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# The Photoconductivity of Poly($N$-vinylcarbazole). II. Dark Conductivity in a Sandwich-type Cell

Kenichi OKAMOTO,* Shigekazu KUSABAYASHI,* and Hiroshi MIKAWA
*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565*

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The dark conductivity in a sandwich-type cell of PVCz films was investigated in a high vacuum, taking the temperature, the applied voltage, and the film thickness as parameters. In low fields, the conductivity was proportional to the applied voltage. In high fields, however, it was proportional to the fourth power of the applied voltage. This nonohmic dark conductivity in high fields may be attributed to the Pool-Frenkel effect. A model of the energy-level diagram is presented which can explain the dark conductivity in both low and high fields.

In the previous paper the authors have reported the photo and dark conductivities in a surface-type cell of poly-$N$-vinylcarbazole (PVCz) films.[1] Although PVCz has a large $\pi$-electron system as a pendant group, its dark conductivity is too small to be measured at moderate temperatures in a high vacuum. In the present paper, the dark conductivity was investigated in a sandwich-type cell. Interesting behavior was observed in the high-field conductivity, as will be mentioned below.

## Experimental

PVCz was prepared as has been described in the previous paper.[1] A certain amount of a 5 wt% benzene solution of the polymer was poured onto a nesa-coated quartz plate, and the solvent was evaporated slowly in the dark. Films 8, 15, and 24 $\mu$ thick were thus prepared, to which three lead wires were attached by using silver paste, as is shown in Fig. 1 (a). The film with lead wires was set in the apparatus

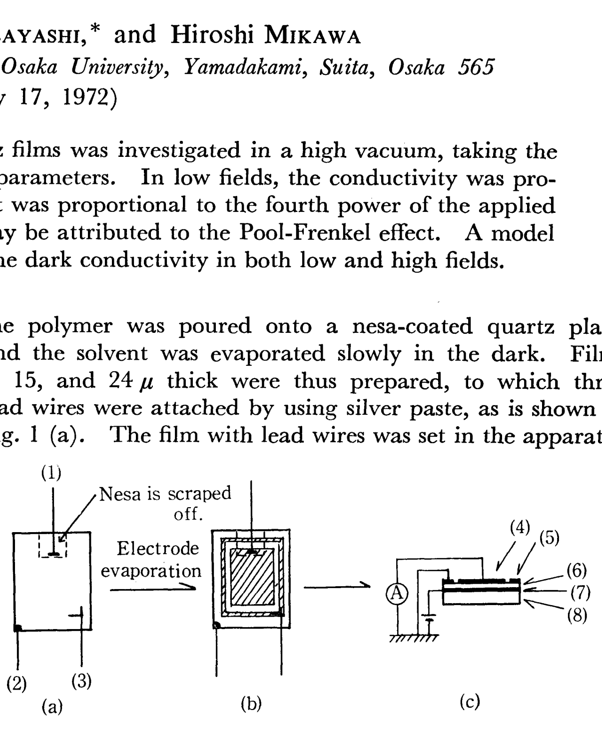

Fig. 1. Sandwich-type cell.
(1) metal electrode lead wire, (2) nesa-electrode lead wire, (3) guard ring lead wire, (4) evaporated metal electrode, (5) evaporated guard ring electrode, (6) PVCz film, (7) nesa-electrode coated on quartz plate, (8) quartz plate (20×25×1 mm).

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* Present address: Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755.

[1] K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 1948 (1973).

for the electrical measurement described in the previous paper and was kept in a high vacuum ($10^{-7}$ mmHg) for several hours. Semitransparent main and guard electrodes were evaporated on the film to prepare the sandwich-type cell, as is shown in Fig. 1 (b, c). Several kinds of metals, such as Au, Ag, Cu, and Al, were used as the electrode material. The sandwich-type cell thus prepared was subjected to the electrical conductivity measurements after it had stood for a day in the dark in a high vacuum, without exposure to air after the evaporation of the metal electrodes. The measurements were carried out by means of a vibrating-reed electrometer (Takeda Riken TR 84M) in a high vacuum ($10^{-7}$ mmHg).

## Results

*Time-dependence of the Dark Current.* The dark current slowly decreased with the time after applying the voltage, as is shown in Fig. 2. The dark current requires from several hours to a day to reach a steady-state value. After the voltage was taken off, a fairly large back current was observed in the short circuit.

