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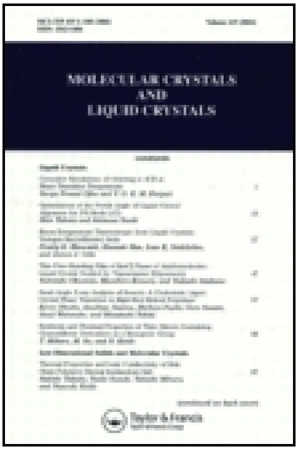

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Determination of the Lowest Electron Conduction Levels in Organic Semiconductors by Tunneling Spectroscopy

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The lowest electron conduction levels of organic semiconductors have been explored with the technique of tunneling spectroscopy. Very thin films of violanthrene-A (VEA), which is known as a typical organic semiconductor, have been prepared as tunneling barriers in Al-VEA-Al tunnel junctions. Conductance measurements on these junctions showed that the conductance depended exponentially on the thickness of the VEA barrier within the thicknesss range studied, 15-90 Å. From this thickness dependence of the tunnel conductance, the position of the lowest levels for electron conduction was estimated to be about 0.2 eV above the Fermi level of the VEA.

1 INTRODUCTION

In the studies on the electronic properties of organic semiconductors, many investigations to determine the position and width of the conduction band have been carried out. By the analysis of intrinsic photoconduction spectral responses,[1] internal photoemission spectra from a metal to organics,[2] external photoemission spectra,[3] or temperature dependence of a dark conductivity,[4] several data for "conduction bands" characteristics have been obtained. Nevertheless, the problem does not seem to be solved completely yet. Thus, we propose in this report a more direct method, a tunneling spectroscopy, for determining the position of a lowest conduction level in an organic semiconductor.

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In the case of inorganic substances, several investigators have shown that it is possible for electrons to tunnel through thin layers of semiconducting materials which are sandwiched between two metal films.[5] Lubberts and Shapiro also demonstrated that a reasonable value for the potential barrier height was obtainable by the analysis of electron tunneling conductances in Sn-CdSe-Sn junctions.[6] This barrier height can be considered to be the energy difference between a lowest conduction level in the semiconductor and a Fermi level of the electrode metal.

We applied this notion for organic semiconductors and tried to measure a tunneling current through an evaporated organic thin film. Violanthrene-A (VEA)[7] and quaterrylene (Q)[8] were used as typical organic semiconductors. In Al-VEA-Al junctions having VEA thickness ranging from 15 to 90 Å, we have demonstrated that electron tunneling through the VEA barrier is the conduction mechanism. In terms of the obtained barrier height, we can reasonably elucidate the electron energy diagram for violanthrene-A solid. Corresponding barrier height obtained for Al-Q-Pb junctions was quite low. This fact is tentatively explained by the structure difference in both films.

2 EXPERIMENTAL

2.1 Materials

The molecular structures of organic substances used in this experiment are shown in Figure 1. Violanthrene-A ($C_{34}H_{18}$)[9] and quaterrylene ($C_{40}H_{20}$)[8] were purified several times by recrystallization and sublimation respectively.

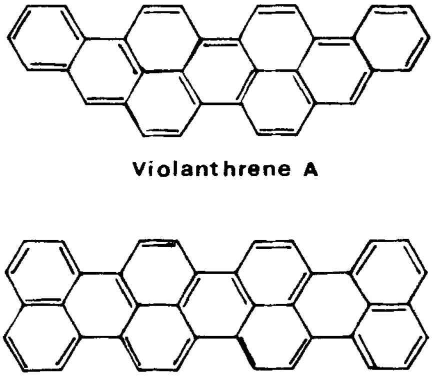

FIGURE 1 Molecular structures for violanthrene-A and quaterrylene.

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2.2 Junction Fabrication

Tunnel junctions were prepared on glass slides. After chemical cleaning, the substrates were placed in a vacuum system and gold strips were deposited to which lead-wires were adhered with silver paste prior to the junction preparation. Then the substrates were again placed in the vacuum system.

