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Threshold Switching of Violanthrone in a Sandwich-type Cell

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Synopsis. Threshold switching between two impedance states has been observed at room temperature in a sandwich-type cell of violanthrone thin film with the use of silver electrodes. The conductivity of the "on state" is larger than that of the "off state" by a factor of 10^4.

Memory- and threshold-switching phenomena have recently received considerable attention. They were observed in many inorganic compounds,[1,2] memory-switching being observed in evaporated aromatic hydrocarbon thin films[3,4] and in electron-beam-deposited polymer films.[5] In a previous paper[6] we reported the memory switching in a surface-type cell of pyranthrone film.

In the present work threshold switching has been observed in evaporated thin violanthrone film sandwiched between silver electrodes.

Experimental

Violanthrone was purified by sublimation *in vacuo* (10^{-6} Torr). The geometry of the sample was of sandwich type, where violanthrone was deposited over a silver electrode prepared by vacuum evaporation onto the glass substrate through an etched stainless steel mask, the counter silver electrode being plated on top of the film. A schematic illustration of the sample is given in Fig. 1. The lead wires were placed on the electrodes by means of silver paste. The area of the electrode was *ca.* 0.01 cm^2 and the thickness of the violanthrone layer *ca.* 100 nm. Switching behaviour was observed with an AC generator and a synchroscope. Electrical measurements were carried out in the atmosphere.

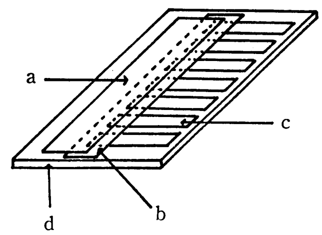

Fig. 1. Sandwich-type cell.
(a) silver electrode, (b) violanthrone film, (c) counter silver electrode, (d) microscope slide.

The microscopic distribution of the temperature on the surface of the sample during the course of switching was recorded with a Nikon 725 thermal plotter having an InSb infrared detector. The detectable spot size with this apparatus is 22 μm and the position of the view can be shifted with the aid of a mobile stage. The state of the film during switching was also observed with an optical microscope. Inspection under the polarizing microscope and the scanning electron microscope showed that the freshly prepared violanthrone films are essentially amorphous.

Results and Discussion

A typical current variation with the applied voltage of 60 Hz for the reversible threshold switching device of violanthrone of the sandwich type is shown in Fig. 2. The film has very low conductance ("off state") as long as the applied voltage is lower than a certain value, so that the current-voltage curve can not be observed in this region. When the voltage exceeded the threshold value, the conductance abruptly increased to the order of 10^{-5} ohm^{-1} and the curve (a) in Fig. 2 appeared. This state is called "on state". The threshold voltage for this device was estimated to be *ca.* 10 V.

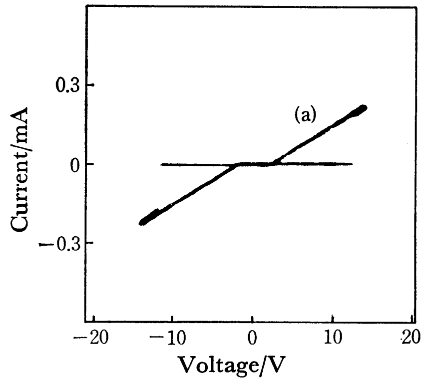

Fig. 2. Response of switching device to 60 Hz voltage.

In general, switching has been interpreted in terms of either a purely electronic effect or a thermal effect. The thermal effect interpretation is based on the premise that the highly localized Joule-heating is occasionally accompanied by structural changes such as crystallization. However, in the present case no difference in temperature was observed on the sample between the switching state and the non-switching state with the aid of a thermal plotter. Inspection of the film under the optical microscope showed no changes after the stable switching had occurred. In some cases unstable switching curves were obtained. In such cases the structural changes were observed during the switching. Observation with the thermal plotter revealed that an electrothermal breakdown had occurred. Thus the electronic effect is distinguishable from the electrothermal effect.

In order to elucidate the switching mechanism, it is desirable to investigate the effect of the film thickness on the switching. However, since it was difficult to prepare a thick and uniform film, surface type cells with various electrode distances were prepared. The minimum distance was 4×10^{-3} cm. In the surface type cell having an electrode distance of 4×10^{-3} cm or more, the high field conduction in the high resistance state was found to agree with the Richardson-Schottky equation,[7] $\sigma = \sigma_0 \exp(\beta_s V^{1/2}/d^{1/2}kT)$. This indicates the existence of the potential barrier at the violanthrone-electrode contact. The thickness of the space-charge-layer was estimated to be 10^{-3} cm.

No reversible threshold switching* occurred in the surface type cell of violanthrone having an electrode distance larger than the thickness of the space-charge-layer and an inspection of the film under the optical microscope showed no change after the threshold switching had occurred in the sandwich type cell of violanthrone. Therefore the threshold switching in the sandwich type cell having an electrode distance smaller than the thickness of the space-charge-layer may be interpreted in terms of the electronic effect such as space-charge-overlap.

* Although the transformation from the "off state" to the "on state" accompanied by structural changes at both interfaces of violanthrone-metal contacts was observed in the surface type cell, the "on state" could not be quenched by lowering the applied voltage in contrast to the case of pyranthrone.[6]

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