In low fields the dark current showed the time-dependence given by Eq. (1), where $n$ was 0.4—0.7, and reached the steady-state value in scores of minutes or in a few hours at room temperature, as is shown in Fig. 3.

$$i_d \propto t^{-n} \tag{1}$$

In high fields the dark current obeyed Eq. (1) for only a short period after the voltage was applied and the current continued to decrease slowly with the time even after ten hours. It reached the steady-state value after more than 20 hr at room temperature.

*Voltage-dependence of the Dark Current.* The voltage-dependence of the forward dark current (abbreviated as "dark current") is shown in Fig. 4(a), taking the time after the application of voltage as a parameter, and in Fig. 4(b), taking the temperature and the polarity of the electrode as parameters. The voltage-dependence of the dark current showed a dramatic change at a certain voltage (transition voltage, $V_t$); that is, the dark current was proportional to the applied voltage below the transition voltage and to the fourth power of the applied voltage above that. This voltage-dependence was observed for the dark current (charging absorption current) within several minutes after the application of the voltage as well as for the steady-state dark current. The transition voltage changed with the temperature, the polarity of the electrode, and the thickness of the film. In the asymmetric Au–PVCz–Nesa sandwich-type cell of the film 15 μ thick, the transition voltage was about 35 V at room temperature or 60 V at 106 °C when the nesa-electrode was biased positively, while the transition voltage was about 90 V when the nesa-electrode was biased negatively at 20 °C. On the other hand, it was 60—80 V at 20 °C in the symmetric Au–PVCz–Au sandwich-type cell. Sandwich-type cells with other electrode materials (Ag, Cu, and Al) acted the same.

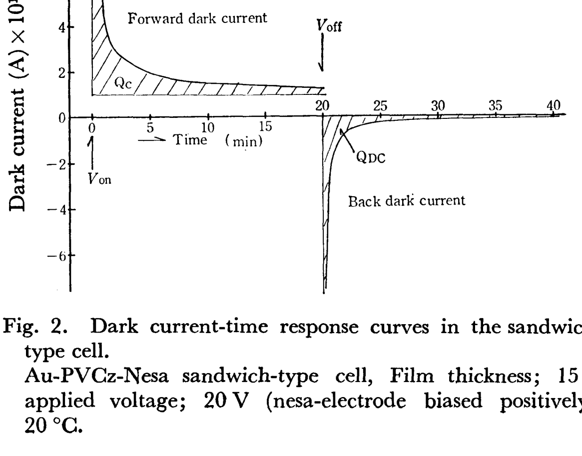

Fig. 2. Dark current-time response curves in the sandwich-type cell.
Au-PVCz-Nesa sandwich-type cell, Film thickness; 15 μ, applied voltage; 20 V (nesa-electrode biased positively), 20 °C.

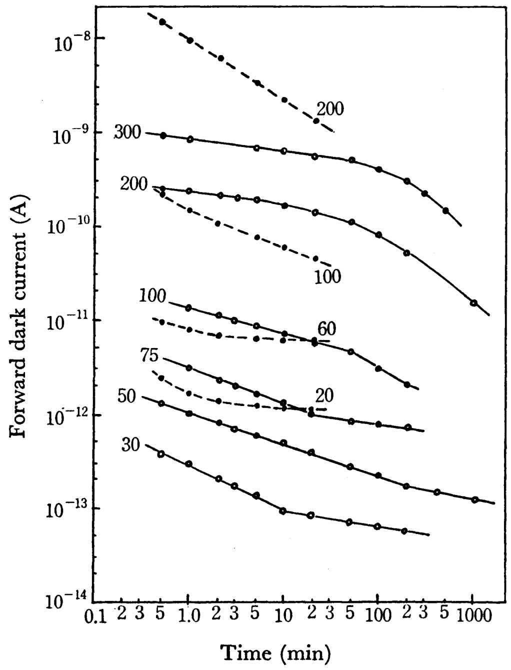

Fig. 3. Time dependence of the dark current in the Au-PVCz-Nesa sandwich-type cell.
The numerical values show the applied voltage when the nesa-electrode was biased positively. Solid lines; at 20 °C, dotted lines; at 106 °C. Film thickness; 15 μ.

At a constant applied voltage, the dark current was inversely proportional to the thickness of the film below the transition voltage and apparently so to the fourth power of the thickness above the transition voltage, as is shown in Fig. 5(a). The transition voltage was proportional to the thickness of the film, as is shown in Fig. 5(b).