The tunnel junctions were prepared in a manner similar to Gieaver's.[5] A metallic film of Al was deposited on the substrate through a rotatable mask by evaporation at a pressure of about 2×10^{-6} mm Hg. Metals were evaporated from a tungsten wire. Next, VEA was evaporated from a glass vase with a tungsten heater onto a glass slide maintained at room temperature to a thickness ranging from 15 to 90 Å.

Since very thin evaporated VEA films are usually not continuous, it is necessary to form an oxide in those areas of the film which are not covered by the VEA.[5] The oxidation step consisted of introducing room air into the bell-jar to 760 mm Hg and being left about 20 hours at room temperature.

The junction was completed by evaporating another Al strip as a counter electrode. The two Al electrodes crossed each other at right angles so that four probes measurements could be made. At no time during any electrical measurements was the sample exposed to room air. A schematic junction fabrication process is given in Figure 2.

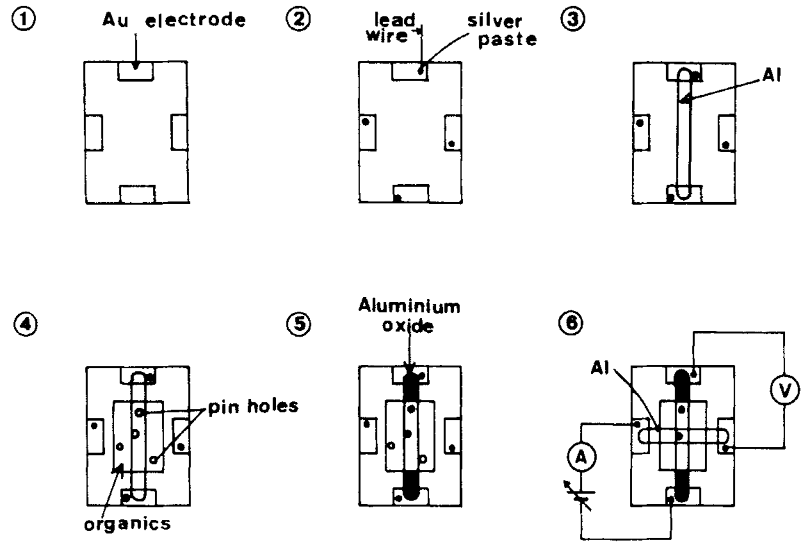

FIGURE 2 Junction fabrication procedure.

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2.3 Thickness Measurement

The VEA thickness was determined by measuring the capacitance C of each junction with an Ando Universal Bridge Type LCR-6. In mks units the thickness t of the VEA layer is given by

$$t = \frac{\varepsilon_0 \varepsilon_r A}{C} \tag{1}$$

where A is the area of the junction, $\varepsilon_0 = 8.8\dot{5} \times 10^{-12}$ F/m and ε_r is the low frequency dielectric constant of VEA, which was estimated to be 3.0.†

2.4 Determination of Pinhole Area

Very thin evaporated semiconductor films are usually not continuous and contain pinholes. By eliminating the oxidation step in our sample preparation procedure and using bismuth instead of the second Al electrodes, the pinholes in our junction were filled with Bi, of which resistance was measured.

Since the pinhole filaments are in a parallel configuration, we write for the total junction resistance

$$R = \frac{\rho t}{A_p} \tag{2}$$

where ρ is the resistivity of Bi, A_p is total pinhole area, and t is the thickness of the barrier. The resistivity ρ was obtained by measuring the resistance of Al-Bi strip which was prepared simultaneously with the junction (see Figure 3). We obtained a value of $\rho = 1.22 \times 10^{-4}\ \Omega$ cm at room temperature which is in a reasonable agreement with published value, $1.07 \times 10^{-4}\ \Omega$ cm. Using this value of ρ and Eq. (2), we determined the total pinhole area from values of junction resistance ($\sim 10\ \Omega$) with approximate VEA thickness of 50 Å. This measurement indicates that the pinhole area is an extremely small fraction (on the order of 10^{-12}) of the total junction area. Thus, we could neglect the effect due to pinhole area in the following analysis of the obtained results.

