BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1418—1422 (1966)

The Effect of Oxygen on the Semiconductivity of Quaterrylene

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(Received November 30, 1965)

The electrical conductivity of an evaporated film of quaterrylene varied with the pressure of the ambient oxygen. The resistivity was 1.1×10^{12} Ωcm. in a vacuum of 4×10^{-8} mmHg; this was very large compared with the previously-reported value, $\sim 10^6$ Ωcm., which was obtained after exposing the film to the air of an atmospheric pressure. The temperature dependence of the resistance of the film was also affected by the ambient oxygen. The intrinsic semiconductor model could be applied only in the case of a high vacuum ($\sim 10^{-8}$ mmHg); the band gap, $\Delta\varepsilon$, was 1.7 eV. in this case. From the resistance-temperature relations at the various oxygen pressures, it seems that two acceptor levels, 0.03 eV. and 0.6 eV. above the valence band respectively, exist.

The effect of an impurity on the semiconduction of organic molecular crystals is very important and has been studied by several workers. Adsorbed oxygen, as one kind of impurity, is known to modify the semiconductivity and the photoconductivity of organic semiconductors. Anthracene, one of the most frequently-investigated organic semiconductors, is also rather sensitive to oxygen$^{1)}$; this fact is partly responsible for the difficulty of interpreting experimental results reliably.

Recently, Heilmeier and Harrison observed the Hall effect in copper phthalocyanine single crystals and explained their results in terms of an extrinsic band model, in which the oxygen impurity formed a donor or an acceptor level.$^{2)}$ Kuroda and Flood also reported on the effect of ambient oxygen on the semiconductivities of the evaporated films of mesonaphthodianthrene and mesonaphthodianthrone.$^{3)}$

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1) H. Pick and W. Wissman, *Z. Physik*, **138**, 436 (1954); A. Bree and L. E. Lyons, *J. Chem. Soc.*, **1960**, 5179.

2) G. H. Heilmeier and S. E. Harrison, *Phys. Rev.*, **132**, 2010 (1963).

3) H. Kuroda and E. A. Flood, *Canad. J. Chem.*, **39**, 1475, 1981 (1961).

In this experiment, we will report how a high vacuum of the order of 10^{-8} mmHg has been employed to ascertain the dark conductivity of the evaporated films of quaterrylene; the conductivity and also the band gap, $\Delta\varepsilon$, have thus been found to be strongly sensitive to ambient oxygen.

The applied hydrocarbon, quaterrylene $C_{40}H_{20}$, is a very stable organic substance, unlike anthracene or mesonaphthodianthrene;* it is, therefore, hard to subject it to ordinary chemical oxidation. The electronic properties of quaterrylene were reported by the present authors some years ago.4) As will be described below, the oxygen effect on the semiconduction of quaterrylene is so large and so decided that the interpretation in terms of the extrinsic band model is rather reasonable quantitatively.

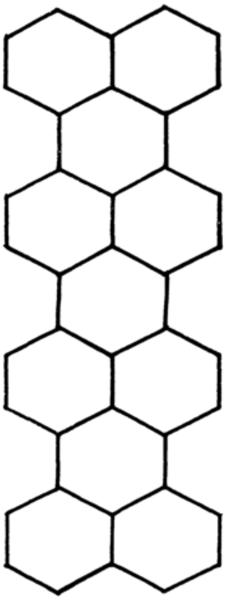

Fig. 1. The molecular structure of quaterrylene.

Only a little of the absorbed oxygen can be removed by evacuation without heating, and its adsorption energy may be expected to be fairly large compared with the usual van der Waals' energy. Therefore, careful treatment is needed in order to measure the intrinsic properties after the substance has been exposed to air.

Experimental Procedures

The high-vacuum evaporation apparatus was designed to obtain a clean vacuum of the order of 10^{-8} mmHg. As the main pumping system, a NEC 40 1./sec. ion pump (1) was employed, while a usual rotary pump was applied as the fore-line. An oil trap (2) containing a molecular sieve was used in the fore-line system. An ultra-high-vacuum cut-off valve (3) between the fore-line and the high-vacuum chamber separated the latter from the atmospheric pressure during the operation. A Bayard-Alpert gauge (5) on the top of the chamber recorded the degree of vacuum.