*Temperature-dependence of the Dark Current.* Figure 6(a) shows the temperature-dependence of the ohmic dark current below the transition voltage. Though the measurement was carried out after the cell had stood with an applied voltage of 7000 V/cm for a day in the dark, on the first heating the dark current behaved in a manner similar to that of the thermally stimulated current. After the subsequent cooling and heating cycles, the dark current showed a reproducible temperature-dependence. The activation energy[2] was

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[2] The activation energy ($\Delta E$) is represented by the equation: $i_d \propto \exp(-\Delta E/kT)$.

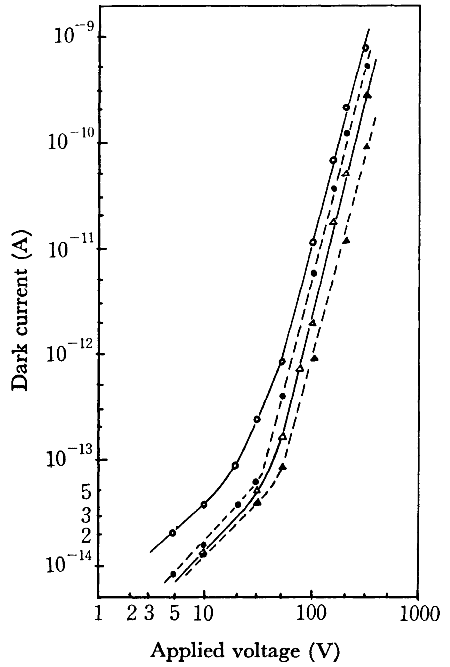

Fig. 4(a). Voltage dependence of the dark current in the sandwich-type cell.
Au-PVCz-Nesa sandwich-type cell, film thickness 15 μ. The nesa-electrode was biased positively at 20 °C. Dark current was measured the following minutes after application of the voltage; —○— 2 min., ---●--- 20 min., —△— 180 min., and ---▲--- 1000 min.

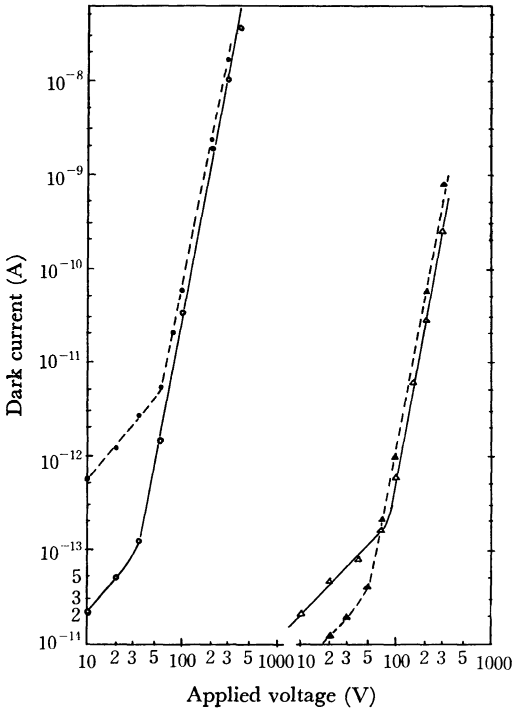

Fig. 4(b). Voltage dependence of the dark current in the sandwich-type cell. Dark current was measured 10 minutes after applying voltage.
Au-PVCz-Nesa sandwich-type cell (film thickness 15 μ); —○— at 20 °C, nesa-electrode biased positively, ---●--- at 106 °C, nesa-electrode biased positively, —△— at 20 °C, nesa-electrode biased negatively. Au-PVCz-Au sandwich-type cell (film thickness 15 μ); ---▲--- at 20 °C.

