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Semiconductivity and Photoconductivity of TCNQ Crystal

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The results of a preliminary investigation on the semiconductive and photoconductive behaviors of the TCNQ crystal are described. The single crystal of TCNQ shows a resistivity of the order 10^{11} $\Omega\cdot$cm at room temperature with an activation energy of about 0.6 eV. The photoconductive sensitivity of a TCNQ crystal is comparatively high. There are two types of crystal with respect to sensitivity to visible light. In both cases, the low-energy tail is extended up to about 1.5 eV. It is shown that both the activation energy of photoconduction and the light-intensity dependence of photocurrent differ appreciably in visible and ultraviolet regions.

Although extensive investigations have been carried out on the electrical properties of anion radical salts of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[1] a good organic semiconductor, little is known on the properties of a TCNQ crystal itself. We could expect some interesting aspects on the electrical conduction in a TCNQ crystal. First, a low energy for the conduction state could be expected as will be discussed later. If this is the case, a TCNQ crystal will show a relatively good conductivity as well as some characteristic photoconductive behaviors. Secondly, we could easily inject electrons into a TCNQ crystal because of its high electron affinity.

In a previous paper,[2] we reported the polarized absorption spectra of the single crystal of TCNQ. We will report the results of a preliminary experiment on the semiconductivity and photoconductivity of a TCNQ crystal.

Experimental

TCNQ was synthesized by the method described by Acker and Hartler,[3] and purified first by recrystallization and then by repeated sublimation *in vacuo*. Because of the high electron affinity of TCNQ, it is apt to take donor-type impurities to form TCNQ ion radical. The purified specimen was checked with ESR, and confirmed to show no detectable signal. This means that the concentration of TCNQ ions, if present at all, might be less than 8×10^{-16} g^{-1}.

Single crystals were prepared by slow sublimation *in vacuo*, or by crystallization from ethylacetate solution. Most crystals thus obtained were a parallelepiped bounded with (001), (110). The developed face was usually (001). The size of a typical crystal used for the measurement was 0.5 cm$\times$ 0.5 cm$\times$0.05 cm.

For electrical measurements, electrodes were put on the

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[1] W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963); L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965); J. P. Farges, A. Brau, D. Vasilescu, P. Dupuis, and J. Neel, *Phys. stat. sol.*, **37**, 745 (1970).

[2] S. Hiroma, H. Kuroda, and H. Akamatu, This Bulletin, **43**, 3626 (1970).

[3] D. S. Acker and W. R. Hartler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

developed face of the crystal to form a sandwich-type arrangement. Although several different electrode materials were tested, most photoconductivity experiments were carried out by using a vacuum-deposited gold film as an illuminating electrode and carbon-paint electrode as another one.

DC currents were measured with a Toa Dempa Microvolt-ammeter Model PM-18. For illumination with a monochromatic light, a quartz-prism monochrometer was used with a Ushio 500 W Xe-lamp, or a tungsten lamp as the light source. The light intensity was measured with a calibrated germanium phototransistor, or a photomultiplier tube. Most measurements were carried out by placing the crystal in a vacuum of 10^{-4}—10^{-5} mmHg.

Results and Discussion

Dark Conduction. A TCNQ crystal shows a relatively high dark conduction. The single crystal showed a resistivity of 5×10^{11} Ω·cm at room temperature. The resistivity measured with a powder sample under compression of 116 kg/cm^2 was 1×10^{11} Ω·cm. These values are considerably low in comparison with the resistivity reported for polycyclic aromatic hydrocarbons of comparative molecular size, such as pyrene[4] and perylene.[5]

