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ACTIVATION ENERGY FOR HOLE INJECTION AND ANALYSIS OF THE SPACE CHARGE LAYER IN ANTHRACENE CRYSTALS

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It was found that the activation energy for hole injection at Ce^{4+}/anthracene interface depends on the applied voltage. From an analysis of the voltage dependence the thickness of the space charge layer and the charge concentration in it could be estimated.

Numerous experiments have been reported on the conductivity of a variety of organic crystals. It has been found that, in many cases, the current exhibits an expnential dependence on the reciprocal temperature. Thus an activation energy can be defined. The physical basis of the activation energy is, howwver, not well understood. The value of this energy is often poorly reproducible; The factors affecting the conductivity may not well be recognized. Oxygen and water vapor have been known to affect seriously the conductivity of organic crystals.

In most dark conduction measurements the mechanism of the charge carrier generation is not clear. Carriers can be generated thermally in the bulk of semiconductors with narrow band gaps. They can also be created at electrodes; The observed current can be carried by positive holes injected from the positively biased electrodes, or by electrons originated at the negative electrodes, or by both. Only with injecting electrodes the origin, and therefore the sign, of the charge carriers can be known with certainty.

We have investigated the dark injection of holes at Ce^{4+}/anthracene interface to elucidate the nature of the electrical contacts.

Zone refined, solution grown crystals, 50-200 μm thick, were cemented with epoxy resin on a conductivity cell made of Pyrex glass. Cerium sulfate dissolved in dilute aqueous sulfuric acid was used as hole injecting electrodes. The electrode area was about 10^{-2} cm^2. The other electrode was painted silver.*) The absence of the electron injection from silver electrode was confirmed with experiments using non-injecting aqueous solution of NaCl (0.1 M) as the counter electrode.

The current-voltage characteristics observed for a 190 μm thick crystal is shown in Fig. 1. At low applied voltages the current proved to be space charge limited. According to the theory developed by Mark and Helfrich, the space charge limited current, J, is expressed by Eq. 1,[1)]

$$J \propto V^{\ell+1} \qquad \left(\ell = \frac{T_c}{T} + 1 \right) \qquad (1)$$

if the trap depth distribution is assumed to be described by Eq. 2,

$$h(\epsilon) = N \exp\left(- \frac{\epsilon}{kT_c} \right) \qquad (2)$$

whre $h(\epsilon)$ is the number of traps the depth of ϵ. From the slope of the V-J plots in the space charge limited region in Fig. 1, T_c around 500K is obtained. This implies that the shallow traps are exceedingly large in number, suggesting the structural nature of existing traps. For the applied voltages exceeding 2×10^2 V, i.e., above the field strength of 10^4 V/cm, the current shows saturation.

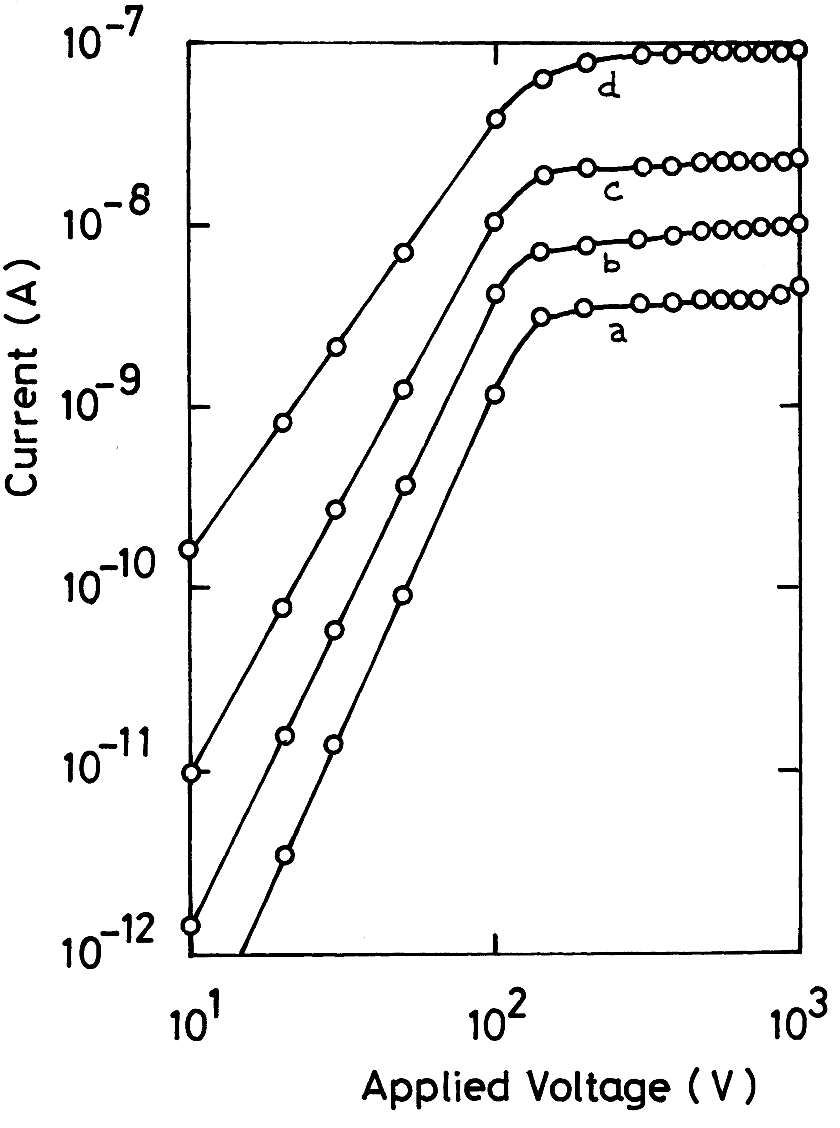

Fig. 1. Current-Voltage characteristics and its temperature dependence of Ce^{4+}/anthracene/Ag system.
a; 24°C, b; 36.0°C, c; 49.0°C, d; 65.0°C

