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Effect of the Trap Density on Switching in Naphthacene Thin Films

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Switching phenomena were observed in Au(+)–naphthacene (crystalline-state)–Al(−). The threshold voltage was found to be expressable as $V_{\text{th}} \propto (\text{thickness})^2$; in amorphous films no reproducible switching phenomena were observed within the same region of the field strength. The differences between them were discussed in terms of the trap density, which is closely related to the crystallinity of the evaporated films.

Szymanski *et al.*1) reported bistable switching in naphthacene thin films with Au and Al electrodes, but the conditions required were not reproducible, while reproducible switching in aromatic hydrocarbon films was observed by Kevorkian *et al.*2) when a mobile electrode material was used. Although some authors have proposed the *turn-on* to be due to either metallic filament formation, or the formation of carbonized materials,3) Kasica *et al.*4) have proposed that the reproducibility of the switching curves is strongly affected by the surrounding conditions and that the switching is interpretable in terms of the double injection mechanism.

This paper deals with the influence of the trap density on the bulk-limited switching characteristics in naphthacene films, because the state of the naphthacene film can be easily controlled by varying the substrate temperature during the evaporation and the bulk-type high field conduction is expected in Au–naphthacene–Al cell. Also, since the heat of sublimation is larger and the melting point of this material is much higher than that of anthracene, the reproducibility of switching should be much better in naphthacene than in anthracene.

Experimental

The geometry of the cell was of the sandwich type, where naphthacene was deposited over a glass substrate on which thirty strips of gold electrodes of 1 mm in width and 1 mm in separation had been evaporated through an etched stainless steel mask. The upper electrodes(Al) were deposited by the same method. The temperature of the substrate was controlled in the range of −120 to 110 °C. The film thickness of naphthacene was measured with the aid of an interferometer. D.c. conductivities and/or switching curves were measured by means of the circuit described in the previous paper.5) The load(protective) resistor in the circuit can be varied in the range of 10^3—10^8 Ω to control the current which flows in the high conductivity state. All the electrical measurements were carried out in vacuum.

The state of the films was examined using a scanning electron microscope and a polarizing microscope. Polycrystalline structure was observed for the film prepared by the deposition onto the glass substrate kept at a high temperature (≈100 °C). However, an amorphous film was obtained when the glass substrate was kept at a low temperature(≤−100 °C) during evaporation. The scanning electron microscopic views of the films are shown in Fig.1. In addition, the absorption spectra of the film deposited on the quartz substrate also indicated that a crystalline state was obtained when a substrate was held at a high temperature and an amorphous state when a substrate was held at a low temperature(≤−100 °C) at the time of evaporation. These results are consistent with that reported by Maruyama and Iwasaki.6) In some cases the substrates were kept at room temperature during evaporation. These films were found to be partly crystallized.

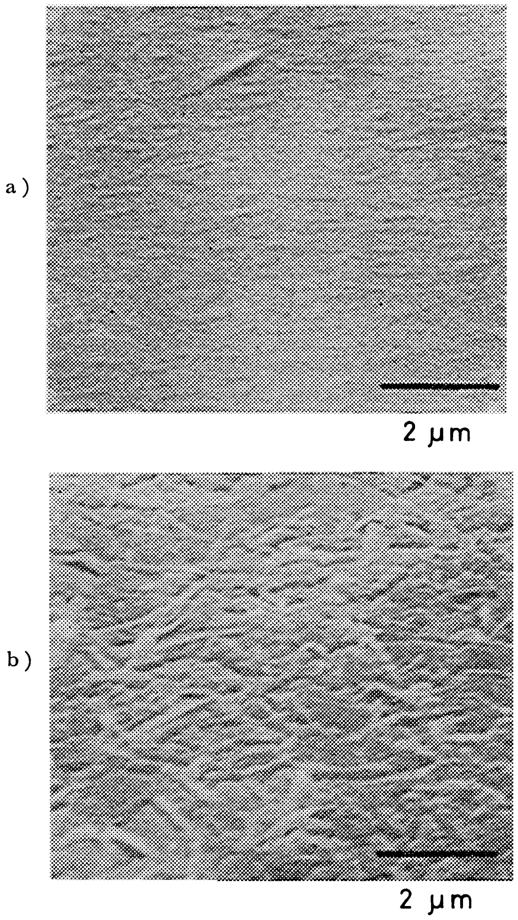

Fig. 1. Scanning electron microscope pictures of film.
a) Low-temperature-evaporated amorphous films,
b) high-temperature-evaporated crystalline film.