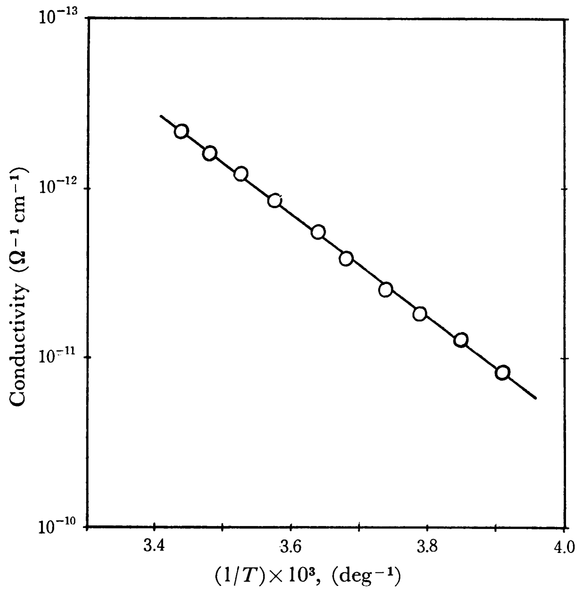

Fig. 1. Temperature dependence of conductivity of TCNQ crystal.

The temperature dependence of dark conduction was measured in the temperature range 200—290°K. An example is shown in Fig. 1. The results can be well described with the exponential equation

$$i = i_0 \exp(-\Delta E/kT) \tag{1}$$

The values of activation energy, ΔE, were found to differ a little with different crystals, but all of them fall in the range 0.45—0.6 eV. The highest value obtained in the present experiment was 0.6 eV.

Thus, if we assume that the carriers are formed by the intrinsic mechanism, not from impurity, the energy gap can be taken to be about 1.2 eV. The energy gap ε can be related to the ionization potential I and the electron affinity A of the component molecule by the relation

$$\varepsilon = I - A - 2P \tag{2}$$

where P is the polarization energy. From the magnetron experiment, Farragher and Page[7] have determined the electron affinity of TCNQ to be 2.88 eV. No experimental value is known for the ionization potential. From a molecular orbital calculation,[8] we predicted that I=7.83 eV and A=2.35 eV. Thus, the difference I—A will be 5.48 eV if we take our theoretical values, and 4.95 eV if we take Page's value for A.[9] Although we have not estimated the polarization energy in a TCNQ crystal, it does not seem unreasonable to assume it to be about 2 eV according to the known data for various organic crystals.[7] Thus, we can predict that the energy gap in a TCNQ crystal might be in the range 1—1.5 eV. Hence the energy gap determined from the temperature dependence of dark conduction is not inconsistent with this estimation. Naturally, we can not exclude the possibility that the observed dark current is due to the impurity effect or the injection from electrode. The observed variation of the activation energy from crystal to crystal suggests that such extrinsic effects are not negligible. We only wish to point out that our highest experimental value, 1.2 eV, is not unreasonable for the true energy gap.

Spectral Response of Photoconduction. A TCNQ crystal exhibits a rather high photoconductive sensitivity as compared with usual polycyclic aromatic hydrocarbons. The photocurrent was found to be proportional to the applied field up to 10^3 V/cm.

The photocurrent *vs.* wavelength curve directly obtained with our experimental set-up is shown in Fig. 2(a). On examining a number of crystals, we found that TCNQ crystals can be classified into at least two types with respect to their spectral response of photoconduction, one which shows a lower sensitivity (*curve A*), and the other a higher sensitivity (*curve B*) in the visible region. We shall denote these two types by A and B, respectively.[11]

If we normalize the observed photocurrent to a constant light intensity, we obtain the curves shown in

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[4] H. Inokuchi, This Bulletin, **29**, 131 (1956).

[5] M. Sano and H. Akamatu, *ibid.*, **34**, 1569 (1961).

[6] In the case of powder sample, ΔE was measured to be 0.45 eV.

[7] A. L. Farragher and F. M. Page, *Trans. Faraday. Soc.*, **63**, 2369 (1967).

[8] c. f. T. L. Kunii and H. Kuroda, *Theor. Chim. Acta* (Berl), **11**, 97 (1968).