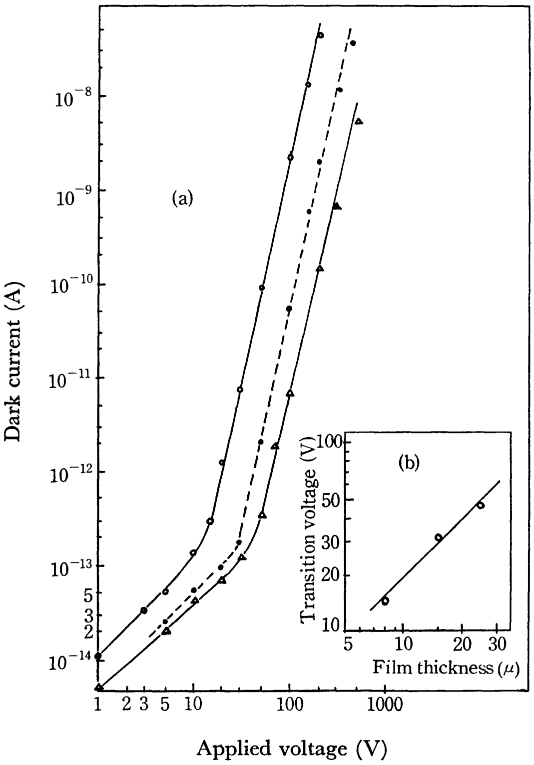

Fig. 5. Effect of the film thickness on the dark conductivity in the sandwich-type cell.
Dark current was measured in Au-PVCz-Nesa sandwich-type cell (film thickness 15 μ) 15 minutes after applying voltage at 27 °C.
(a) Dark current *vs.* applied voltage.
—○— 8 μ thick, ---●--- 15 μ thick, —△— 24 μ thick.
(b) Transition voltage *vs.* film thickness.

1.1—1.3 eV, which was identical with that measured in the surface cell in the high-temperature range (100—200 °C) in a high vacuum. After the thermodynamic equilibrium had been built up, the dark conductivity was very small; the specific conductivity was only $1\times10^{-18}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 90 °C.

Figure 6(b) shows the temperature-dependence of the nonohmic dark current above the transition voltage. In the applied field (200000 V/cm), the activation energy of this dark current was 0.6—0.8 eV, which was considerably smaller than that of the ohmic dark current.

*Discharging Absorption Current.* When the applied voltage was taken off, the back dark current was observed in the short circuit. This back dark current is referred to the discharging absorption current. For many cells this current followed Eq. (1), as is shown in Fig. 7(a), and the $n$ value was 1.0—1.4 regardless of the field strength. The discharging absorption current, was proportional to the pre-applied voltage in any voltage region, as is shown in Fig. 7(b). It should be noted that the discharging absorption current showed a linear dependence on the pre-applied voltage even in the high-voltage region, where the dark current showed the nonohmic dependence.

The temperature-dependence of the discharging absorption current was small in comparison with that of the dark current; that is, the discharging absorption

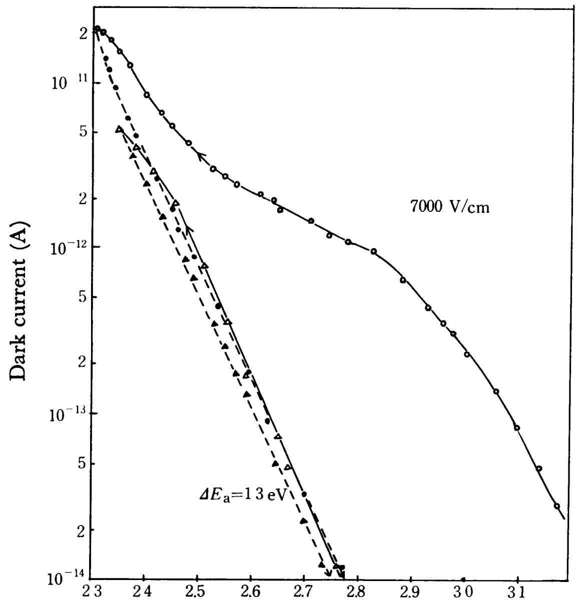

Fig. 6(a). Temperature dependence of the ohmic dark current at low field in the PVCz sandwich-type cell.

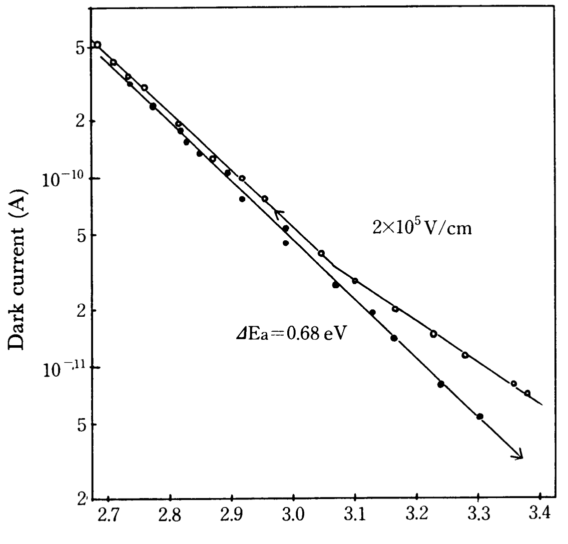

Fig. 6(b). Temperature dependence of the nonohmic dark current at high field in the PVCz sandwich-type cell.

current was approximately doubled in magnitude with a rise in the temperature from 20 to 100 °C.