Results and Discussion

A typical current-voltage characteristic in the low-conductivity state is shown in Fig. 2 for an Au–naphthacene–Al cell. This curve is typical for a rectifying contact, *i.e.*, the current increases non-linearly with applied voltage. Similar asymmetry in its characteristic has been reported by Ghosh and Feng.7) Under the forward-bias condition, the V^n dependence of current on voltage due to an exponential trap distribution was found for all samples prepared in various conditions. Rectification ratios as high as 10^4 was observed in the high-field region.

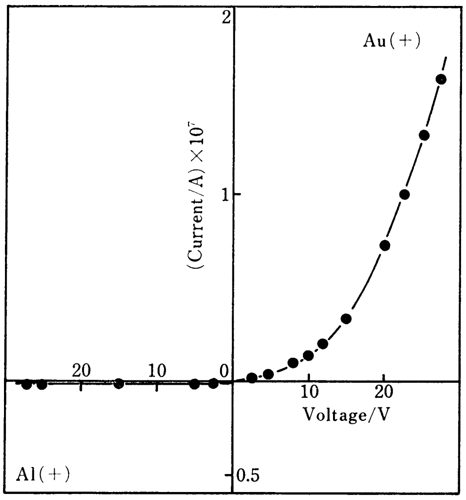

Fig. 2. A typical *I-V* characteristic in the Au–naphthacene–Al cell.

More than 600 films were used for the electrical measurements under the forward-bias conditions in order to clarify the influence of the trap-density on the threshold voltage for the bulk type switching phenomena. Although no switching phenomena were observed in the low-temperature-evaporated films, the switching without any structural changes were observed in the high-temperature-evaporated crystalline-state films in most of the samples. The observed switching characteristics are shown in Fig. 3. When the applied voltage exceeded a critical value (V_{th}) which is poorly dependent on the value of the load resistor R_L, the current abruptly increased, and simultaneously the field dropped (negative resistance region), so that a new high-conductivity state was formed. Since the conductance of this new state is strongly influenced by the value of the load resistor and this dependence on the load resistor cannot be explained by the usual non-linear-conduction mechanisms, this state should be formed in a filamentary way *i.e.* the effective area of this state increases upon decreasing the value of the load resistor.

In addition, the holding voltage (*turn-off* voltage) was observed in the switching characteristics when the load resister R_L was $10^8\,\Omega$, while the memory effect was observed when R_L was $10^5\,\Omega$. After the applied voltage had been taken off, the state with its memory effect quenched off in *ca.* 3 h or more and the initial low-conductivity state was recovered. Such a high-conductivity state with a memory effect may be related to the density of deep trapping levels, and not be caused by any structural changes.

In the low-conductivity state for the crystalline films the current increased rapidly in proportion to V^n with $n \approx 4$. This characteristic is interpretable in terms of the space-charge-limited current (SCLC). According to Mark and Helfrich[8] the SCLC for exponential distribution of traps with energy should follow the equation

$$J = N_0 \mu e^{1-l}\left\{\frac{\varepsilon\varepsilon_0 l}{H(l+1)}\right\}^l \left(\frac{2l+1}{l+1}\right)^{l+1} \frac{V^{l+1}}{d^{2l+1}}, \tag{1}$$

where N_0 is the effective density of states in the valence band, μ is the hole mobility, ε is the dielectric constant, ε_0 is the vacuum permittivity, e is the electron charge, H is the total hole trap density, d is the film thickness, and $l = T_c/T$. The parameter T_c characterizes the trap distribution. Furthermore, one can obtain an expression for the position dependence of the quasi-Fermi level for holes. It is

$$E_F = kT_c \ln\left[\frac{(l+1)^2}{l(2l+1)} \frac{eHd^2}{\varepsilon\varepsilon_0 V}\left(\frac{x}{d}\right)^{1/l+1}\right], \tag{2}$$

where x is the distance from the injecting electrode (anode). The measurement of the temperature dependence of SCLC yields the value of $E_F(x=d)$, while the density of free carriers, which is proportional to the current, is given by the relation $n \propto \exp(-E_F/kT)$. In Fig. 4, the relation between the activation energy and the value of $\log(d^2/V)$ is shown. From the results in Fig. 4 the total hole trap density was estimated to be 1—2×10^{16} cm^{-3} for thicker films(line I) and 1—$2\times$

