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Threshold Switching in Anthracene Thin Films

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Threshold switching was observed in anthracene thin films (<3 μm) using a circuit with a high protective resistance. On the other hand, when the protective resistance was small, the switching was erratic and irreproducible. In the latter case, the switching was occasionally accompanied by filamentary damages caused by the excess current focused at the electrically weak spots, and the threshold voltage was poorly dependent on the protective resistance. The threshold-switching characteristics for thin films are interpretable in terms of the transition from the trap-limited SCLC to the trap-filled SCLC. The thermal breakdown model is not adaptable.

In general, switching phenomena may be classified into two categories: memory and threshold switching. The threshold switching has no memory effect, and a *turn-off* can be achieved below the critical voltage, called the holding voltage. This type of switching has been observed in several organic thin films.[1,2] On the other hand, many authors[3—5] have reported memory-switching characteristics which arise from the formation of a metallic filament or a carbonized conducting channel. However, our understanding is still incomplete.

The purpose of this study is to report that a non-destructive switching in anthracence can be observed by means of circuit with an appropriate protective resistor and to discuss the mechanism of the switching.

Experimental

Pure anthracene was prepared by a method similar to that described by Nakada[6] and was then further purified by zone melting. The geometry of the cell was of the sandwich type, where anthracene was deposited on a glass substrate with an evaporated silver electrode through an etched stainless steel mask. The temperature of the substrate was controlled in the range from −70 to −50 °C.

The film thickness of anthracene was varied in the range of 5×10^{-6}—1.0×10^{-3} cm. The thickness was measured with the aid of an interferometer when the films were thin, while for the thicker films an ac bridge was used. Silver was deposited as the upper electrode by vacuum evaporation through the mask. The area of the electrode was *ca.* 0.01 cm^2.

The *I-V* characteristics were observed by means of the circuit described in a previous paper.[7] The protective resistor in the circuit can be varied in the range of 10^3—10^8 Ω in order to control the current which flows in the sample.

The states of the sample before and after the switching were observed using a scanning-electron microscope and an optical microscope.

Results and Discussion

Initially the anthracene film has a very high resistance, but when a certain value of voltage (threshold voltage, V_{th}) is applied, the current increases drastically; simultaneously, the voltage applied to the sample descreases and a new high conductivity state is formed. Figure 1 shows the relationship between the protective resistance, R_p, and the resistance, R_A, at the high conductivity state formed by applying the threshold voltage. It may be observed that the value of R_A increases with the protective resistance; consequently, non-linear current-voltage characteristics can be predicted in the high

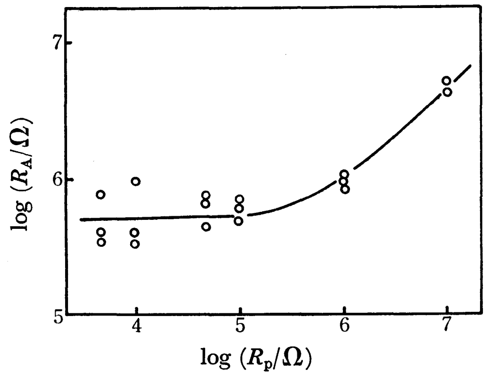

Fig. 1. Relationship between R_p and R_A.

conductivity state.

More than 500 thin films were used for the current-voltage-characteristic measurements. When N_s and N represent respectively the total number of cells used in the measurements for a given protective resistor and the number of the cells with which the threshold switching without any structural changes were observed, the ratio of N/N_s increases with the value of the protective resistor, while the value of V_{th} is poorly dependent on the value of the protective resistor. Erratic and irreproducible switching characteristics, accompanied by structural changes, were occasionally observed. In these cases a stable high conductivity state with a memory effect was observed. The results of a scanning-electron-microscopic inspection of the cell after the erratic memory switching are shown in Fig. 2. The transformed area may be formed by the localized excessive current flow at the weak spots in the film.

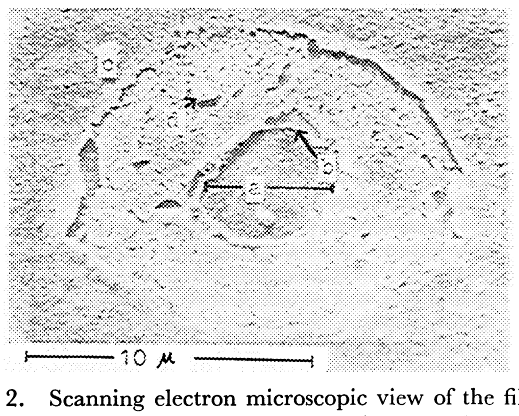

Fig. 2. Scanning electron microscopic view of the film. a) Center void, b) lower electrode, c) upper electrode, d) anthracene.