3 RESULTS AND DISCUSSION

With tunnel junction prepared as outlined above, we always obtained current vs voltage (I-V) curves such as that shown in Figure 4. The qualitative features of this I-V curve are very similar to that of metal-insulator-metal tunneling structures. At low voltage, the I-V curves is fairly linear, and at high applied

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† Dielectric constant of VEA has not been reported yet. The estimated value seems to be a reasonable one.

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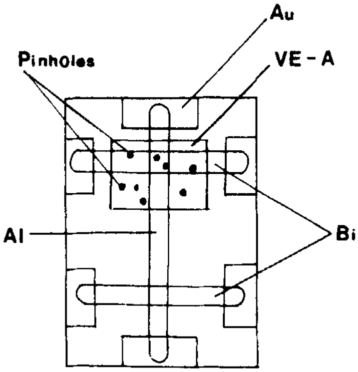

FIGURE 3 Determination of pin hole areas using an Al-VEA-Bi junction.

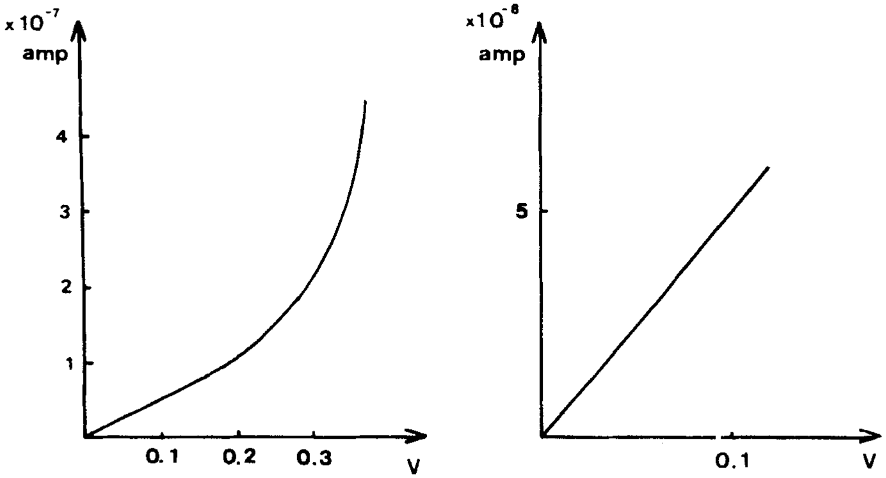

FIGURE 4 Current vs voltage characteristics in an Al-VEA-Al junction (thickness of VEA: 45 Å).

voltages (a few hundred mV) the current increases rapidly with applied voltage which is indicative of a field emission type of tunneling.

To obtain more quantitative information for these tunnel junctions, we investigated the conductance near the origin of the I-V curve as a function of the barrier thickness. At low voltages the theory of tunneling through a barrier between metal films indicates that the conductance G of the tunnel junction depends in an exponential fashion on the thickness of the tunneling barrier,[6, 10]

$$G \propto \exp\left[-\frac{4\pi t(2\varphi m^*)^{1/2}}{h}\right] \qquad (3)$$

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where m^* is the effective mass of the tunnel electron in the VEA, φ is the barrier height between the metal and the VEA layer, and h is Planck's constant.

