Switching in Copper-Phthalocyanine Films

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Bistable switching between two impedance states was observed in copper-phthalocyanine films. The *turn-on* can be interpreted in terms of the steady thermal breakdown model. The stable high conductivity in the *on-state* is attributed to the partly carbonized copper-phthalocyanine which was formed by Joule heating along the filamentary paths. The *J-V* characteristic in the *off-state* and the threshold-field strength were found to be expressed as $J \propto V^6/d^{3.8}$ and $E_{th} \propto 1/d^{0.46}$ respectively.

The memory- and threshold-switching phenomena have recently received considerable attention as a practical application of organic semiconductors.[1,2] Although similar phenomena have been reported in thin films of inorganic semiconductors,[3-5] our understanding of switching is still incomplete, particularly in organic semiconductors.

In the present work the preswitching conduction and the memory-switching characteristics have been investigated in thin films of α-copper-phthalocyanine (CuPc).

Experimental

Pure copper-phthalocyanine was prepared by repeated sublimations *in vacuo* at 380 °C, followed by washing with acetone to remove any thermal decomposition products.

The geometry of the cell was of a sandwich type, where copper-phthalocyanine was deposited from a Pyrex crucible on a cleaned glass substrate with a silver electrode which had been evaporated through an etched stainless steel mask. The upper electrodes (Al) were deposited by vacuum evaporation through the mask. The vacuum evaporation was performed at pressures below 10^{-6} Torr. The film of CuPc was confirmed to be α-type crystalline by the methods described in a preceding paper.[6]

The film thickness of the copper-phthalocyanine, as measured with the aid of an interferometer, varied over the range of 10^{-6}—10^{-4} cm. The current-voltage characteristics were obtained by applying step voltages using a high-voltage dc power supply (John-Fluke, model 412 B), an electrometer, and a picoammeter (Takeda Riken, models TR8651 and TR8641 respectively). A series resistor ($10^6\Omega$) was used to limit the current flow in the circuit. The measurements were performed at a pressure of *ca.* 10^{-3} Torr.

The states of the film before and after the switching were observed using a scanning electron microscope (Hitachi and Akashi, model MSM-4).

Results and Discussion

In the Al–CuPc–Ag cell, the current with the forward-bias voltage (Ag(+), Al(−)) was much higher than that with the backward-bias voltage in the high-field region (Fig. 1). Its marked asymmetry can be explained by a pin-structure at the CuPc–Al junction, a detailed discussion of which has been given by Tantzscher and Hamann.[7] In the present paper the results with the backward-bias voltages will not be discussed.

Initially the film has a very high resistance (*off-state*), and the non-linear current-voltage characteristic is observed, as is shown in Fig. 1, as long as the applied voltage is lower than a certain value (threshold voltage; V_{th}). When the applied voltage exceeds V_{th}, the current abruptly increases, and simultaneously the field drops, so that a new low-resistance state (*on-state*) with a memory effect appears. This new state can be easily quenched by applying a short current pulse (pulse width, 10 μs, maximum voltage, 180 V) from a capacitor of 0.047 μF. The scanning electron microscopic inspection of the film in the *on-state* shows that this state is accompanied by the formation of conducting channels (Fig. 2). The upper electrode (Al) was partly molten (A), and the region of CuPc (B) transformed by the localized Joule heating was confirmed in this figure, so

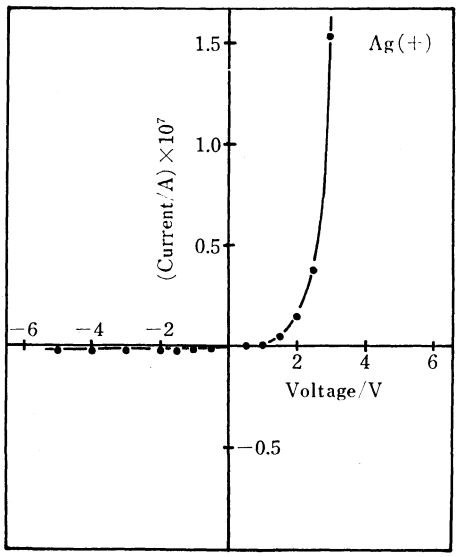

Fig. 1. A typical *V-I* characteristic in the Ag-CuPc-Al cell. Film thickness 1.7×10^{-5} cm.

