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Thermally Stimulated Current in Perylene Crystals

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Synopsis. A single current peak characteristic of thermally detrapped holes was observed at 220 K, the depth of the traps being determined to be 0.50±0.02 eV. This value showed no apparent correlation with the activation energy for photoconduction, 0.18±0.01 eV.

In many high-resistivity semiconductors, localized states in the forbidden energy gap play a dominant role in the mechanism of transport of charge carriers. Perylene crystals show a photocurrent under illumination of light in the visible and ultraviolet spectral regions.[1] A photocurrent signal induced by a light pulse, however, shows a diffused shape with a long tail of decay, indicating the presence of charge carrier traps. The low mobility of charge carriers in perylene crystals has been attributed to the trapping of carriers in an excess-electron-dimeric state.[2] In this note we would like to report a trap level of perylene crystals studied by means of thermally stimulated currents.

Single crystal platelets of chromatographically purified perylene, thickness *ca.* 100 μ, were obtained by sublimation. A crystal platelet, *ca.* 8×5 mm^2, was sandwiched between two electrodes, one with semitransparent gold coating and the other lead foil covered with a 6 μ Mylar film. The crystal was mounted on the top of a copper block which could be cooled by a stream of cold nitrogen gas. The whole assembly surrounded by an electric heater was accommodated in a glass chamber (Fig. 1).

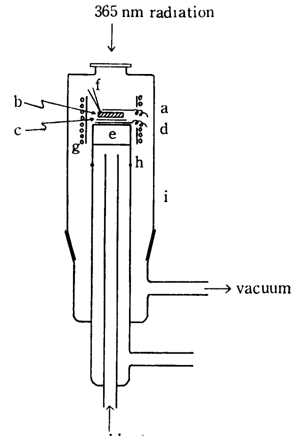

Fig. 1. Experimental arrangement.
(a) gold film electrode, (b) crystal, (c) Mylar film, (d) lead foil electrode, (e) copper block, (f) thermocouple, (g) electric heater, (h) Kovar seal, (i) glass chamber.

The gold electrode was connected to the positive side of a 90 V battery. The crystal was cooled to about 170 K and then illuminated through the electrode with 365 nm mercury radiation. After illumination for ten minutes, the polarity of the applied voltage was reversed, and thermally stimulated currents at a predetermined uniform heating rate were subsequently measured in the dark. The heating rate was controlled with an electric heater, an appropriate amount of helium gas being introduced into the chamber. The current through a 10^{10} ohm input resistor was recorded by a Takedariken vibrating reed electrometer, the temperature of the crystal being recorded simultaneously with a copper-constantan thermocouple junction pasted to the crystal surface with silicone rubber.

In the range 170—245 K, a single current peak characteristic of thermally detrapped holes was observed, indicating that there is one kind of trapping center observable in this temperature range. At a heating rate of 0.38 K/s, the peak appeared at 220 K. As the heating rate was increased to 0.45 K/s, the peak shifted to a higher temperature and became narrower (Fig. 2). Garlick and Gibson's method[3] was adopted for evaluation of the trap depth, on the assumption that the trapping centerslie with a uniform depth E. The thermally stimulated current i is expressed by the equation

$$i = n_t \nu \exp\left(-\frac{E}{kT}\right), \tag{1}$$

where n_t is the number of carriers in the traps and ν is the effective attempt-to-escape frequency.

Plots of the logarithm of current against the reciprocal of the temperature gave a straight line in the initial current rising region. From the slope of the line, the depth of traps for holes was evaluated to be 0.50± 0.02 eV. When the crystal was illuminated through a

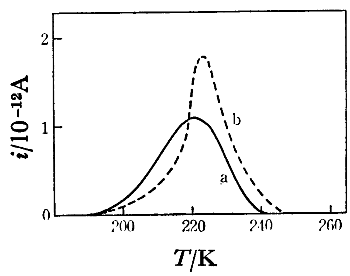

Fig. 2. Thermally stimulated currents.
Heating rate: (a) 0.38 K/s, (b) 0.45 K/s.

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negatively biased gold film electrode, no thermally stimulated current could be observed. This means that electrons could not be injected from the electrode or the injected electrons were trapped too deeply to be released thermally. The nature of trapping centers could not be determined from the present experiment. The depth of hole traps for melt-grown anthracene crystals was determined to be 0.76 eV with the same experimental arrangement. This is in good agreement with the value obtained previously.[4] Similarity in the trap depths for organic crystals; 0.50 eV for perylene, 0.53—0.76 eV for anthracene,[4,5] and 0.36 eV for metal-free- and lead-phthalocyanine crystals[6] suggests that a physical cause of the same kind might be responsible for trapping of holes.

Variation of a photocurrent with temperature has been considered to be an evidence for the existence of trapping centers.[7] We measured the temperature dependence of a photocurrent for perylene single crystals by the method given in the leterature.[8] The photocurrent was found to increase with an increase in temperature in the range 200—330 K. Plots of the logarithm of photocurrent against the reciprocal of the temperature gave a straight line, the activation energy for photoconduction being evaluated to be 0.18 ± 0.01 eV. The value of the activation energy was found to be independent of the exciting wavelength in the visible spectral region. The activation energy for photoconduction, however, showed no apparent correlation with the trap depth. It might be associated with the process of carrier generation rather than the process of c arrier transport.

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