The observed values of log G in the linear region of I-V curves are plotted against the thickness t in Figure 5. The linearity of log G vs t in Figure 5 seems to be so well that we can calculate the value of φm^* from the slope of this line which is drawn by a least square method, using Eq. (3). At higher voltage region where the current rises steeply, theoretical current density J can be

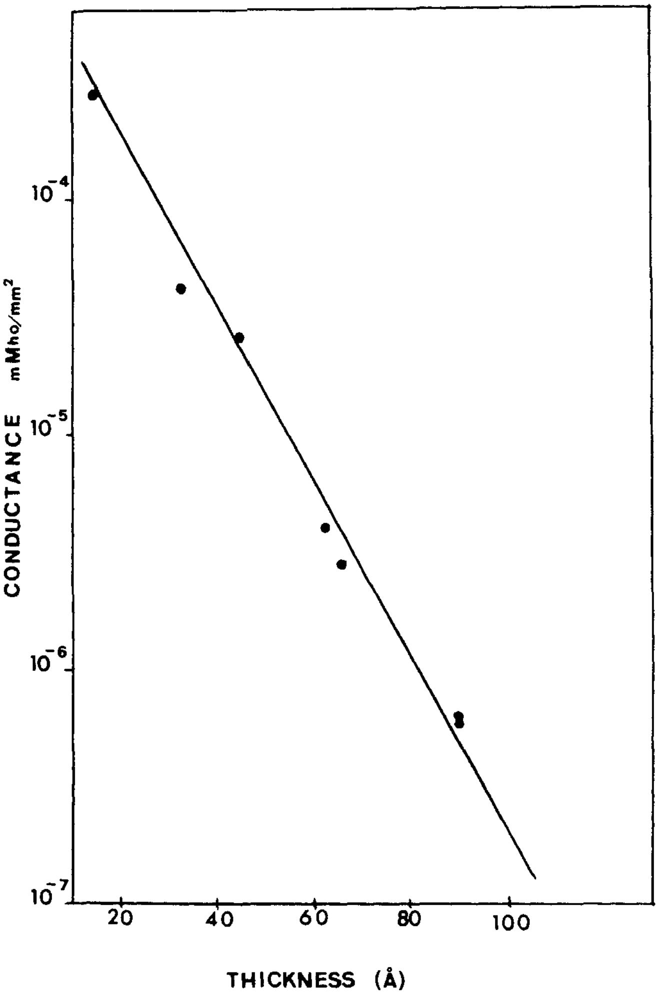

FIGURE 5 Conductance of Al-VEA-Al tunnel junctions as a function of VEA thickness.

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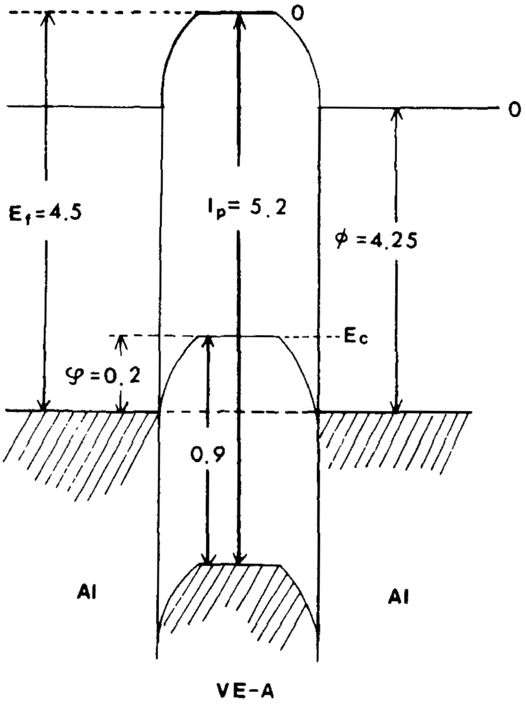

FIGURE 6 A schematic electron energy diagram for an Al-VEA-Al system.

expressed as,[6,10]

$$J = \frac{3e}{4\pi h t^2}\left(\varphi - \frac{1}{2}\text{eV}\right)\exp\left[-\frac{4\pi t}{h}(2m^*)^{1/2}\left(\varphi - \frac{1}{2}\text{eV}\right)^{1/2}\right]. \tag{4}$$

The observed value of J could be fitted with that of Eq. (4) by choosing a relevant φm^*. Comparing this φm^* value with that derived from foregoing treatment (Eq. (3)), we obtain the barrier height $\varphi = 0.2$ eV and effective mass $m^* = 0.1m_0$† respectively, where m_0 is a free electron mass.