[9] From the contact potential measurement, Kotani has determined the Fermi level of TCNQ crystal as 5.1 eV (M. Kotani, PhD Thesis, 1970). The values of I and A mentioned above give the prediction of Fermi level at 5.1—5.3 eV, in agreement with this experimental value.

[10] L. E. Lyons, *J. Chem. Soc.*, **1957**, 5001; F. Gutman and L. E. Lyons, "Organic Semiconductors," John-Wiley, New York (1967); M. Batley and L. E. Lyons, *Molec. Cryst. Liqu. Cryst.*, **6**, 299 (1970).

[11] At present, we do not know the reason for their appearance. Both types were found among crystals prepared by the same procedure. They can not be distinguished either from appearance or from the crystallographic character of the prominent face of the crystal.

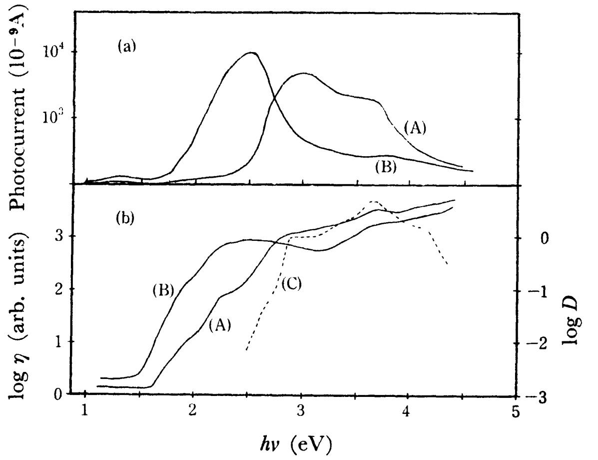

Fig. 2. Spectral response of photoconduction of crystal of A (*Curve A*), and crystal of B (*Curve B*). In Fig. 2(a), the photocurrent directly obtained without any correction for light intensity is plotted against the photon energy ($h\nu$). In Fig. 2(b), the logarithm of the apparent photoconductive sensitivity (η) is plotted against $h\nu$, together with the logarithm of the optical density (D) of the absorption spectrum of the crystal (*Curve C*).

Fig. 2(b), where the logarithm of η(Photocurrent/light intensity) is plotted against photon energy. The absorption spectrum of a TCNQ crystal is also shown. It can be seen that the spectral response curve of the A-type crystal corresponds to the absorption spectrum as regards the locations of the maxima, whereas there is an extra band in the 20—25 kK region in the case of the B-type crystal. It should be noted also that, in both cases, the tail of spectral response curve is extended into the lower energy region well outside the absorption edge. Such a tail seems to have a threshold at about 1.5 eV, which nearly coincides with the energy gap experimentally estimated from the temperature dependence of dark current.

We have examined the presence of electrode effect by using evaporated-film electrodes of different kinds of metal, *i.e.*, Au, Al, Pb, and Mg and a conducting glass electrode. But no specific effect of electrode material was found as far as the spectral response curve is concerned.

At present we do not know the reason for the difference in spectral response between A and B. It could be associated with the defect concentration of crystal. Another possibility might be the effect of impurity, or that of TCNQ ions which are produced either by impurity or the injection from electrodes. However, we have found that no marked change is produced in the spectral response curve, even if a large amount of TCNQ ions are introduced into the crystal by the doping of Li or ammonia.

Effects of Temperature and Light Intensity on Photocurrent. Photocurrent increases exponentially with temperature. An example of the experimental results obtained for crystal of A is shown in Fig. 3. From the results, the activation energy for photoconduction is estimated to be 0.15 and 0.03 eV for the wavelength of light 400 mμ and 500 mμ, respectively. The same results were obtained also for crystal of B.

