad (1)$$

where D is diffusion constant and t is time.

In the beginning of diffusion, the electron does not reach Al electrode but it diffuses through d (the thickness of LB film including the thickness of Al_2O_3 30 Å). Therefore, it is possible to apply equation (1) of semi-infinity circle. The potential drop of Au electrode V(t) can be expressed as equation (2).

$$V(t) = -(2 q_0 D^{1/2} / \pi^{1/2} \varepsilon) t^{1/2} \quad (2)$$

From equation (2) , the generated voltage V is proportional to the square root of time t. This explains the result of Figure 5.

Calculation of diffusion constant

In case of t_1=60(sec) in Figure 5 is selected the generated voltage is as follows;

$$V (t_1) = 0.01 \text{ (V)} \quad (3)$$

In addition, the permittivity can be obtained as equation (4).

$$\varepsilon = \varepsilon_r \times \varepsilon_0 = 3.5 \times 8.85 \times 10^{-14} = 3.1 \times 10^{-13} \text{ (F/cm)} \quad (4)$$

The thermal equilibrium voltage[3] of the specimen Al/PI(7 layers)/Au used in this experiment was 0.1 V and the capacity was 0.14 μF^2. Therefore, the charge q_0 generated in Au electrode per 1 cm^2 considering 2 cm^2 of area of electrode is as follows(sign is neglected).

$$q_0 = C \times 0.1 \times 5 = 0.070(\mu C) = -7.0 \times 10^{-8} \text{ (C)} \tag{5}$$

Then, from equation (3), (4), (5) the diffusion constant can be calculated.

$$D \fallingdotseq 2.5 \times 10^{-17} (cm^2/sec) \tag{6}$$

CONCLUSIONS

The study is attempted to search for the origin of the generation of voltage in LB film with MIM device and to discuss the diffusion of electron in the LB film. In this research, the diffusion of electron is verified and the diffusion constant is obtained. In addition, it is verified that the calculated value of diffused current and measured value are almost same. It is considered that this diffusion is deeply related to the origin of voltage generation in LB film with MIM device.

It is presumed that the thickness of LB film of several tens of Å is proper for the generation of voltage. If the film is thinner, the carrier moves immediately through the film like a junction of semiconductor. Therefore, the generation of voltage would not occur since the potential of both of the electrodes becomes the same. And, if the film is thicker, the effect of diffusion on the voltage generation becomes very small.

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