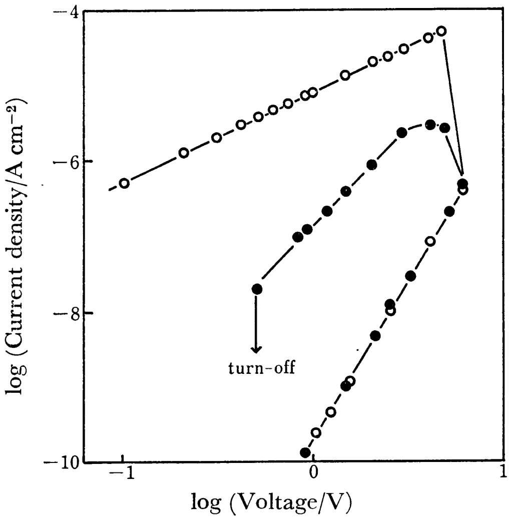

Fig. 3. Current-Voltage characteristic in switching. (○) with $R_L(10^5\,\Omega)$, (●) with $R_L(10^8\,\Omega)$, film thickness: 3.5×10^{-5} cm.

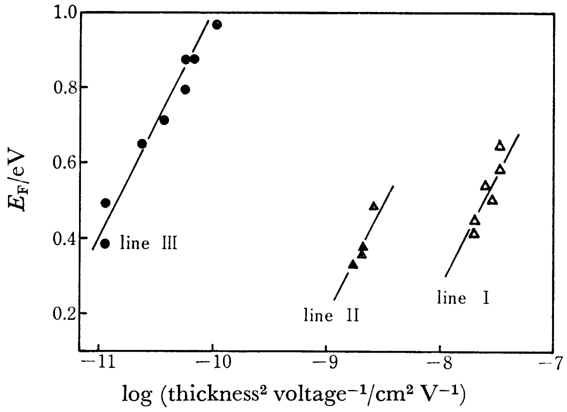

Fig. 4. Plot of E_F against log (d^2/V) relationship.
(●) Low-temperature-evaporated amorphous film,
(▲) high-temperature-evaporated crystalline film, film thickness: 5.0×10^{-5} cm,
(△) high-temperature-evaporated crystalline film, film thickness: 1.0×10^{-4} cm.

10^{17} cm^{-3} for thinner films(line II), respectively, by substituting $\varepsilon=3.8$ and, $x=d$. The values of l obtained from the slope of the lines in Fig. 4 are consistent with those obtained from the current-voltage curves. The values of H for the crystalline films are reasonable ones, although they are somewhat higher than that for single crystals grown by sublimation in nitrogen ($H=3\times10^{15}$ cm^{-3}).[9] The fact that the value of H for a thinner film is somewhat larger than that for a thicker film suggests that the traps caused by residual gas molecules and/or defects are located in the surface regions close to the electrode. In addition, in the case of the amorphous films prepared by low-temperature deposition, similar current-voltage characteristics ($l\approx8$) caused by SCLC for an exponential distribution of traps with energy was obtained and a linear relation (line III) between E_F and $\log(d^2/V)$ was also found. The total hole trap density was estimated to be 4×10^{18} cm^{-3}. Since it is well known that lowering the substrate temperature increases structural disorder, the structural irregularity must be the cause of such trapping-levels rather than the chemical impurities because the low- and high-temperature-evaporated films were deposited from the same evaporation source.