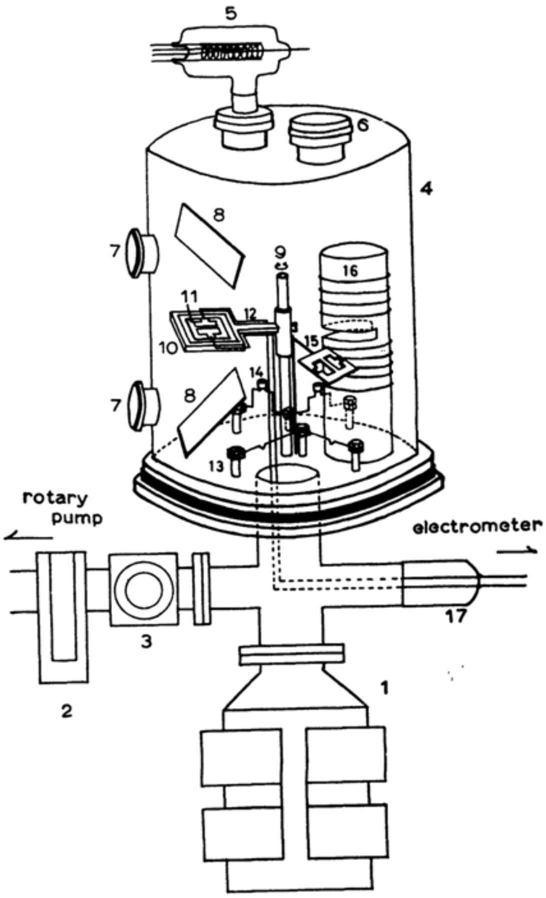

Fig. 2. The high-vacuum evaporation apparatus.
1. NEC 40 1./sec. ion pump
2. molecular sieve
3. ultra-high-vacuum cut-off valve
4. stainless-steel bell-jar
5. Bayard-Alpert gauge
6. viewing port
7. window
8. mirror
9. rotary axis
10. sample holder
11. glass plate cell
12. silver lead wire
13. electrodes for evaporation
14. gun
15. mask
16. electric heater for temperature control
17. high-resistance glass seal

Figure 2 illustrates the whole system schematically.

The sample holder (10) was supported by the rotary axis in the center of the base plate. Four pairs of electrodes (13) were placed on the base plate; two of them

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* A farily strong oxidation of these two aromatic hydrocarbons is found under atmospheric circumstances.

4) Y. Maruyama, H. Inokuchi and Y. Harada, This Bulletin, **36**, 1193 (1963).

served for the metal evaporation, and the other two, for the evaporation of organic substances. Above the electrodes the appropriate masks for evaporation (15) were applied. Metals for the cell electrodes and the samples of organic compounds were successively evaporated on the clean glass plate fitted on the sample holder by rotating it magnetically from the outside around the center axis (9).

The glass plate mentioned above had been thoroughly cleaned with a chromic acid mixture in advance. The surface conductivity of the plate was lower than 10^{-16} Ω^{-1}. No difference in electrical resistance between the two surface-type cells, arranged as glass plate - electordes - organic film and also as glass - organic film-electrodes, could be found.

The stainless-steel bell-jar (4) was heated to about 200°C under evacuation for a few days in order to remove the adsorbed gases, mainly water vapor; the inside of the jar also warmed to about 120°C. The evaporation sources (14), the gun and the sample, were also degassed by preheating in order to make them capable of maintaining a vacuum in the order of 10^{-8} mmHg during the evaporation.

In order to measure the conductivity of the cell which had been kept in a high-vacuum evaporation vessel, silver lead wires (12) were attached to the edges of the glass plate cell by silver paste before evacuation; these wires were connected at the other ends to a Cary-31 vibration-reed electrometer through a high-resistance glass seal (17). The evaporation velocity of the organic substances was about 10—50 Å in thickness per second; the value was calculated from the increase in the electrical conduction of the film specimen during evaporation.

Either side, the top or the bottom, of the cell could be irradiated by appropriate light sources through the two windows (7) and the mirrors (8).

It took five hours to evacuate the cell from an atmospheric pressure up to about 10^{-7} mmHg, and then a few days to obtain a high vacuum of 2×10^{-8} mmHg; during this time the vessel was kept at a fairly high temperature (120°C) to facilitate degassing.