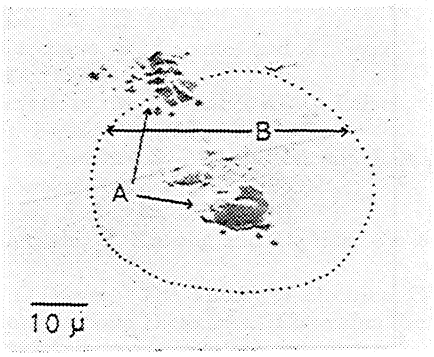

Fig. 2. Scanning electron microscope picture of damaged region. A) Partly molten electrode (Al), B) transformed region.

that it may be presumed that a temperature higher than 660 °C (the melting point of aluminium) has been temporarily attained in this region.

Souma[8] has reported that, when CuPc was heated at 625 °C, the carbonization and/or the condensation occurred and the conductivity increased rapidly. It has also been reported that poly-CuPc has a conductivity about 10^6 times larger than that of the monomer, and the activation energy (E) in $\sigma=\sigma_0 \exp(-E/kT)$ was estimated to be 0.06 eV[9] in a sample previously heated to 450 °C. In the present work, the activation energy in the high-conductivity state was estimated to be 0.05 eV from the temperature dependence of the current obtained in the range of 15—70 °C. Since this value is in fair agreement with the value for poly-CuPc, the conducting channels may be made up of the poly-CuPc.

Although many authors[10-12] have reported that the stable *on-state* in some organic compounds arises from the formation of metallic filaments or carbonized paths, the exact mechanism for the formation of such filaments is not clear.

The various models proposed to explain the memory-switching process for chalcogenide glass, *etc.* can be classified into two categories: (1) the electronic effect and (2) the thermal effect. In the former case, the *on-state* without a memory effect is formed first, and the *lock-on* occurs after a certain time by the excessive current flow in this state, while in the latter case, the switching occurs by means of the local Joule heating in the *off-state.*

The measurement of the thickness dependence of the threshold-field strength, E_{th}, which equals V_{th}/d, is a very powerful method of distinguishing between the thermal effect and the electronic effect.[13] If the switching is caused by the electronic mechanism, as explained by the space-charge-overlap model[14] or the one-carrier space-charge limited-current (SCLC) model,[15] in which the concentrations of the injected carriers are sufficient to exceed the critical concentration, the threshold-field strength can be expressed as $E_{th} \propto$ (thickness). Since Fig. 3 shows that E_{th} is not proportional to the thickness, the electronic model can be excluded.

On the other hand, according to the steady-state thermal-breakdown model,[16] the *turn-on* occurs when the temperature derivative of the power input exceeds that of heat loss. Below the critical point, Eq. 1 holds:

$$J \cdot V = \lambda(T - T_0), \tag{1}$$

where J is the current density; V, the applied voltage; λ, a constant external thermal conductivity, and T_0, the ambient temperature. At the critical point where thermal breakdown commences, the following equations are given:

$$\partial(J_c \cdot V_c)/\partial T = \lambda, \tag{2}$$

$$J_c \cdot V_c = \lambda(T_c - T_0), \tag{3}$$

where J_c and V_c are the critical current density and the voltage for breakdown respectively, and where T_c is the critical temperature.

To resolve these relations, the voltage and the thickness dependence of the current density in the preswitching state were observed (Figs. 4 and 5). The results are experimentally expressed as $J \propto V^{6.0}$ and $J \propto 1/d^{3.8}$ respectively in the high-field region, while the relation

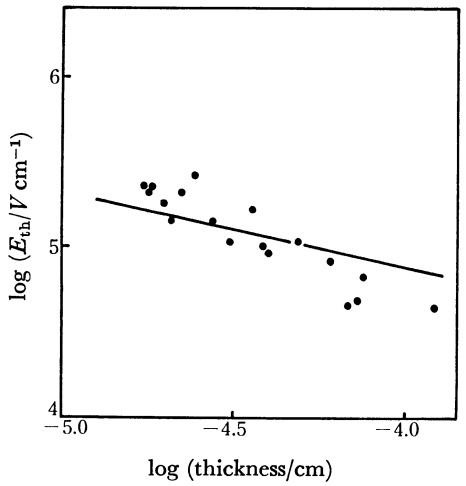

Fig. 3. The relation between log(E_{th}) and log(thickness).