The amount of the electric charge carried by the charging absorption current, which is indicated by the symbol $Q_C$ in Fig. 2, did not depend on the structure of the electrodes, but that carried by the discharging absorption current ($Q_{DC}$ in Fig. 2) was affected by the structure of the electrodes. In the asymmetric Au–PVCz–Nesa sandwich-type cell, the $Q_{DC}$ value was about three times that in the symmetric Au–PVCz–Au sandwich-type cell. Furthermore, the $Q_{DC}$ value was much smaller than the $Q_C$ value; that is, the $Q_{DC}/Q_C$ ratio was 1 : 2 in the asymmetric sandwich-type cell and 1 : 6 in the symmetric one in the ohmic voltage region.

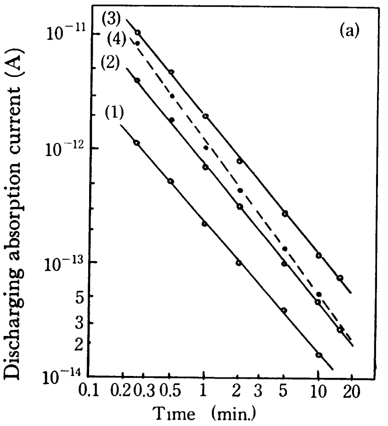

Fig. 7(a). Time dependence of the discharging absorption current in the Au-PVCz-Nesa sandwich-type cell. $i_{DC} = i_0 t^{-n}$, $n=1.1-1.4$.
Film thickness; 15 $\mu$, nesa-electrode biased positively.
(1) 35 V, 20 °C, (2) 100 V, 20 °C, (3) 300 V, 20 °C,
(4) 100 V, 106 °C.

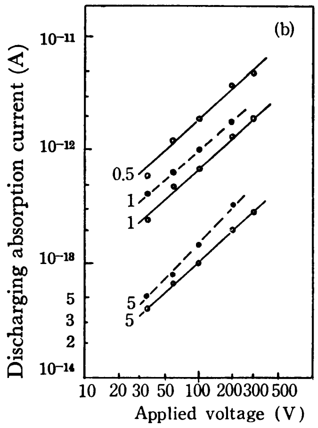

Fig. 7(b). Voltage dependence of the discharging absorption current in the Au-PVCz-Nesa sandwich-type cell.
Film thickness; 15 $\mu$. The numerical values show the time (min.) after closing the external circuit. Solid lines are measured at 20 °C and dotted lines at 106 °C.

## Discussion

*Absorption Current.* It is well known that, for many insulating polymers, both charging and discharging absorption currents obey Eq. (1), where the $n$ value is equal to 0.7—1.1.[3-5] In the case of the polymers such as polymethylmethacrylate, the two absorption currents equal one another in magnitude (superposition principle) and are attributable to the slow orientation of the permanent electric dipoles or ionic charges by the applied voltage.[3] On the other hand, for the polymers such as polyethylene the superposition principle fails to hold and the $Q_C$ value is usually several times larger than the $Q_{DC}$. Another mechanism besides the orientation of the permanent electric dipoles (for example, the accumulation or dissipation of space charge) must, therefore, be used

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5) G. Lengyel, *J. Appl. Phys.*, **37**, 807 (1966).

for both absorption currents of these polymers.[3,6]

In the case of PVCz, the discharging absorption current had an $n$ value, 1.1—1.4, similar to those of polyethylene and others, but the charging absorption current showed a very small $n$ value, 0.1—0.7, especially in the high-voltage region. The $Q_{\mathrm{C}}$ value was two or six times larger than the $Q_{\mathrm{DC}}$ value, and the superposition principle failed to hold. Both absorption currents in a PVCz sandwich-type cell, therefore, should not be attributed to the orientation of the permanent dipoles by the applied voltage, but to another mechanism in the same manner as in the case of polyethylene. The accumulation of space charges could be the reason for the charging absorption current in the low-voltage ohmic region, but not for that in the high-voltage nonohmic region, because the back electromotive force which would be caused by that is too large compared with the applied voltage.