After these treatments, the metal to be used for electrodes, aluminum or gold, was evaporated to bring it in contact with the silver paste which was stuck to the silver lead wire, and then an organic substance was evaporated to form a surface-type conductivity cell. The sample dimensions were 15 mm. × 3 mm. × a few microns (thickness). Dried oxygen passed through active charcoal, itself cooled by liquid nitrogen, was then introduced into the vessel, and its effect on the conductivity was examined.

Results

Some previous results of measurements of the resistivity of quaterrylene are listed in Table I.

TABLE I.

Sample	Resistivity, Ωcm.	$\Delta\varepsilon$, eV.
Powder	10^{10}	0.6
Single crystal	10^{6}	
Sandwich-type cell	10^{13}	0.6
Surface-type cell	10^{6}	0.6

The present results show a large discrepancy from the previous ones; particularly, the effect of oxygen is rather extraordinary. The resistivity, however, fluctuated according to the conditions of the preparation of the conductivity cell. One of the typical results for the quaterrylene films was as follows: The resistivity of the film, when it was kept in a high vacuum of 4×10^{-8} mmHg, reached 1.1×10^{12} Ωcm.; this was very large compared with the previously-obtained value, $\sim10^{6}$ Ωcm.

When the evaporated film was brought in contact with a trace of oxygen at room temperature, the resistance gradually decreased with the time. When the increase in oxygen pressure was large, the decrease in resistance was also large during a short initial period; after this period, however, the rate of decrease fell off, and the resistance approached a constant value. The resistance of the quaterrylene film varied with the pressure of the ambient oxygen, as is shown in Fig. 3.

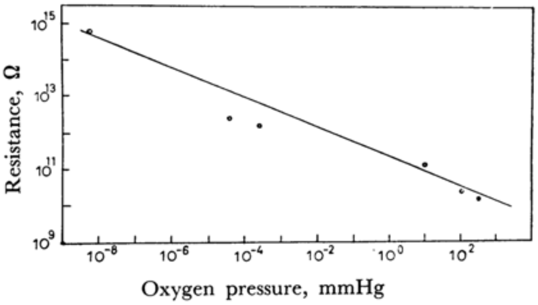

Fig. 3. The resistance of the quaterrylene film as a function of the pressure of the ambient oxygen.

When the pressure of the oxygen was lower than about 10^{-4} mmHg, the change in the resistance was reversible at room temperature. However, when the oxygen pressure increased to a point higher than this value, the process of recovering the sharply-decreased resistance was a very slow one at room temperature. Particularly when the film was exposed to oxygen in the air of an atmospheric pressure, the reduced resistance hardly increased at all after more than 1×10^{3} hrs' evacuation at room temperature; that is to say, the adsorption of oxygen on the organic crystal was practically irreversible. During this evacuation, however, when the cell was heated at about 100°C, the recovery of the resistivity was nearly attained after about 30 hr.

In Table II the resistivities of a quaterrylene surface-type film are summarized according to the ambient pressure of oxygen, P_{O_2}. No change in the resistance of the films was found when herium gas was introduced. Further, only a small effect of hydrogen gas in increasing the resistivity, or

TABLE II. THE RESISTIVITY OF THE QUATERRYLENE FILM AS A FUNCTION OF THE PRESSURE OF OXYGEN (P_{O_2})

Pressure, mmHg	Resistivity (15°C, Ωcm.)
$P_{O_2}=8\times10^{-9}$	1.1×10^{12}
$P_{O_2}\sim2\times10^{-5}$	3.5×10^{9}
$P_{O_2}\sim2\times10^{-4}$	2.7×10^{9}
$P_{O_2}=10$	2.1×10^{8}
$P_{O_2}=100$	5.0×10^{7}
$P_{O_2}=152$	3.3×10^{7}

the $\Delta\varepsilon$ value, of the oxygen-exposed film was observed.

Figure 4 shows the temperature dependence of the resistance of the quaterrylene film. The resistance was observed at temperatures from 23°C to about 120°C. With an film prepared under a vacuum of the order of 10^{-8} mmHg (Curve 1 of Fig. 4: $P_{O_2}=8\times10^{-9}$ mmHg), a linear relation was obtained between $\log R$ and $1/T$. The temperature dependence of Curve 1 can be expressed by an exponential function such as is usually found with intrinsic semiconductors:

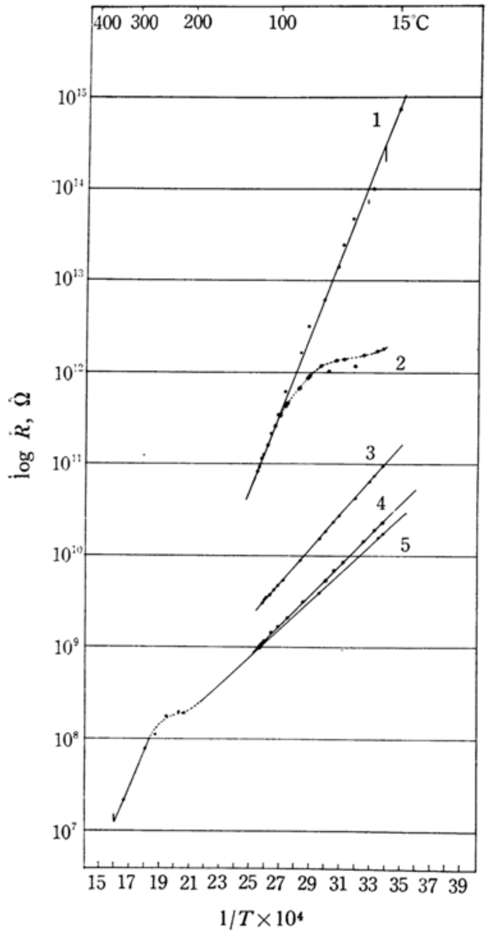

Fig. 4. The temperature dependence of the resistance of the quaterrylene film.

Curve 1 : $P_{O_2}=8\times10^{-9}$ mmHg, $\Delta\varepsilon=1.7$ eV.
Curve 2 : $P_{O_2}\sim2\times10^{-4}$ mmHg, $\varepsilon_A\sim0.03$ eV.
Curve 3 : $P_{O_2}=10$ mmHg, $\varepsilon_A=0.74$ eV.
Curve 4 : $P_{O_2}=100$ mmHg, $\varepsilon_A=0.66$ eV.
Curve 5 : $P_{O_2}=152$ mmHg, $\varepsilon_A=0.6$ eV.

$$R=R_0\exp(\Delta\varepsilon/2\boldsymbol{k}T) \qquad (1)$$

where $\Delta\varepsilon$ is the band gap for the semiconductivity. The value of $\Delta\varepsilon$ determined from the experimental results was 1.7 eV. After the ion pump had been switched off, the pressure in the vessel gradually increased to about 10^{-3} mmHg after five days. For this pressure ($P_O\sim2\times10^{-4}$ mmHg), the resistance-temperature relation curve, Curve 2, was obtained; it showed a large departure from Curve 1 in the low temperature region, which seemed to be the saturation region, but in the high temperature region it coincided exactly with Curve 1. When dried oxygen gas was introduced into the jar, linear relations, Curve 3 and Curve 4, were again obtained over the temperature range measured. However, their inclinations and resistance values were much smaller than those of Curve 1. Curve 3 was found to hold for $P_{O_2}=10$ mmHg, and Curve 4, for $P_O=100$ mmHg. Curve 5 was obtained in 10^{-3} mmHg after exposure to air under an atmospheric pressure; it corresponded to $P_{O_2}=152$ mmHg.

This behaviour seems to be due to the adsorption of oxygen; it may be analysed by the method for extrinsic semiconductors:

$$R=R_0'\exp(\varepsilon_A/2\boldsymbol{k}T) \qquad (2)$$

where ε_A is the depth of the acceptor or donor levels from the valence or conduction band. The values of ε_A calculated from the slope for each curve (Curves 3, 4 and 5) are also shown in Fig. 4. When we extended Curve 5 to the high temperature region (up to 350°C), a sharp kink in the curve was found at around 250°C; the curve at high temperatures lay exactly on the line extraporated from Curve 1.

Other organic compounds, circumanthracene,⁽⁵⁾ tetrathiotetracene,⁽⁶⁾ and violanthrene,⁽⁷⁾ were also investigated briefly. The effects of oxygen were not as evident as for quaterrylene, but a decrease in the resistivities caused by the ambient oxygen was found in all compounds.

The time-response curves of the current when the electric field was applied to the specimen film were also affected by the ambient oxygen pressure. In a high-vacuum region the response curve was of a rather square type, but above 10^{-3} mmHg it was an exponential-decay curve which corresponded to the establishment of the polarization field by trapping the carriers. The photoconduction response curves against the time were also of the

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5) H. Inokuchi, N. Matsubara, Y. Maruyama and E. Clar, *Nature,* **205**, 64 (1965).
6) H. Inokuchi and M. Kochi, unpublished results.
7) N. Imatake, private communication.

decay type above 10^{-3} mmHg, in contrast to the clear-cut square-type response in a high vacuum.

