

MIS SCHOTTKY BARRIER PARAMETERS OF Al/*MESO*-TETRAPHENYL-  
PORPHINATOMAGNESIUM(II)/Ag CELL

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Integral capacitance measurements of Al/*meso*-tetraphenylporphinatomagnesium(II)/Ag cells, where the Al and porphyrin are separated by a thin Al<sub>2</sub>O<sub>3</sub> film, have been made by the capacitor discharge method. The  $1/C_i$  vs.  $Q$  plots yield a good straight line. The apparent diffusion potential  $V_o$  estimated from the slope and the  $1/C_i$  axis intercept is in the range 0.8-1.3 volts. The derived values for the barrier width  $w_o$  and the density of ionized impurity  $N$  are 11-17 nm and  $1.2-1.6 \times 10^{18}$  cm<sup>-3</sup>.

Recently, Popovic<sup>1)</sup> has suggested that the capacitor discharge method is appropriate for capacitance measurements of organic semiconductor cells, where the use of the conventional ac method often encounters some difficulties due to the high resistance, trapping effects *etc.*<sup>2)</sup>

In this paper the parameters of MIS Schottky barrier for the Al/MgTPP/Ag cell, where MgTPP denotes *meso*-tetraphenylporphinatomagnesium(II), are determined using the capacitor discharge technique. In the capacitor discharge experiments the Al/MgTPP/Ag cell is charged to an applied dc bias and then discharged. Applied voltages were provided by a Fluke 415B power supply. The charge accumulated in the sample was measured by a Takeda TR-8651 electrometer. MgTPP used was a product of Strem Chemicals and purified by sublimation if necessary. The film of MgTPP was prepared by sublimation under  $10^{-5}$  Pa and the film thickness was about 150 nm.

In the previous paper,<sup>3)</sup> we have found that the Al-MgTPP interface in the sandwich cell is photoactive and best described as a metal-insulator-semiconductor (MIS) diode consisting of Al/Al<sub>2</sub>O<sub>3</sub>/MgTPP. Then the thickness of the interfacial layer was estimated to be a few nm.

According to the theoretical work of Cowley,<sup>4)</sup> the differential capacitance ( $C_d$ ) of the MIS Schottky barrier with reverse bias is mostly represented by the following equation as same as that for the ideal Schottky barrier,

$$C_d = A \left( \frac{e \epsilon_s \epsilon_o N}{2} \right)^{1/2} (V + V_o)^{-1/2} \quad (1)$$

where  $A$  is the sample area,  $e$  the electronic charge,  $\epsilon_s$  and  $\epsilon_o$  the dielectric constant of the semiconductor and free space,  $N$  the density of ionized impurity and  $V_o$  is the apparent diffusion potential at zero applied bias, which is always larger than the actual diffusion potential  $V_{do}$  when the interfacial layer is present.<sup>5)</sup> On the other hand, the integral capacitance ( $C_i$ ) can be defined by

$$C_i = \frac{Q}{V} \quad (2)$$

where  $Q$  is the total charge accumulated in the cell measured at the applied bias  $V$ . The quantity  $Q$  is correlated with the differential capacitance by

$$Q = \int_0^V C_d dV' \quad (3)$$

Hence, by introducing Eq. (1) into (3) we obtain

$$\frac{Q}{Q_0} = \left(1 + \frac{V}{V_0}\right)^{1/2} - 1 \quad (4)$$

where  $Q_0 = A(2\epsilon_s \epsilon_0 eNV_0)^{1/2} = AeNw_0$  is the amount of charge in the barrier at zero bias and  $w_0 = (2\epsilon_s \epsilon_0 V_0 / eN)^{1/2}$  is the applied-bias independent barrier width. Furthermore, Eqs. (2) and (4) can be rewritten as

$$\frac{1}{C_i} = \frac{1}{C_0 Q_0} Q + \frac{2}{C_0} \quad (5)$$

where  $C_0 = Q_0/V_0$ . Eq. (5) indicates that plots of  $1/C_i$  vs.  $Q$  yield a straight line with the slope  $1/C_0 Q_0$  and the intercept  $2/C_0$ . From these data we can estimate the parameters such as  $V_0$ ,  $N$  and  $w_0$ .

Figure 1 shows the time dependence of the accumulated charge in the Al/MgTPP/Ag cell with reverse bias. The total charge  $Q$  was measured by extrapolating the linear portion to zero. The time necessary to measure  $Q$  was about 20 s. If the ac technique was used, the necessary frequency would be of the order of 0.01 Hz as same as in the case of  $\alpha$ -phthalocyanine.<sup>1)</sup> The capacitance measurements at such low frequencies become remarkably difficult due to sensitivity and acquisition problems.

In Fig. 2 plots of  $1/C_i$  vs.  $Q$  are shown. The derived value for  $V_0$  ranges from 0.8 to 1.3 volt, depending on the age of the sample. This seems to be correlated with increase in the interfacial-layer thickness. The values of  $N$  and  $w_0$  estimated on the assumption of  $\epsilon_{\text{MgTPP}} = 2.0$  are in the range  $1.2\text{--}1.6 \times 10^{18} \text{ cm}^{-3}$  and 11-17 nm, respectively.

#### References and Notes

- 1) Z.D. Popovic, *Appl. Phys. Lett.*, **34**, 694 (1979).
- 2) A.K. Gosh, D.L. Morel, T. Feng, R.F. Shaw, and S.H. Rowe Jr., *J. Appl. Phys.*, **45**, 230 (1974).
- 3) F.J. Kampas, K. Yamashita, and J. Fajer, *Nature*, **284**, 40 (1980).
- 4) A.M. Cowley, *J. Appl. Phys.*, **37**, 3024 (1966).
- 5) For example,  $V_0 = V_{d0} + V_1/4 + (V_1 V_{d0})^{1/2}$  for the MIS model without surface states, where  $V_1 = 2e\epsilon_s N \delta^2 / \epsilon_i^2 \epsilon_0$ .  $\delta$  and  $\epsilon_i$  are the thickness and dielectric constant of the interfacial layer. For details see ref. (4).

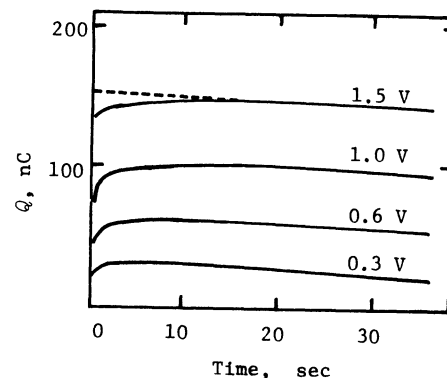


Fig. 1 Time dependence of  $Q$ .

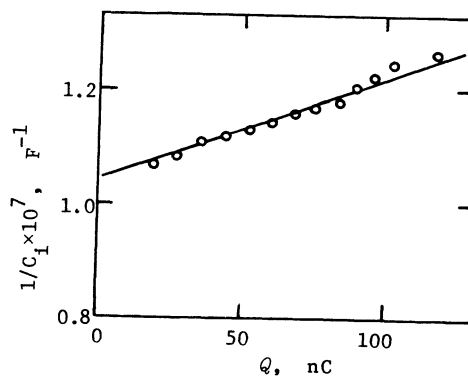


Fig. 2 Plots of  $1/C_i$  vs.  $Q$ .

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