The current-voltage relation in single crystals of anthracene, expressed as $I\propto V^n$, where $n>2$ in the high-field region, has been explained on the assumption that current carriers are trapped by the local states exponentially distributed within an energy region; the reduction of the value of n with the density of the trapping centers has previously been reported by Thomas *et al.*[8] On the other hand, Williams *et al.*[9] interpreted the precipitous transition from the ohmic region to the cubic region for the carbon fiber diode in terms of the trap-filled-limit.

Since, in this work, it is confirmed that the current obeys the scaling law in the preswitching state (Figs. 3 and 4), the current-voltage relation obtained in the high-field region may be expressed as:

$$J_{\mathrm{off}} \propto \frac{V^{l+1}}{d^{2l+1}}\exp(-\phi/kT), \tag{1}$$

where J_{off} is the current density in the preswitching state; d the film thickness: ϕ, the activation energy; k, the Boltzmann constant, T, the temperature, and l, the constant. The averaged value of l was, from the results shown in Figs. 3 and 4, estimated to be 1. This behavior can be interpreted in terms of the space-charge-limited current in an insulator with a single type of traps.

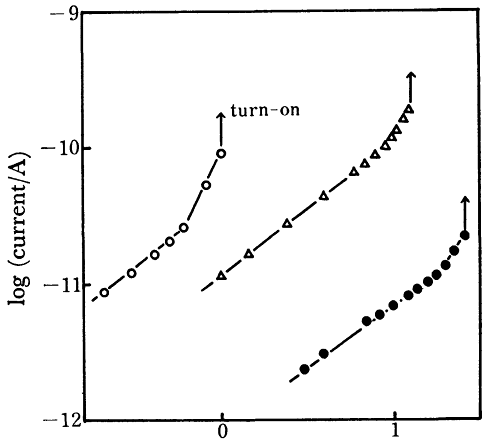

Fig. 3. Current-voltage characteristics in the *off state* for three different thickness.
○) 0.34 μm, △) 0.64 μm, ●) 0.99 μm.

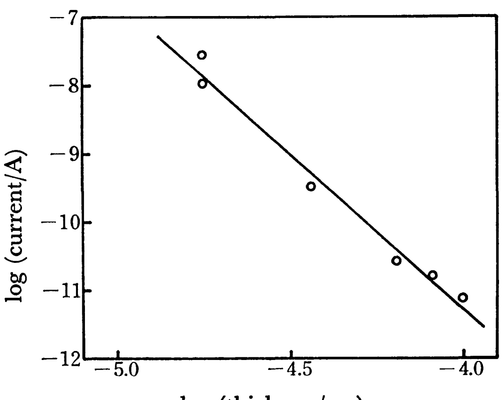

Fig. 4. Relation between the current and the film thickness in the *off state*.

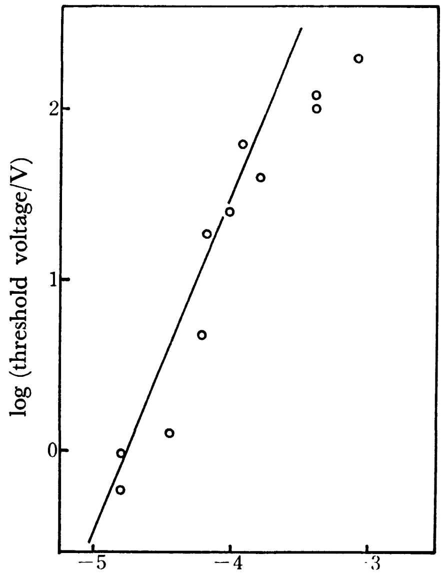

Fig. 5. Relation between the threshold voltage and the film thickness.
Solid line; $V_{\mathrm{th}}\propto d^2$.

It is well known that the causes of switching and/or breakdown proposed by many authors can be classified into two categories; (1) the thermal effect and (2) the electronic effect. In order to determine which of these effects is the cause of the switching in the case of anthracene, the relation between the threshold voltage, V_{th}, and the film thickness, d, was observed. The results are plotted in Fig. 5. This figure shows that V_{th} is proportional to d^2.

In the thermal-breakdown model, the temperature of the film may be expected to be uniform for a thin film, so the switching conditions can be determined by the use of Eqs. 2, 3 and 4. These equations are induced by assuming that the thermal breakdown occurs when the temperature derivative of the power input exceeds that of the heat loss:[10]

$$J\cdot V = \lambda(T-T_0), \tag{2}$$

$$\partial(J\cdot V)/\partial T = \lambda, \tag{3}$$

$$J_c\cdot V_c = \lambda(T_c-T_0), \tag{4}$$

where λ is a constant external thermal conductivity; T_0, the ambient temperature; J_c, the current density at the critical temperature (T_0), and V_c, the breakdown voltage. The substitution of the current density in Eq. 1 into Eqs. 2, 3, 4 and subsequent rearrangement give:

$$V_c^{l+2}\propto d^{2l+1}. \tag{5}$$

However, the experimental results shown in Fig. 5 do not agree with this equation, unless $l=\infty$. Therefore, the possibility of the thermal breakdown was excluded.

