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The Electro-motive Force Generation in Langmuir-Blodgett Films

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The Electro-motive Force Generation in Langmuir-Blodgett Films

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Abstract Even 20 years ago, it was suggested that the electro motive force is generated in the MIM-structured LB ultra-thin film element. It is known that the current-voltage curve does not pass the origin. In addition, the reason for the generation of voltage is considered to be the chemical reaction taking place in the LB film etc.. In this paper, it is proposed that with chemical reaction it may be difficult to explain the fact that the same phenomenon of voltage generation and electric properties can be investigated for the sample fabricated 6~7 years ago and the new sample. Thus, it is considered to be necessary to clarify the characteristics of voltage generation with a point of view of utilization or removal of voltage generated.

INTRODUCTION

It is well known that D.C. voltage is generated at the elements of MIM structure which is sandwiched between two electrode of Langmuir-Blodgett (LB) ultra-thin films.[1] It is considered that the voltage generation is caused by LB films only or a chemical reaction between LB films and electrode. We also found the generation of the voltage for a long time ago. We already reported [2] that

1) In case of nonpolar Y type LB films sandwiched between same materials, the voltage is not generated; However, 2) In

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different kind of electrode materials such as Al and Au, the voltage is generated. The positive voltage is generated at Au, which has high work function; 3) In case of hetero structure of Y type LB films and polarized Z type LB films, the voltage is generated at the same kind of electrode materials.

In this paper, the experiments are processed for the sample which is left in the atmosphere since its fabrication in 1986. We measured the same voltage as at the time of fabricating the LB films. The thickness of LB films and evaporated electrode used for the experiments is about 20~30Å and 2000Å, respectively.

Therefore, we can not think that the chemical reaction, which is generating several hundred milli-volts, takes place continusly for 6~7 years. It is proper that the chemical reaction has terminated. In our experimental results, the cause is due to some kind of electro-motive force (EMF) which is occurred at elements.

Anyhow, the voltage, several hundred mV, is generated for a long time. It can't ignore the phenomena for the possibility of its use and characteristics of elements or materials.

EXPERIMENTALS

Materials

Samples, shown in Figure 1, are MIM-structured elements made by the process of vacuum evaporation of Al and Au on a glass-substrate. In the other type of element, SnO_2 film was used as a lower electrode and Al, Au as upper electrode and LB film was deposited on it. For the molecule of the LB film sandwiched, Arachidic Acid(C_{20}), Long alkyl chain additioned tertracyano-quinodimethane (CnCTNQ, n=12, 15, 18, 20, 22), Polyamide(PA), Polyimide(PI) etc., and natural oxidized films Al_2O_3 were also used. LB film of PI was obtained by the imidization of LB film of PA.[3)]

Measurement

In Figure 2, the circuit of measurement used in this study is shown. The D.C voltage generated in the sample charges

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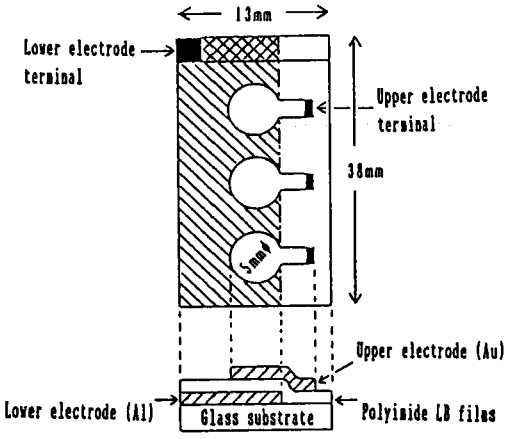

FIGURE 1 Structure of MIM element.

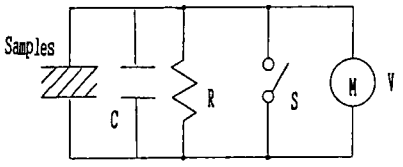

FIGURE 2 Schema of the measuring circuit.

first condenser C and sample itself (about 0.136 μF) and makes current flow through the resistance R. At this time, the voltage V generated at both ends of C and R was measured by eletronic-voltmeter M. The inner resistance of the electronic-voltmeter is very high about $10^{14}(\Omega)$ and the output of power was recorded by X-Y recorder. 10^{11}, 10^{10}, 10^{9}, 10^{8} (Ω) etc. were used as resistance R and the measurement was also performed for the circuit without R or Condenser C.

The characteristics of temperature of a MIM-structured sample was investigated and the effect of the resistance inserted externally was also examined. It was heated from room temperature(24℃) to 70℃ for 30 minutes in an electronic-temperature controller using the experimental apparatus shown in Figure 3.

