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CHARGE CARRIER GENERATION IN AURAMINE THIN FILM UNDER ILLUMINATION

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The current-voltage characteristics, activation energies of dark-conduction and photoconduction and light intensity dependence of photocurrent of Al-auramine hydrochloride-n-type SnO_2 sandwich cell were measured. It was suggested that charge carriers of photocurrent were generated by electric field assisted ionization of excited molecules.

In a previous report[1)] we studied electric conduction phenomena of n-type SnO_2-auramine hydrochloride (sublimed film)-Al sandwich cell and found that charge carrier transport through the interface between the semiconductor and auramine-hydrochloride (AurHCl) film mainly determined the electric properties of the cell such as the rectifying characteristics of dark conduction and a drastic increase of photocurrent in the reverse direction. Transfer of charge carriers through such junctions was controlled by relative positions of hole and electron bands and the sign of the majority carriers of both components. Although charge transfer processes in the cell had considerably been elucidated, no information was obtained at that time about charge carrier generation process under illumination of the cell. In this report a possibility of charge carrier generation by electric field assisted ionization of an excited molecule is suggested referring to current-voltage characteristics, activation energies of the electric current, and light intensity dependence of photocurrent.

In the present experiments electric measurements were made at 10^{-6}Torr with the same sandwich cell[1)] and the same technique[1,2)] as reported before. Current (J)-voltage(V) characteristics of dark conduction and photoconduction in the case where the SnO_2 electrode was positively biased were shown in Figure 1 in which log (J/V) was plotted against $V^{1/2}$. Dark conduction of the cell was ohmic regardless of bias direction. From Figure 1 photoconduction characteristics can be expressed as follows.

$$J_p = AV \qquad V < 0.7 \text{ volt} \qquad (1\text{-a})$$

$$J_p = BV\exp(\beta\sqrt{V}) \qquad V > 0.7 \text{ volt} \qquad (1\text{-b})$$

The value of β in eq.(1-b) was 5.1[$\text{volt}^{-1/2}$]. In addition, photocurrent density was proportional to light intensity. Activation energy of dark current was 0.70eV (-10°C - +80°C), while that of photocurrent was 0.25eV (-70°C - +60°C) and 0.72eV (+60°C - +80°C). The above values of the activation energy were obtained from Arrhenius plots when the applied voltage was 1 volt.

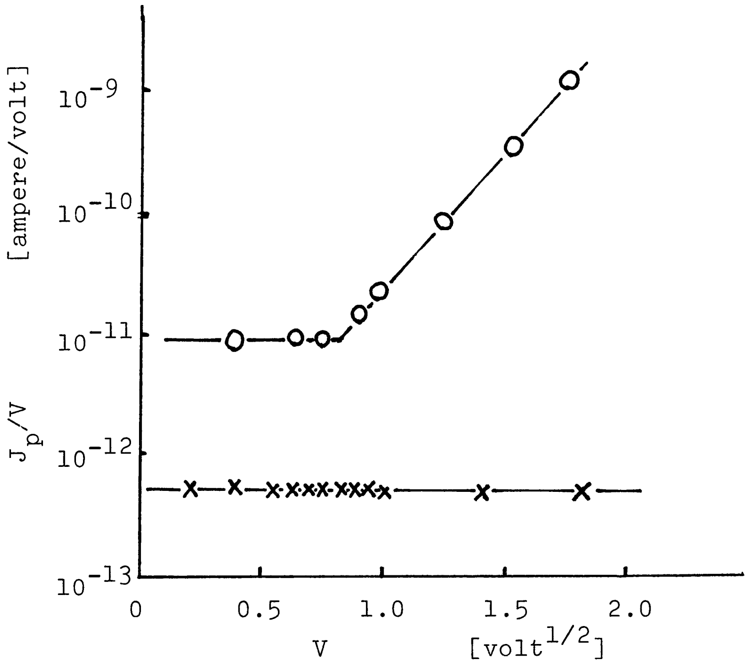

Figure 1 Current-voltage characteristics of dark conduction and photoconduction

O : photoconduction

X : darkconduction

The exponential term in eq.(1-b) may be attributed to a charge carrier liberation process from trap levels and/or to a charge carrier generation process from an excited dye molecule. The same value of the activation energy at higher temperatures in both the dark- and photoconduction suggests that the majority carriers are same in the both cases as reported previously$^{1)}$. Measurements of thermally stimulated currents at 1 volt bias revealed the presence of trapped state at 0.31 eV below conductive state. So far, there is no reason to exclude the possibility that the shallow traps are charged but the deep traps are uncharged when trapped carriers are liberated. Then, when the shallow traps (deep traps) mainly contribute to conduction, J-V characteristics of the cell will obey to eq.(1-b)$^{3)}$ (eq.(1-a)). This mechanism, together with the J-V curve in Figure 1, leads to the prediction that activation energy of the photocurrent must be different, i.e. 0.25 eV or 0.72 eV, according to whether the bias voltage is above or below 0.7 volt. However, the measured values of the activation energy did not show such discontinuity. Now we consider the effect of electric field on the charge carrier generation process from the excited dye molecules. A charge carrier of the steady state photoconduction should be generated from an excited dye cation (AurHCl^+) and disappear as a first order process, since the photocurrent density was proportional to light intensity which was sufficiently small (10^{13} - 10^{14} photons/$\mathrm{cm}^2\cdot$sec). Thus, the steady state density of charge carriers may be given by the following equation,

$$n = \phi I + KI\exp(\beta\sqrt{V}). \qquad (2)$$

The first term in the right hand side of eq.(2) represents the generation of charge carriers at dissociation centers, and the second term in eq.(2) means that the carriers are generated by the electric field assisted ionization of excited cations. When electric field becomes sufficiently high, the second term in eq.(2) will become dominant. This mechanism gives the following expression for β in a similar way to the case of Poole-Frenkel effect$^{3)}$,

$$\beta = (2^3 e^3/4\pi\varepsilon_o \varepsilon \ell)^{1/2}/kT, \qquad (3)$$

where ε and ℓ are the dielectric constant and the effective thickness of the AurHCl film. The optical dielectric constant of sublimed AurHCl film was estimated by Takeda to be 2.0$^{4)}$. As the value of β was 5.1 at 300°K, the effective thickness, ℓ, should be 0.8μ. This value seems to be reasonable since the thickness of the sublimed film was approximately 1μ$^{1,2)}$. Thus, it is strongly suggested that, under certain condition, field assisted ionization of an excited molecule plays a dominant role in charge carrier generation process in a thin film of organic material under illumination.

In the case where the SnO_2 electrode was negatively biased, the situation was rather complicated. In this case, $\log(J_p/V^2)$ was proportional to the square root of bias voltage and the slope of the $\log(J_p/V^2) - \sqrt{V}$ curve coincided to that of the $\log(J_p/V) - \sqrt{V}$ curve in the case of the reverse bias. It is very probable that the space charge layer at the interface of SnO_2 and auramine affected the probability of the ionization of an excited molecule in the similar manner as the coupling of space charge and Schottky emission which was theoretically treated by Frank and Simmons$^{5)}$.

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