On the other hand, the measurement of the thickness dependence of the threshold voltage(V_{th}) was carried out for the high-temperature-evaporated crystalline films in order to determine whether the *turn-on* is based on the thermal effect or the electronic effect, since such a measurement is a very powerful method[10] to distinguish one from the other. As shown in Fig. 5, the threshold voltage is proportional to the square of the thickness (line I), though other line II different from line I was obtained from the films thinner than *ca.* 3×10^{-5} cm. This relation indicates that the *turn-on* is caused by an electronic mechanism such as the space charge overlap model[11] or the one carrier SCLC model[12] in which the concentration of the injected carriers is sufficient to exceed the critical concentration (N_{th}). And this interpretation is confirmed by the fact that the *turn-on* does not occur in the amorphous films at the conditions under which the *turn-on* occurs in the crystalline films. In the space charge overlap model, it is expected that the current-voltage characteristic in the *pre*-switching state is caused by the double injection and the *turn-on* is achieved by the formation of the space charge overlap region. However, in the one carrier SCLC model the *turn-on* may be expected when the space charge density caused by injected holes in the *pre*-switching state reaches a critical value and the injection of electrons begins.[4,12] Since in the *pre*-switching state the current-voltage curve in Au(+)–naphthacene–Al(−) is similar to that in Au–naphthacene–Au, the electric conduction in the *pre*-switching state is most likely due to one carrier SCLC with traps. This current in the high resistivity state may entirely consist of the holes injected from the Au electrode into naphthacene, as was suggested by Ghosh and Feng.[7] Consequently, the *turn-on* is interpretable in terms of the one carrier SCLC model rather than the space charge overlap model based on the double injection in the *pre*-switching state.

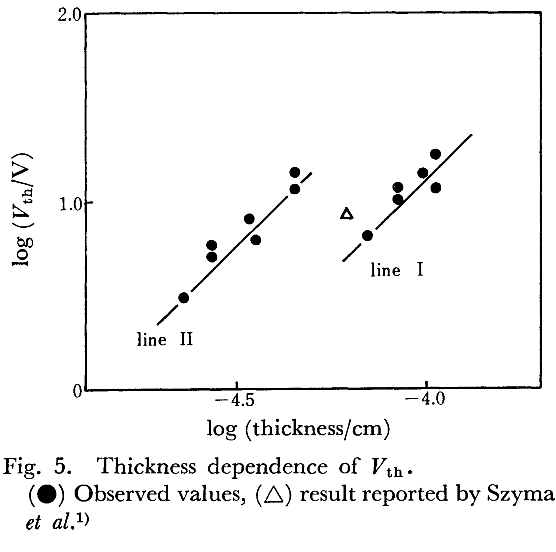

Fig. 5. Thickness dependence of V_{th}.
(●) Observed values, (△) result reported by Szymanski *et al.*[1]

If Q_{th} represents the space charge density formed by the injected holes, the potential distribution in the bulk can be expressed as Eq. 3:

$$V(x)=\frac{Q_{th}}{2\varepsilon\varepsilon_0}x^2. \tag{3}$$

Consequently, the threshold voltage may be introduced as Eq. 4 by substituting $x=d$:

$$V_{th}=\frac{Q_{th}\cdot d^2}{2\varepsilon\varepsilon_0}. \tag{4}$$

The corresponding values of N_{th} and Q_{th} were estimated to be 6×10^{15} cm^{-3} and 9.7×10^{-4} C/cm^{-3} for line I and 2×10^{16} cm^{-3} and 3×10^{-3} C/cm^{-3} for line II, respectively. Since no switching phenomena were observed in the amorphous films and the values of N_{th} obtained by using Eq. 5 for the crystalline films are roughly in agreement with the values of total hole trap density, the *turn-on* can occur when the traps are filled by the injected holes and under such conditions the Al electrode will become an electron-injecting contact. In this case Eq. 4 can be replaced by Eq. 5:

$$V_{th}=\frac{eHd^2}{2\varepsilon\varepsilon_0}. \tag{5}$$

The same relation between the threshold voltage and the trap density was reported in the previous works for poly(N-vinylcarbazole)[5] and anthracene.[13]

From the results thus obtained it is concluded that the lack of switching phenomena for the amorphous film is caused by the fact that the number of the trap density is much larger than that in the crystalline films; in these circumstances, the thermal breakdown caused by Joule-heating may occur before the trap-filled state is achieved, since the threshold voltage for the amorphous film of 5×10^{-5} cm in thickness is estimated to be *ca.* 2×10^3 V and the value of l is much larger than that for the crystalline films ($l=4$).

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