RESULTS AND DISCUSSION

Voltage Generation in LB Films[2,4]

In Figure 4, a characteristic current-voltage curve of the sample made by deposition of polyimide LB film (10 layers), on the electrode. As shown in Figure 4, this curve does not pass through 0 point of both axis. This suggests that another D.C. voltage except the external voltage V (applied voltage) is

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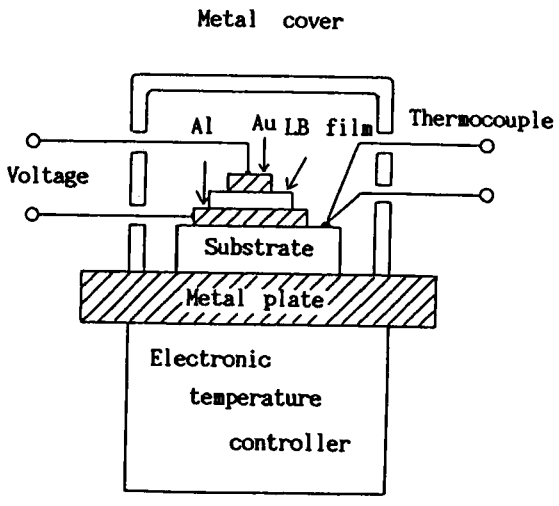

FIGURE 3 Schematic diagram of experimental apparatus.

generated in the sample. The current that flows from the upper electrode to the lower electrode is assumed to be positive and the measurement is performed on the voltage of upper electrode with the datum voltage of lower electrode. Therefore, it is inferred that the positive voltage is generated in the upper electrode for the case of Figure 4. The voltage generated mentioned in this paper means just the voltage described as above. It is found that the difference of the magnitude of the voltage generated depends on the sample, and is about 100 to several 100 mV. In addition, it is observed that the direction of voltage generated does not change for the same type element even though the magnitude ofvoltage is more or less different. In Figure 5, the result of the voltage generated measured for a long-period is shown.[2] At the point when evident decrease of voltage was not observed in 2 years, about 0.2 V of constant voltage was maintained. The experiments were simultaneously attempted on several tens of substances in type of $Al/Al_2O_3/C_{12}TCNQ/Al$, $Al/Al_2O_3/C_{20}/Al$ with the variation of the number of layers. The voltage, however, was generated in all samples for a long-period. In addition, both of the electrodes of sample was short when the measurement was not carried out. Later, as the measurement was resumed by connecting a voltmeter between two electrodes, the voltage of

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electrode starts to increase up to the constant value as shown in Figure 5. The time t0 required to reach the constant value of voltage generated is about 100 minutes and the time t0 becomes small as the resistance of sample decreases.

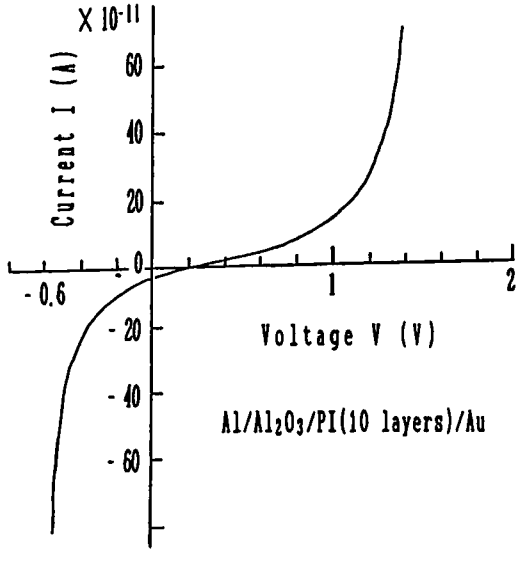

FIGURE 4 An example of current-voltage characteristics.

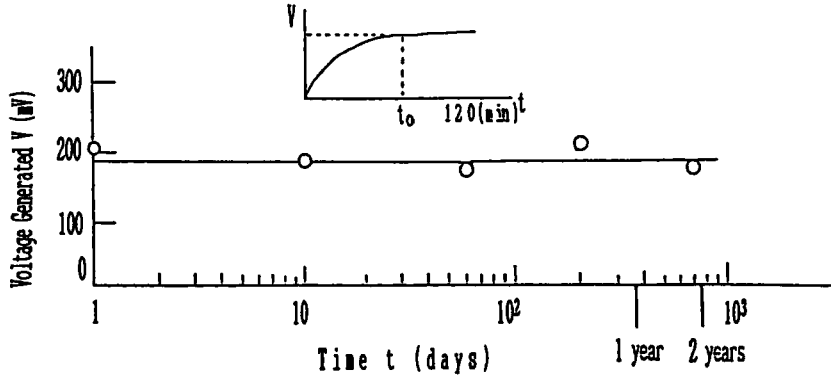

FIGURE 5 Voltage generation over long period.