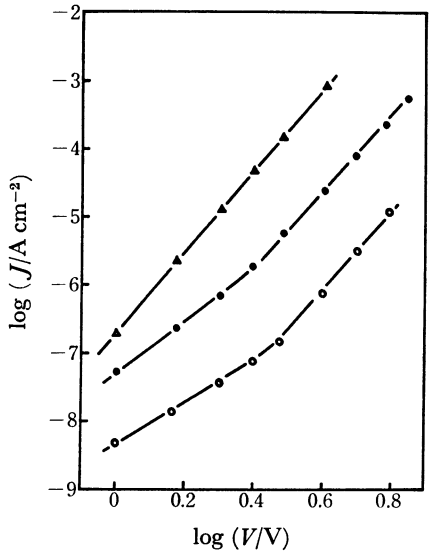

Fig. 4. The voltage dependence of the current.
△) 0.18 μm, ●) 0.48 μm, ○) 1.2 μm.

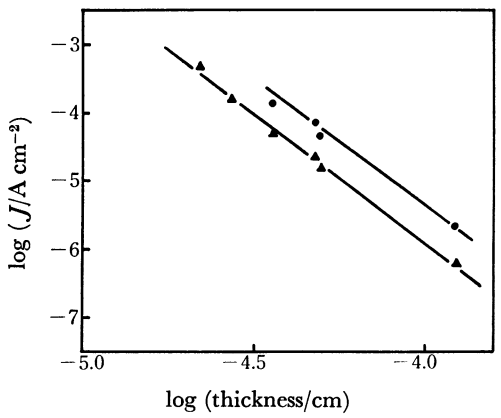

Fig. 5. The thickness dependence of the current.
▲) 4 V, ●) 5 V.

between the current density and the applied voltage expected from the scaling law[17] ($J \propto V^{l+1}/d^{2l+1}$) was confirmed in the low-field region for thicker films. Since the observed J-V characteristics were reversible with an increase and then a decrease in the voltage, the possibility of a thermal effect may be excluded. The high value of l in the high-field region may be attributed to the other conduction components, such as the emission limited current (ELC). A quantitative analysis of the J-V characteristics for ELC under the conditions of SCLC flow was reported by the Frank and Simmons.[18] According to this analysis, the transition from SCLC to ELC for the M–I–M junction can be expected to occur when a negative charge begins to appear on the cathode as well as inside the insulator, and the contact changes from an Ohmic to a blocking one with an increase in the voltage. As is shown in Fig. 6, the straight line in the plot of log J *vs.* $(V/d)^{1/2}$ indicates that the high-field conduction is predominantly governed by ELC in the preswitching state.

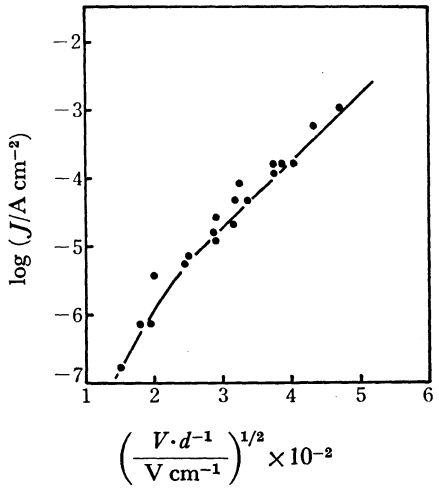

Fig. 6. The plots of log J *vs.* $(V/d)^{1/2}$.

If it is assumed that the I-V characteristic is expressed as Eq. 4* and that the *on-state* is formed filamentarily as is shown in Fig. 2, the critical current density in the area of the filamental paths is proportional to the current density geometrically obtained (J_G):

$$J_G = C \cdot \frac{V^{6.0}}{d^{3.8}} \exp(-\phi/kT), \tag{4}$$

$$J_c \propto J_G \tag{5}$$

where C is a constant; ϕ, the activation energy, and k, the Boltzmann constant.