Discussion

The experimental results described above suggest that the semiconduction of quaterrylene films may be identified as of the extrinsic type except for the case of a high vacuum. In this case it may be classified as an intrinsic type from the linear relation between $\log R$ and $1/T$; its energy gap is about 1.7 eV.

As was described in presenting the results, at high temperatures the experimental points for different specimens lie on a single line, a line which coincides with Curve 1. This is a reason to assume that the energy gap, $\Delta\varepsilon=1.7$ eV., is an intrinsic one. Further, in the optical absorption spectrum of quaterrylene film, Fig. 5, the long-wavelength-side shoulder at 710—760 mμ seems to correspond to this fundamental absorption threshold. These peaks may correspond to the 564—668 mμ peaks in the solution state spectrum of quaterrylene. The 668 mμ peaks (1.86 eV.) may be assigned to the lowest singlet excitation of the quaterrylene molecule. We obtained $-0.3691\,\beta$ (β: resonance integral) as this excitation energy by means of the Simple Molecular Orbital (SMO) calculation of the quaterrylene molecule. In order to fit this calculated value to the 668 mμ observed peaks, one must assume the value of -5.01 eV. for β. For the case of perylene, β is estimated as -4.11 eV. to obtain the agreement between the observed spectrum and the SMO calculation; therefore, this large value of β for quaterrylene is not unreasonable. Thus, the value of 1.7 eV., which corresponds to the lowest singlet excitation energy for the quaterrylene molecule in the solid state, can be considered to be the intrinsic band gap.

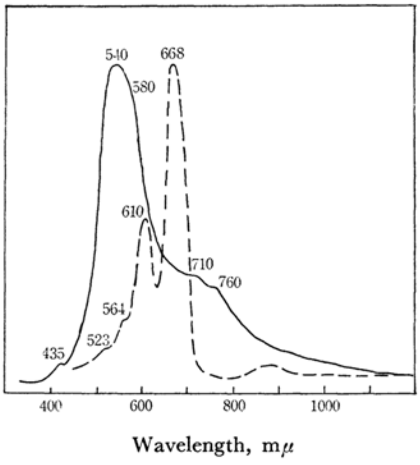

Fig. 5. The absorption spectra of the evaporated film (full line) and the solution (dashed line) of quaterrylene.

For the extrinsic semiconduction, it is not clear whether the oxygen impurity forms an acceptor or a donor level, but the former may be more likely in view of the fact that the electronegativity of oxygen is larger than that of the hydrocarbon. Therefore, as has been well established for the *p*-type semiconductor, the carrier density, n, may be given by the formula:

$$\frac{n(n+N_{\mathrm{D}})}{N_{\mathrm{A}}-N_{\mathrm{D}}-n}=\frac{N_{\mathrm{C}}}{2}\exp(-\varepsilon_{\mathrm{A}}/\boldsymbol{k}T) \qquad (3)$$

where N_{A} or N_{D} is the density of the acceptors or donors, ε_{A} is the energy depth of the acceptor level measured from the top of the valence band, and N_{C} is the effective state density. When $N_{\mathrm{A}}\gg n\gg N_{\mathrm{D}}$, Eq. 3 is reduced to the form:

$$n=\left(\frac{N_{\mathrm{C}}N_{\mathrm{A}}}{2}\right)^{1/2}\exp\left(-\frac{\varepsilon_{\mathrm{A}}}{2\boldsymbol{k}T}\right) \qquad (4)$$

This corresponds to Eq. 2.

The adsorption of oxygen may occur not only on the surface of the film, but also in its bulk. This was verified by the measurement of the oxygen effect on a cell which had a guard ring electrode* applied to its surface.

The electrode effect is also important in this experiment.8) The details of the study of this effect will be presented in due time.

One of the present authors, Y. M., would like to express his thanks to financial support of Sakkokai Fundation in performing study.

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8) H. Inokuchi, Y. Maruyama and H. Akamatu, This Bulletin, **34**, 1093 (1961).

* The electrodes and guard ring were evaporated onto the organic film. The guard ring was located in the center line portion between two electrods; it was grounded to prevent any surface current.