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The Electric Capacity of MIM element

In the MIM element, natural oxidized film of $A_{12}O_3$ about 30 Å in thickness and the relative dielectric constant of which is 8 is formed on the surface of inner eletrode of Al vacuum-evaporated film.[5] Thus, the electric capacity of circular-type MIM element of 5 mm in diameter is calculated as follows.[6]

$$\frac{1}{C} = \frac{1}{C_{OX}} + \frac{1}{C_{PI}} \qquad \text{-------- (1)}$$

$$C_{OX} = (\varepsilon . s/d) = 0.345 \times 10^{-6} \text{ [F]}$$

$$C_{PI} I = 0.210 \times 10^{-6} \text{ [F]}$$

Then $C = 0.136$ [μF] -------- (2)

Here, S is the area of electrode and d is the thickness of LB film. In addition, the electric capacity of hetero-structured element of arachidic acid LB film(C_{20}) and TCNQ LB film(C_{15}.TCNQ) is calculated by the use of equation (1) and the result is as follows.

$$C = 7.68 \times 10^{-12} \text{ [F]} \qquad \text{-------- (3)}$$

Time Characteristics of Voltage generated

In Figure 6, the voltage generated in the circuit without R is shown. The voltage is generated as the electric charges of condenser C and sample are discharged, and the measurment is performed by switching S on for a second with time interval 1 minute. At this time, the short was accomplished through 10^8 (Ω) since switch S built in the voltmeter was used for short. Thus, the voltage is generated to some degree in a moment of switch open as the electric charges of the condenser and sample were not discharged enough. After that, however, the voltage generated increases with the time interval of 1 minute. In addition, the voltage generated decreases with the number of discharges, however, the rate of decline of voltage decreases considerably after 10 charge - discharge, cycles.

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In Figure 7, the results of voltage generated just before short by the switch S are shown. It includes three kinds of results. The 1st run was performed without leaving time in the air, and the 2nd and 3rd run were attempted after 30-minute and 10-minute of leaving time in the air. In other words, the voltage generated becomes much smaller than that of Figure 6 as the leaving time in the air increases. Thus, about 1 day of leaving time was required for the recovery of voltage.

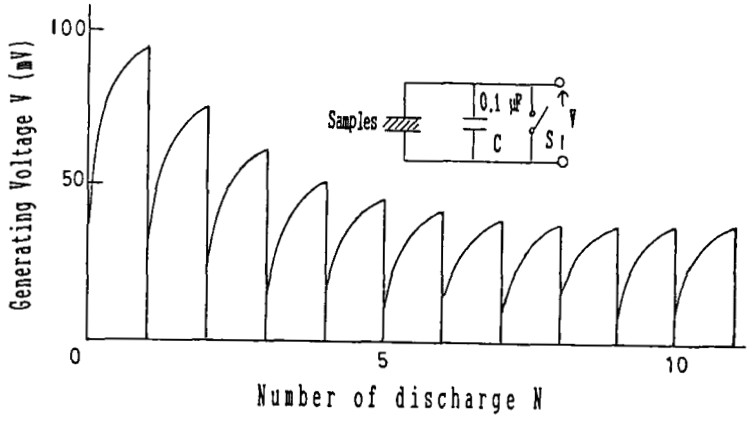

FIGURE 6 Characteristics of charging and discharging of condenser by generating voltage.

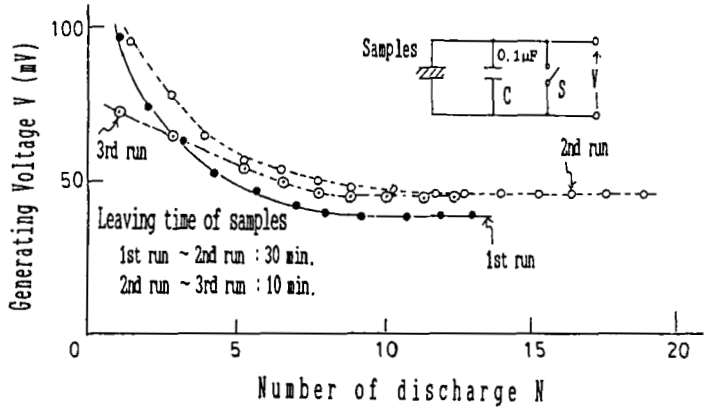

FIGURE 7 Recovery of generating voltage during the time.

