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ELECTRONIC SWITCHING IN PYRANTHRONE THIN FILM

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Bistable field- and thermal-induced switching between a "ON" state and a "OFF" state was observed in pyranthrone thin film by using surface type cell with gold electrodes. The transformation from the "OFF" state to the "ON" state is caused by the avalanche of electrons at the negative biased electrode.

Introduction

Field-induced switching between a high impedance state and a low impedance state has been reported for naphthalene, anthracene[1], tetracene and perylene[2] thin films when a mobile electrode such as gallium-indium alloy is used. Garrett et al.[1] observed that after the first transition to the low impedance state a Ga-In alloy-filled crater was formed and carbonized walled craters were observed for films with evaporated gold or aluminium counter electrodes. Kevorkian et al.[2] concluded that pure organic films undergo switching via electrode diffusion leading to filament formation of a metallic nature. In the previous paper[3] we reported the electronic switching phenomenon for dibenzo-18-crown-6 thin film with silver electrodes.

In this work we studied the electronic switching mechanism and the electrode dependence of the conductance in evaporated thin films of pyranthrone.

Experimental

Pyranthrone was purified by repeated sublimation in vacuo (10^{-6} Torr). The surface type cell was prepared by vacuum evaporation (10^{-6} Torr) of electrode (Pt, Au, Ag, Al) and pure pyranthrone on microscope slide glass. The surface type cell is convenient to observe the transformations of the film. Electrical properties were measured with an electrometer and a dc power supply (max 3 kV). The sample was held in vacuo (10^{-6} Torr). The temperature was measured by use of copper-constantan thermocouple. The state of the film was observed with a polarizing microscope.

Results and Discussion

"OFF" state

The typical current-voltage characteristic observed for "OFF" state is shown in Fig. 1. This equilibrium current does show noticeable deviation from Ohm's law and this deviation increases with temperature. At low applied voltages(below 10 volts) the electrode dependence of the activation energy (E') in Eq. (1) indicates that this pyranthrone thin film is one of the n-type semiconductors and the main carriers are the electrons injected from metal electrode.

$$I = \sigma_0 \cdot V \cdot \exp(-E'/kT) \qquad (1)$$

where I is the observed current and V is the applied voltage. The activation energies E' with some electrode materials are 0.92(Al), 1.12(Au), 1.20(Ag), and 1.35(Pt), all in eV. The schematic illustration of energy diagram is shown in Fig. 2, and the value of electron affinity of pyranthrone film is estimated to be about 3.4 eV by the least squares method (Fig. 3). At high applied voltages the current-voltage characteristic is interpreted in terms of the Schottky emission of electron from negative biased electrode to pyranthrone. In the Schottky emission, the current density is given by

$$I = AT^2 \cdot \exp\left[-(E - \beta V^{1/2})/kT\right] \qquad (2)$$

where A is the emission coefficient, E is the zero-field barrier at the electrode-sample interface and is approximately equal to the value of E' in Eq. (1) and

$$\beta = (e^3/4\pi d \varepsilon_r)^{1/2} \qquad (3)$$

where ε_r is the dielectric constant and is estimated to be 5 from the value of the capacitance at 100 kHz and d is the thickness of the space charge layer. Eq. (4) is derived from Eq. (2).

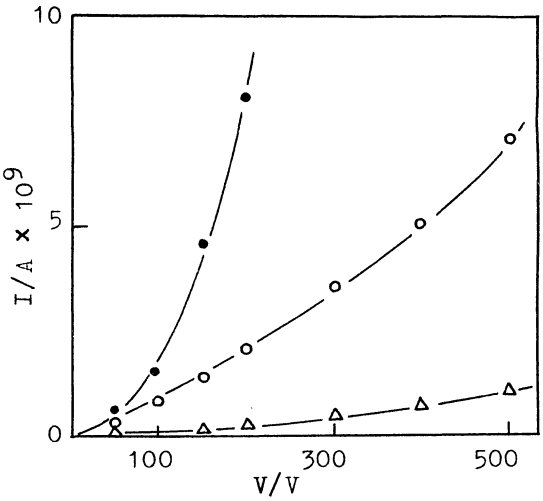

Fig.1. Typical current-voltage characteristic for off state. Electrode;Au. △)71 °C, o)96 °C, ●)121 °C.