Lindmayer has applied Eq. (2) to the discharging absorption current in the Au–SiO$_2$–Si system; he attributed this relation to the asymmetric field caused by the space charges trapped inhomogeneously in the bulk by the trap levels distributed energetically:[7]

$$I_{\mathrm{ext}}(=i_{\mathrm{DAC}})=f\cdot g\cdot C\cdot V_{\mathrm{a}}/t \qquad (2)$$

where $I_{\mathrm{ext}}$, is the discharging absorption current; $C$, the capacity of the sandwich-type cell; $f$, the charge in the insulator divided by $C\cdot V_{\mathrm{a}}$; $V_{\mathrm{a}}$, the applied voltage; $g$, the charge appearing in the discharging current ($Q_{\mathrm{DC}}$) divided by $C\cdot V_{\mathrm{a}}$ and $t$, the time after the electrodes were short-circuited. Now, Eq. (2) was used for the PVCz sandwich-type cell the following $f\cdot g$ values were obtained; $f\cdot g=0.8$—$1.0\times10^{-3}$ (20 °C) or 1.2—$1.6\times10^{-3}$ (106 °C). These values are in agreement with the requirement that $f\cdot g<0.06$.[7]

The $Q_{\mathrm{DC}}$ value in the asymmetric Au–PVCz–Nesa sandwich-type cell was larger than that in the symmetric Au–PVCz–Au one. The asymmetric structure of the electrodes, therefore, seems to contribute to the formation of the asymmetric field to a fairly large extent.

*Ohmic Dark Current under a Low Field Strength.* The ohmic dark current under a low field strength in a sandwich-type cell showed a behavior similar to that in a surface-type cell described in the previous paper.[1] The dark current increased upon UV-light pre-illumination and decreased upon repeated IR-light illumination. The activation energy of the ohmic dark current was quite small, while the dark current was fairly large, because of the effect of the previous history. After the thermodynamic equilibrium was achieved, it was, however, the same value, 1.0—1.3 eV, as that observed in a surface-type cell in a high vacuum in the high-temperature range.[1] These facts suggest that the ohmic dark current in a sandwich-type cell may be due to the thermal reexcitation of the trapped carriers, just as in the case of a surface-type cell.

On the other hand, the considerable effect of air on the dark conductivity observed in a surface-type cell was not observed for a sandwich-type cell; that is, there were no significant differences in the magnitude of the dark current and the dark activation energy between that in the air and in a high vacuum. This suggests that the trap level which gave an activation energy of 0.7—1.0 eV in a surface-type cell (trap level $E_{\mathrm{t2}}$ shown in Fig. 6 in the previous paper[1]) is negligibly small in a sandwich-type cell. This trap level was introduced by air or the irradiation of UV-light or $\gamma$-ray, and may, therefore, be attributed to some surface impurity. In a sandwich-type cell, the layer containing both some surface impurity and adsorbed oxygen molecules will be covered by the evaporated electrode layer.

*Nonohmic Dark Current under a High Field Strength.* The nonohmic dark current under a high field strength was different from the ohmic dark current under a low field strength in the following three characteristics; (1) $i_{\mathrm{d}}\propto V^4$, (2) a small activation energy, and (3) the dark current decreased very slowly with time. The dark current with a superlinear dependence on the applied voltage has often been attributed to the space-charge limited current (SCLC), the Schottky conductivity, or the Poole-Frenkel conductivity.[8]

When there are trap levels with an energetic distribution such as an exponential one, the SCLC is proportional to the $n$-th power ($n>1$) of the applied voltage and the transition voltage from the ohmic current to the SCLC is proportional to the second power of the film thickness.[9,10] This kind of SCLC has been reported for anthracene,[10] stilbene,[11] and polyethylene-terephthalate.[12] In a sandwich-type cell of PVCz film, the nonohmic dark current was proportional to the fourth power of the applied voltage and inversely proportional to the same power of the film thickness. The nonohmic dark current, therefore, showed the same value for films with different thicknesses under the same field strength; that is, there was no effect of the film thickness. Furthermore, the transition voltage was

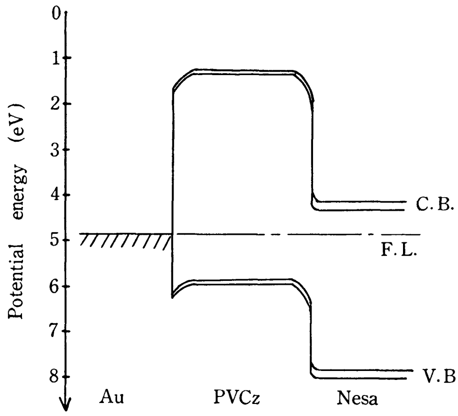

Fig. 8. Energy level diagram of the Au-PVCz-Nesa system.