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The Accumulation of Charge generated

In Figure 6, the short is performed through 10^8 (Ω) since the internal short switch of electronic voltmeter was used for the experiment. In other words, the charge of condenser C and sample could not discharge enough due to short. Thus, by the use of contact relay switch, the charge can be discharged enough. With this condenser, more than 100 times of repetition of charge-discharge were attempted. At first, the voltage generated decreases as that of Figure 6 and it does not become zero, but it maintains almost a constant value. The calculation of total quantity of charge accumulation(total quantity of discharge) generated in the sample under the assumption that all of the charged electric-charge is fully discharged by short is shown in Figure 8. From Figure 8, it is known that the accumulated charge increases almost linearly as the number of charge-discharge increases. This infers that the velocity of charge generation is almost constant.

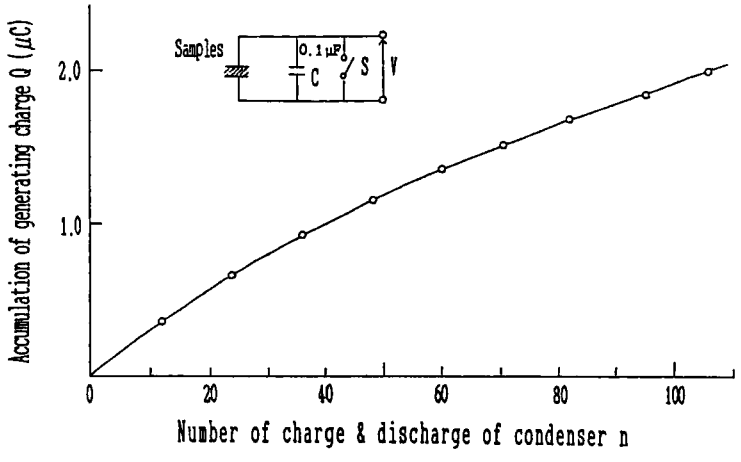

FIGURE 8 Accumulation of charge generated in specimen by charging and discharging of condenser.

Temperature dependence of generating voltage

The temperature-characteristcs that the voltage increases as temperature increases was observed as shown in Figure 9. It is

known from Figure 9 that voltage generated decreases as resistance R decreases. The reason is that the resistance inserted externally is smaller than that of the sample (about $10^9 \sim 10^{10}$ Ω). In addition, it was observed that the linearity between log(V) and 1/T appears very clearly and the slope was measured in a large value as resistance becomes smaller. It is considered that the characteristics of Arrhenius type shown in Figure 9 is related with the cause of generation of voltage. The experiment for this is, accordingly, in progress now.

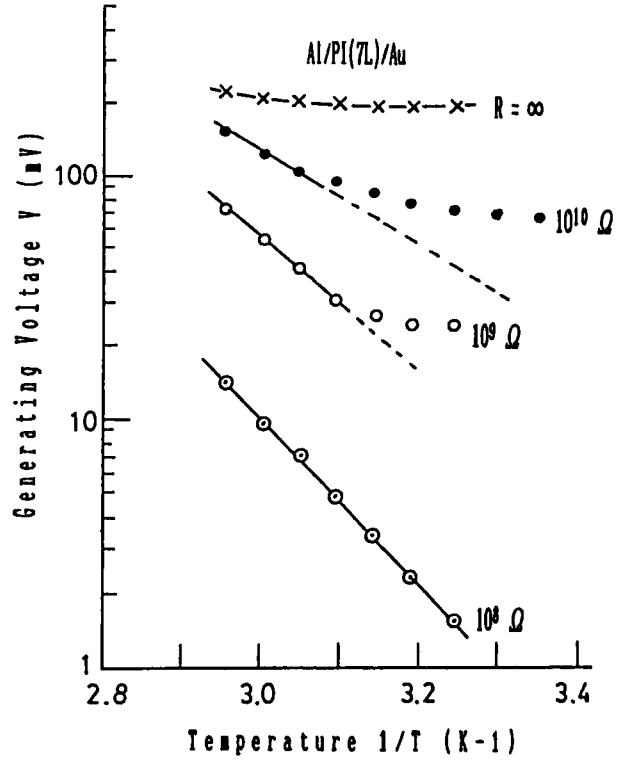

FIGURE 9 Temperature dependence of generating voltage.

CONCLUSIONS

It is well known that voltage is generated in the MIM-structured LB element. The authors have already reported a

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study on the electric phenomenon of voltage generated. The aim of this study is to discuss the same voltage generated and electric properties observed in both the sample left in the air for 6~7 years after fabrication and the new one. The fact that the voltage is generated for the long-term interval raise a doubt in the explanation that the voltage generation is due to the chemical reaction in LB film etc.. Although the reason for the generation of voltage is considered to be the chemical reaction, it is very important to verify the characteristics of voltage generated and its utilization. The attempts to investigate the electrical phenomena of voltage generation are in progress.

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