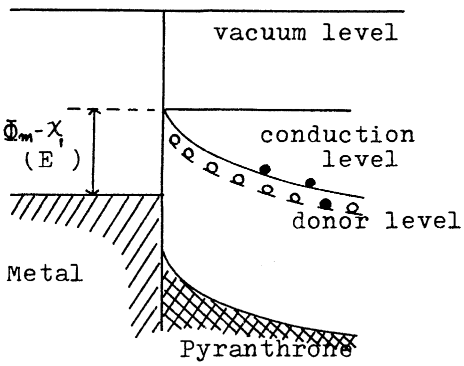

Fig.2. Energy diagram of metal-pyranthrone contact. Φ_m ;work function of metal, χ ;electron affinity of pyranthrone.

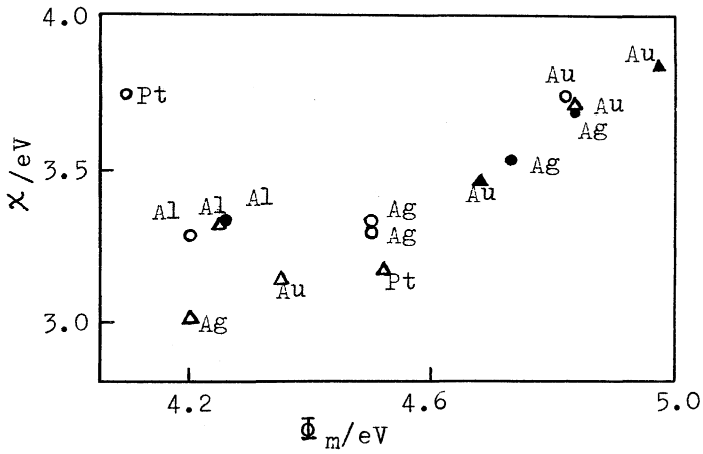

Fig.3. The relation between Φm and χ(=Φm - E')

●) used in ref.(4) by Eley.

▲) used in ref.(5) by Kotani and Ohno.

△) contact potential difference method.[8]

o) photoelectron emission.[8]

$$2.303\ kT\cdot\log(I/T^2) = e^{3/2}\cdot V^{1/2}/(4\pi d\varepsilon_r)^{1/2} + C \qquad (4)$$

Fig. 4 takes the form of the Schottky plot of $2.303\ kT\cdot\log(I/T^2)$ against $V^{1/2}$. The linear plot in Fig. 4 suggests that the field and the temperature dependence of the high field conduction can be interpreted in terms of the field-assisted electron emission at the negative biased metal electrode. The thickness of the space-charge layer is estimated to be 0.015 mm by using Eq. (3). Another possible mechanism of the cathode emission is electron tunneling, viz., Fowler-Nordheim-type mechanism. Since the conductance at high field is strongly dependent on temperature, Fowler-Nordheim-type mechanism, however, is ruled out.

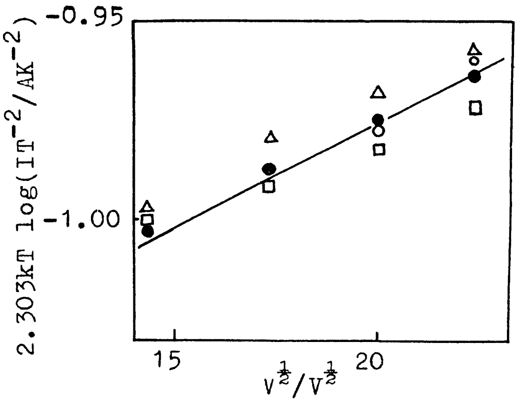

Fig. 4. The Schottky plot for off state. Electrode;Au.
Δ) 96 °C, ●) 121 °C, o) 82 °C, □) 71 °C.