The substitution of Eqs. 4 and 5 into Eqs. 1, 2, and 3 gives:

$$V_c^{7.0}/d^{3.8} \propto \frac{T_c^2}{\phi} \exp(\phi/kT_0) = \text{constant}. \tag{6}$$

Thus,

$$(V_c/d)^{7.0} = K \cdot d^{-3.2}, \tag{7}$$

where K is a constant.

* If the ELC relation ($J_G \propto \exp(V/d)^{1/2}$) is used, the relation between E_{th} and d is expressed as $\log E_{th} = -0.5 \log d + \text{constant}$ instead of by Eq. 8.

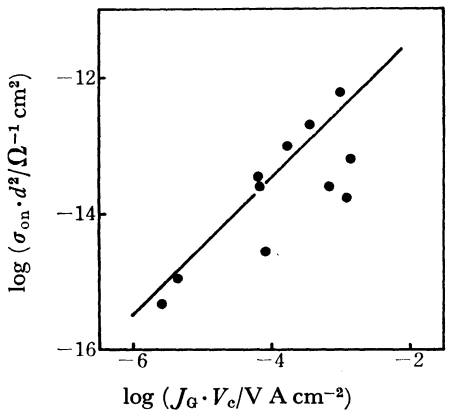

Fig. 7. The plots of $\log(\sigma_{on} \cdot d^2)$ *vs.* $\log(J_G \cdot V_c)$.

Since V_c/d is equal to E_{th}, Eq. 8 is obtained:

$$\log E_{th} = -0.46 \log d + \text{constant}. \tag{8}$$

The solid line in Fig. 3, drawn with a slope of −0.46, is in fair agreement with the experimental data. In addition, Fig. 7 shows that $\sigma_{on} \cdot d^2$ is proportional to $J_G \cdot V_c$, where σ_{on} is the conductance of the sample in the *on-state*. Since $\sigma_{on} \cdot d^2$ is proportional to the volume of the conducting paths and $J_G \cdot V_c$ is the heat evolved by the current, this result is also evidence in support of the thermal-breakdown mechanism.

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References

1) L. F. Pender and R. J. Fleming, *J. Appl. Phys.*, **46**, 3426 (1975).
2) H. Kasica, W. Wtodarski, H. Kurczewska, and A. Szymanski, *Thin Solid Films*, **30**, 325 (1975).
3) P. J. Walsh, R. Vogel, and E. J. Evans, *Phys. Rev.*, **178**, 1274 (1969).
4) S. R. Ovshinsky and H. Fritzsche, *IEEE Trans. Electr. Dev.*, **20**, 91 (1973).
5) A. C. Warren, *IEEE Trans. Electr. Dev.*, **20**, 123 (1973).
6) Y. Sakai, Y. Sadaoka, and H. Yokouchi, *Bull. Chem. Soc. Jpn.*, **47**, 1886 (1974).
7) C. Tantzscher and C. Hamann, *Phys. Status Solidi A*, **26**, 443 (1974).
8) I. Souma, *Nippon Kagaku Kaishi*, **1972**, 1059.
9) A. Epstein and B. S. Wildi, *J. Chem. Phys.*, **32**, 324 (1960).
10) J. Kucirka, D. C. Larson, and M. M. Labes, *Bull. Am. Phys. Soc.*, **18**, 132 (1973).
11) H. Carchano, R. Lacoste, and Y. Segui, *Appl. Phys. Lett.*, **19**, 414 (1971).
12) J. Kevorkian, M. M. Labes, D. C. Larson, and D. C. Wu, *Discuss. Faraday Soc.*, **51**, 139 (1971).
13) B. T. Kolomiets, E. A. Lebedev, and I. A. Taksami, *Soviet Phys.-Semiconductors*, **3**, 267 (1969).
14) H. Iida, *Bussei*, **15**, 295 (1974).
15) T. Shiraishi, T. Kurosu, and M. Iida, *Oyo Butsuri*, **46**, 36 (1977).
16) J. J. O'Dwyer, "The Theory of Electrical Conduction and Breakdown in Solid Dielectrics," Clarendon Press, Oxford (1973), p. 182.
17) P. Mark and W. Helfrich, *J. Appl. Phys.*, **33**, 205 (1962).
18) R. I. Frank and J. G. Simmons, *J. Appl. Phys.*, **38**, 832 (1967).