On the other hand, the space-charge-limited-current (SCLC) in the preswitching state has been taken into consideration in some electronic models.[11,12] In these models, the *turn-on* can be achieved when the space-charge density in the film reaches a critical value. In this case, the relationship between the threshold voltage and the film thickness is given by:

$$V_{th} \propto d^2. \tag{6}$$

The experimental results agree well with this expected relation deduced from the electronic model. Furthermore, the trap density, N_t, was estimated to be 10^{15}—$10^{16}\ \mathrm{cm}^{-3}$ by assuming that the *turn-on* condition is equivalent to the transition condition from the trap limited space-charge-limited current (SCLC) to the trap-filled SCLC. In this case, V_{th} is expressed as:

$$V_{th} = ed^2N_t/2\varepsilon\varepsilon_0. \tag{7}$$

The trap density thus obtained is comparable to the value, $(3-7)\times 10^{13}\ \mathrm{cm}^{-3}$, obtained by Garrett *et al.*,[13] and to that $10^{13}-10^{19}\ \mathrm{cm}^{-3}$, obtained by Thomas *et al.*[8]

On other hand, a typical current-voltage relationship in the high-conductivity state is shown in Fig. 6. The square law holds in the high-field region, while in the low-field region the current is lower than the value estimated by extrapolation from the high-field region on the assumptions that the current obeys the square law and that this deviation from the square law increases with a decrease in the applied voltage. The *turn-off* can be achieved when the applied voltage decreases below *ca.* 1 volt. In the square law region, it was found that the current is proportional to d^{-3}. Therefore, the current density, J_{on}, in the high-conductivity state is expressed by the scaling law, l being 1:

$$J_{on} = \alpha \cdot V^2/d^3, \tag{8}$$

where α is a constant. It was confirmed by the analysis* of an equivalent circuit that the observed R_A is proportional to $R_p^{1/2}$ when a high protective resistance is used in the measurement circuit, whereas R_A is poorly dependent on R_p when a low protective resistance is used. These analytical results are in good agreement with the observed data plotted in Fig. 2.

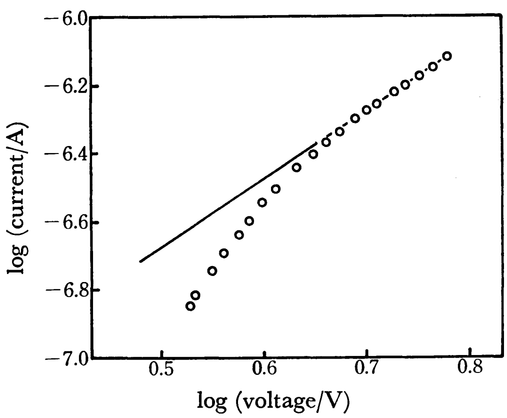

Fig. 6. Current-voltage characteristic in the *on state* solid line; $I \propto V^2$.

* Since the resistance in the preswitching state is much larger than that of the protective resistance, V_{th} is approximately equal to the total applied voltage. When the *turn-on* occurs, the voltage applied to the cell is equal to $V_{th}\cdot R_A/(R_A+R_P)$.

From the results thus obtained, it may be concluded that the threshold switching observed in thinner films is based on the transition from the trap-limited SCLC to the trap-filled SCLC, without any structural changes.

For thicker films (>3 μm), no reproducible threshold switching was observed. In these films, an instantaneous increase of current was observed when measurements were carried out using a circuit with a high protective resistor ($10^8\ \Omega$). On the other hand, a high-conductivity state with a memory effect was observed when a lower protective resistor was used. In this case, the relationship between V_{th} and the thickness is expressed as $V_{th}\propto d^n$, $0.5<n<1$; this relation can be introduced by the thermal-breakdown model (Eq. 5), while the current-voltage characteristics in the prebreakdown region are expressed as $I\propto V^m$, ranging in value of m from 1 to 2 for these thicker samples.

It is well known[14,15] that the thickness dependence of V_{th} for the thick films is different from that for the thin films and that the thermal breakdown occurs in thicker films, while in thinner films the switching caused by the electronic mechanism is predominant, especially for amorphous semiconductors. The results for thicker anthracene films reported in this paper are consistent with those obtained by Garrett *et al.*[13]

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