"ON" state

The "ON" state was not observed at the low applied voltage such as 10 volts at 15 - 140 °C. However when the applied field is 100 volts, as shown in Fig. 5, the current rapidly increases at about 120 °C and is about 10^4 times that of the high impedance state ("OFF" state) at room temperature. The "ON" state could not be quenched at low temperature. The activation energy of the "ON" state conductance takes the lower value (0.3 eV) than that of the "OFF" state. Typical current-voltage characteristic of the "ON" state is formed under the high voltage, the conductance is extremely larger than that of the "OFF" state at low applied voltage and the current is approximately proportional to the square of the applied voltage. According to

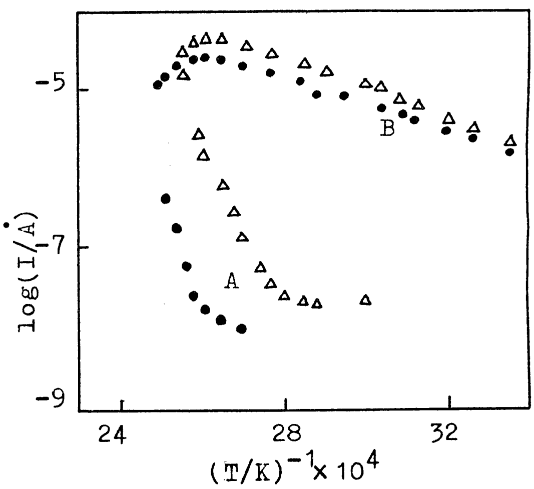

Fig. 5. The field- and thermal-induced switching characteristic. Electrode; Au. Applied voltage; 100V. A) off state, B) on state.
●) denotes the first run.
Δ) is obtained when the voltage is applied in a direction opposite to the first one.

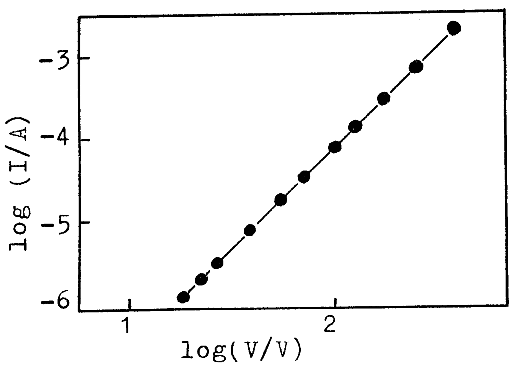

Fig. 6. The log I against log V relationship for the on state at 96 °C. Electrode;Au.

the theory developed by Mott and Gurney[6], the space-charge-limited current is expressed as Eq. (5).

$$I = 10^{-13}\ V^2 \mu \varepsilon_r / d'^3 \qquad (5)$$

where V is the applied voltage, μ is the drift mobility and d' is the thickness. By using Eq. (5), the drift mobility is estimated to be $2 \times 10^{-3}\ cm^2 \cdot V^{-1} \cdot sec^{-1}$.

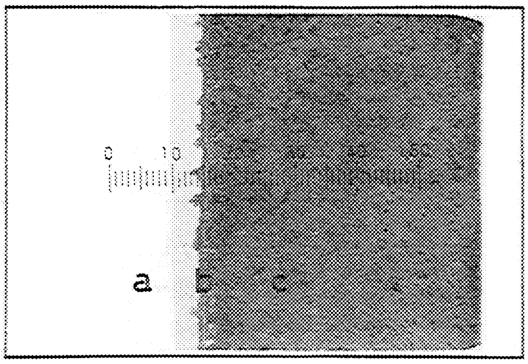

Fig. 7. The polarizing microscopic view of the film in the "ON" state.
a; negative biased electrode(Au),
b; transformed region of pyranthrone,
c; pyranthrone of the original form.
1 div. in photo equals to 0.001 mm.

Polarizing microscopic inspection

The fact that the current-voltage characteristic of the "ON" state is expressed as Eq. (5) indicates that the metal-pyranthrone contact was transformed to ohmic.[7] The polarizing microscopic inspection of the film showed that the transition from "OFF" state to "ON" state is occasionally accompanied by field- and thermal-assisted structual changes at the interface of the negative biased electrode (Fig. 7). Although Garrett et al.[1] reported that after the first transition to the "ON" state in pure naphthalene and anthracene films Ga-In alloy-filled craters were formed with depths that could exceed 80 % of the total film thickness, the depths of the structural changes do not exceed the thickness of the space-charge layer in the "OFF" state and the filament formation of a metallic nature was not observed.

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