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proportional to the film thickness. The carrier injection from the electrodes is difficult, as will be discussed below. The nonohmic dark current can not, therefore, be explained by the SCLC for these three reasons.

Figure 8 shows the energy diagram for the Au–PVCz–Nesa sandwich-type cell. The work function of gold is 4.83 eV.[13] The ionization potential and the electron affinity of nesa coating are 7.2 and 3.6 eV respectively.[14] The ionization potential of PVCz has been reported to be 6.1 eV from the measurement of the photoinjected hole current from the gold electrode,[15] and its electron affinity has been estimated to be only the polarization energy, the estimated value being 1.5 eV.[16] From Fig. 8 the hole injection from a gold electrode to PVCz is most conceivable, and the electron injection from a gold or nesa electrode to PVCz is not conceivable. As the nesa coating is a *n*-type semiconductor, the possibility of a hole injection from a nesa electrode to PVCz can be neglected. When a nesa-electrode was biased positively, the transition voltage was usually smaller and the nonohmic dark current was usually larger, as is shown in Fig. 4(b). For the nonohmic dark current to be attributed to the Schottky emission, an electron injection from a gold electrode to PVCz must be supposed. This injection, however, is difficult, as has been discussed above. The other electrode materials (Ag, Al, and Cu) which have a lower work function than that of Au, did not affect either the magnitude of the dark current or the transition voltage. From these facts, it can be said that the nonohmic dark current can not be explained by the Schottky emission from the electrode.

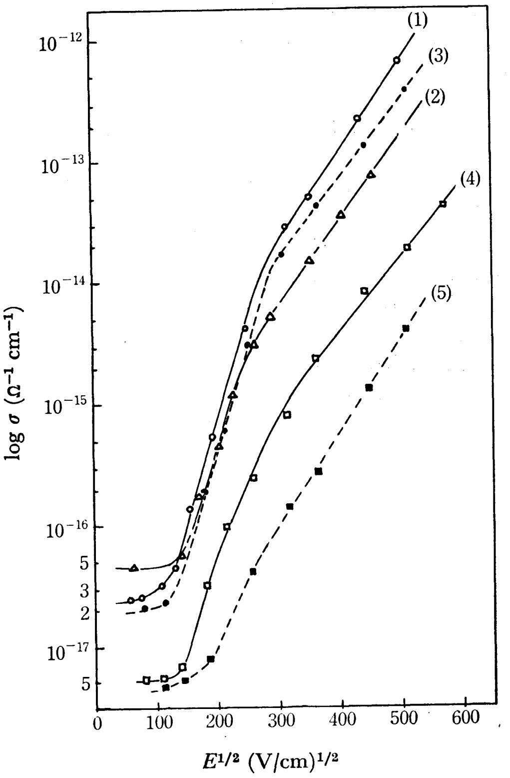

Fig. 9. Poole-Frenkel plot of dark conductivity *vs.* applied field for the PVCz sandwich-type cell.
(1) 8μ thick, 27 °C, 15 min. after application of voltage.
(2) 15 μ thick, 27 °C, 15 min. after application of voltage.
(3) 24 μ thick, 27 °C, 15 min. after application of voltage.
(4) 15 μ thick, 20 °C, 20 min. after application of voltage.
(5) 15 μ thick, 20 °C, steady state value.

Now the application of the Poole-Frenkel effect was attempted in the case of the nonohmic dark current. This effect is not concerned with the electrode limited conductivity, but with the bulk conductivity. The Poole-Frenkel effect gives the conductivity a field dependence of this form:[17]

$$\sigma_{\mathrm{PF}} = \sigma_0 \exp\left(\beta_{\mathrm{PF}} E^{1/2}/kT\right) \tag{3}$$