The logarithm of the observed photocurrent against that of relative light intensity is plotted in Fig. 4. The data shown here were measured on crystal of A, but essentially the same results were obtained also for B type crystals. We can thus conclude that in both A and B types, the photocurrent is nearly proportional to the light intensity in the visible region, whereas it is almost proportional to the square root of the light intensity in the ultraviolet region. It is well known that photocurrent becomes proportional to the square root of light intensity when the concentration of charge carrier is controlled by the recombination of photogenerated carriers.[12] Such an effect is usually observed at very high light intensity. In the present experiments, the intensity of monochromatized light is not high, and is considerably lower in the ultraviolet region than in the visible region. It should be noted, however, that the absorption coefficient of a TCNQ crystal is quite high in the ultraviolet region, so that the incident light is strongly absorbed in a very thin region near the illuminated surface of the crystal, while the light in the visible region can penetrate deep into

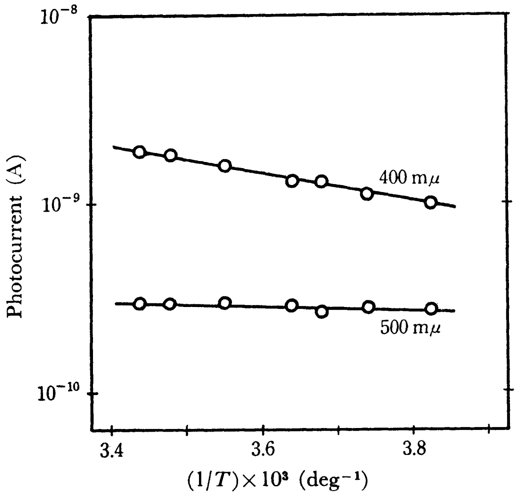

Fig. 3. Temperature dependence of photocurrent. (Crystal of A of TCNQ)

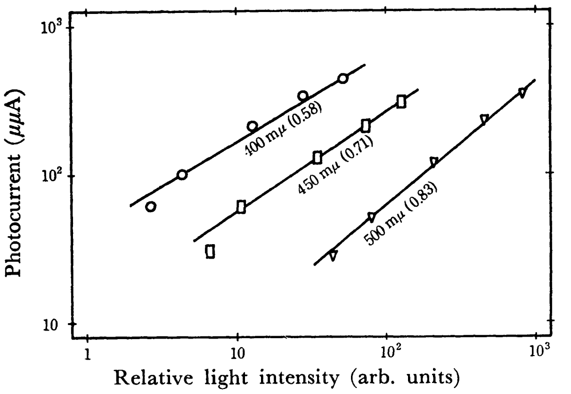

Fig. 4. Dependence of photocurrent (i_p) on the light intensity (L). (Crystal of A of TCNQ); the wavelength of the light is indicated in the figure, the number in the parentheses is the value of n obtained by assuming that $i_p \propto L^n$.

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[12] N. Almeleh and S. E. Harrison, *J. Phys. Chem. Solids*, **26**, 1571 (1965).

the bulk of the crystal. Thus, it is most likely that an ultraviolet light produces a considerably high carrier concentration near the illuminated surface, where recombination could play an important role.

If this is actually the case, the temperature dependence of the steady-state photocurrent with an ultraviolet light will be dependent, not only on the carrier trapping in the bulk, but also on the recombination process. This could be the reason for the difference in activation energy between the visible and ultraviolet regions.

Effect of Electron Donor. We prepared a Li-doped polycrystalline film from a melt of TCNQ containing 1—2 weight percent of Li(TCNQ). The pale-green film thus obtained showed a considerably higher dark current, and the ratio of photocurrent to dark current was markedly reduced. However, no specific change was found in the shape of the spectral response curve of photoconduction. Similarly, a TCNQ crystal showed a pale green color when it was kept for a long period in ammonia vapor. The dark current in TCNQ crystal gradually increased with time on exposure to ammonia vapor. In the case of crystal of A, the photocurrent was lowered to about half of the original value throughout the spectral region after exposure to 15 mmHg ammonia vapor for 22 hr. Again, no specific change was found in the spectral response curve.

These results suggest that the doping of an electron donor, or the introduction of TCNQ ion into the crystal, markedly affects the dark conduction, but does not give rise to additional mechanism of charge carrier formation in photoconduction.