The temperature dependence of the current at a given voltage is also deduced from Fig. 1. The current appears to be expressed by a single activation energy, which depends on the applied voltage, decreasing from 0.96 eV at 10V to 0.66 eV above 2×10^2 V (Fig. 2).

The saturation current, J_s, depends on the cerium concentration as $[\mathrm{Ce}^{4+}]^n$, where n is 0.3 for the concentration range between 5×10^{-4} M and 5×10^{-1} M.

The voltage dependence of the activation energy can be interpreted in terms of the potential barrier to be surmounted by the carriers. Thepotential barrier due to the image charge was discussed by Kallman and Pope.$^{2)}$ This leads to the Schottky effect, and it seems to be the case in the saturation region (above 2×10^2 V) in Fig. 1, where a slight increase of J is noticed. Weattribute the transition from the space charge limited region to the saturation region to the gradual depletion of space charge. Holes are thermally injected from the solution into the crystal and form the space charge layer near the interface. If the density of the space charges, ρ, is assumed to be uniform in the layer, a parabolic potential results (Eq. 3),

$$V(x) = \begin{cases} V_o - \dfrac{2\pi\rho}{\kappa}(L-x)^2 & (L>x>0) \\ V_o & (x>L) \end{cases} \tag{3}$$

where x is the distance from the crystal surface, L is the tjickness of the space charge layer and κ is the dielectric constant of the crystal. V_o represents the energy of the hole band in the interior of the crystal. With the presence of an external field, E, the potential may be approximated by Eq. 4.

$$V(x) = V_o - \frac{2\pi\rho}{\kappa}(L-x)^2 - Ex \tag{4}$$

This potential has a maximum, at $x_o = L - \dfrac{\kappa E}{4\pi\rho}$, of

$$V_o + \frac{\kappa E^2}{8\pi\rho} - LE. \tag{5}$$

The front of the space charge layer is now located at x_o. It constitutes the virtual electrode to the bulk of the crystal. The barrier height decreases with the external field, reaching a minimum at $E = \frac{4\pi\rho}{\kappa}L$. The drop of the barrier height is $\frac{2\pi\rho}{\kappa}L^2$. Extrapolation in Fig. 2 yields 1.2 eV as the activation energy at zero applied voltage. Thus our observation indicates that the drop of the barrier height is 0.54 eV with a field of 1×10^4 V/cm. It enables the estimation of L and ρ to be 2×10^{-4} cm and 6×10^{13} holes/cm^3, respectively. At still higher voltages the space charges are all swept away by the external field and the injection becomes rate determing. Yamagishi and Soma have discussed the activation free energy for the present system.$^{3)}$ They observed activation energy of 0.34 eV for the hole injection and inter preted it as the activation energy for the electron transfer reaction. Our observation that I_s is proportional to $[\mathrm{Ce}^{4+}]^{0.3}$ seems to indicate the participation of some adsorbed states, so the temperature dependence of the adsorption might affect the activation energy for J_s.

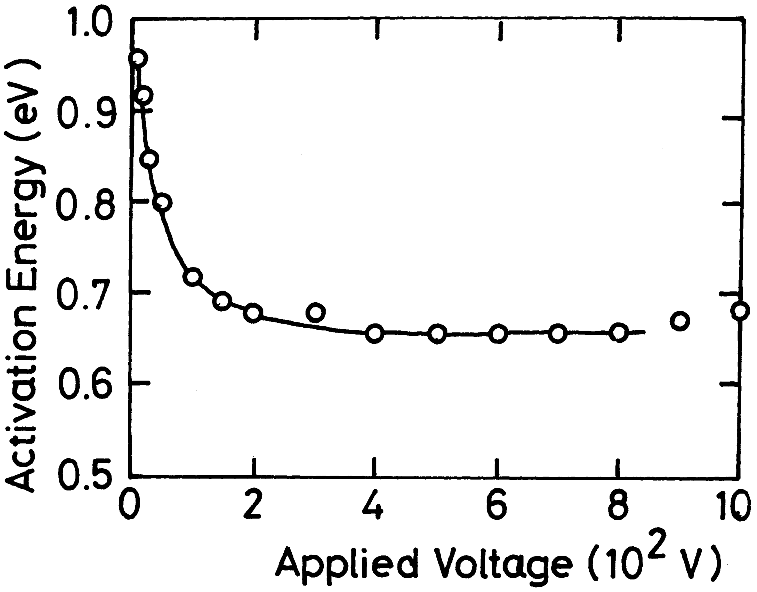

Fig. 2. Dependence of the activation energy on the applied voltage.

*) When aqueous electrodes were used in place of the silver electrodes, cosiderable current obeying Ohm's law was observed at lower voltages, which proved to be a trivial leakage current in most cases.

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