$$\beta_{\mathrm{PF}} = (q^3/\pi K \varepsilon_0)^{1/2} \tag{4}$$

where $\sigma_0$ is the low-field conductivity of the system, $q$ is the unit of electric charge, $\varepsilon_0$ is the permitivity of free space, $K$ is the high-frequency dielectric constant of the film, and $E$ is the electric field strength in the film. When the voltage-dependence of the dark current given in Figs. 4 and 5 is replotted, with log σ as ordinate and $E^{1/2}$ as abscissa, a straight line is obtained in the high field strength region, as is shown in Fig. 9. The Poole-Frenkel constant, $\beta_{\mathrm{FP}}$, was obtained from the slope of the straight line in Fig. 9; it is shown in Table 1. On the other hand, this constant is calculated to be $4.1\times10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ from Eq. (4) by assuming $K$ as 3.0.[18] As is shown in Table 1, the agreement between the calculated and the experimentally found values of the $\beta_{\mathrm{PF}}$ constant are very good. The nonohmic dark current under the high-field strength in the sandwich-type cell of the PVCz film thus satisfies well Eqs. (3) and (4) and may, therefore, be attributed to the Poole-Frenkel conductivity. A similar behavior has been reported for the high-field conductivity of the polymers, such as polyethylene[19] and polyacrylonitrile,[20] and has been attributed to the Poole-Frenkel effect.

In order to exhibit the Poole-Frenkel conductivity under a high-field strength, a trap is required to be

TABLE 1. THE $\beta_{\mathrm{PF}}$ VALUES OBSERVED FOR THE PVCz FILMS

| Film thickness | $\beta_{\mathrm{PF}}$ Observed$^{a)}$ | $\beta_{\mathrm{PF}}$ Calculated |
|---|---|---|
| 8μ | $4.3\times10^{-5}$ eV (m/V)$^{1/2}$ | |
| 15 | $4.4\times10^{-5}$ $^{b)}$ | $4.1\times10^{-5}$ eV (m/V)$^{1/2}$ |
| 24 | $4.0\times10^{-5}$ | |

a) Measured for the dark current in 15 minutes after application of voltage at 27 °C.
b) The same value was obtained for the steady-state dark current at 20 °C.

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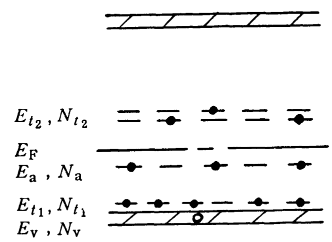

Fig. 10. Energy level diagram explaining the dark conductivity in PVCz sandwich-type cell.
The symbols $E_v$ (=0), $E_{t1}$ (=0.1−0.3 eV), $E_{t2}$ (=2 eV), $E_a$ (=1.0−1.3 eV) and $E_F$ express the potential energy of each level measured above the valence band edge. The values in parentheses were obtained from the activation energy for the dark current. The symbols $N_v$, $N_{t1}$, $N_{t2}$, and $N_a$ express the density of each level.

positively (or negatively) charged; that is, it must be charged when empty and uncharged when filled (donor or aceeptor), and these traps must be the main source of the dark conductivity under a low-field strength. A model must, therefore, be presented which can explain both the low-field and high-field conductivities. The energy level, 0.7—1.0 eV, above the valence band was negligibly small in the sandwich-type cell, as has been mentioned above, and so it has been excluded from Fig. 10. An acceptor level was considered as the trap level causing the Poole-Frenkel effect, because holes are the majority carriers in PVCz.

We located the position of the Fermi level by equating e number of holes missing from the acceptor centers with the number of the deep traps occupied by holes, the number of holes in the valence band being negligibly small. The thermodynamic Fermi level, $E_F$, as measured above from the valence band edge, is therefore, given by Eq. (5).

$$E_F = E_a - kT\log\{(N_a - N_{t2})/N_a\} \tag{5}$$

At a zero (or low) field, the number of free holes, $p$, is given by:

$$P = \{N_v(N_a - N_{t2})/N_a\}\exp(-E_a/kT) \tag{6}$$

The low-field conductivity $\sigma_0$ is, therefore, given by:

$$\sigma_0 = Pq\mu_h = \{q\mu N_v(N_a - N_{t2})/N_a\}\exp(-E_a/kT) \tag{7}$$

where $\mu_h$ is the hole carrier mobility. In the high field, the acceptor barrier is lowered by the Poole-Frankel effect, so that the number of free holes in the valence band increases to:

$$P = \{N_v(N_a - N_{t2})/N_a\}\exp\{-(E_a - \beta_{PF}E^{1/2})/kT\} \tag{8}$$

and the dark conductivity is given by Eq. (3). The magnitude of the lowering of the activation energy for the dark conductivity was 0.3—0.5 eV at the field strength of $2\times10^5$ V/cm, which is in approximate agreement with the calculated value, 0.2 eV. Thus, the energy-level model given in Fig. 10 can give a reasonable explanation of the dark conductivity in the sandwich-type cell of the PVCz film in both low- and high-fields.

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