Using the obtained barrier height value, $\varphi = 0.2$ eV, and the reported values for ionization potential I_c,[11] Fermi energy E_f[12] of violanthrene-A and work function of aluminum metal, we can draw a schematic energy diagram for the Al-VEA-Al system, as shown in Figure 6. Thus, the lowest conduction levels in VEA are estimated to lie at 0.9 eV above the valence

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† $m^*/m_0 = 0.1$ relation seems to be peculiar, since $m^* > m_0$ for a conduction electron is generally believed in an organic semiconductor. However, we may consider that as for a tunneling electron this relation ought not necessarily hold.

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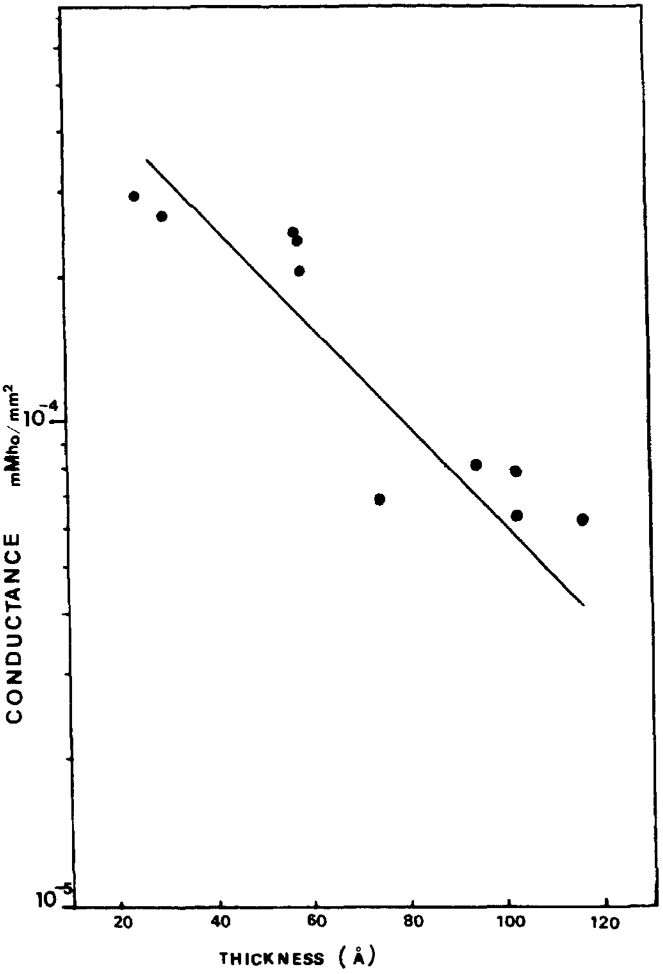

FIGURE 7 Conductance of Al-quaterrylene-Pb junctions as a function of quaterrylene thickness.

band which is in a good agreement with the reported "band gap" energy, 0.9 eV,† by Hori *et al.*[13]

In the Al-Q-Pb junctions, the conductance vs thickness relation is shown in Figure 7. Similar analysis as the foregoing procedure in VEA provided a quite low barrier height, ~0.01 eV. A quaterrylene film has been known to be quite amorphous in structure[14] when it is prepared onto a room-temperature

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† This "band gap" energy may be considered to be an extrinsic one, since the VEA film was necessarily exposed to oxygen in this experimental procedure.

substrate. On the other hand, VEA forms a rather crystalline film under the same condition.[15] Hence, the conduction band edge in a quaterrylene film is likely to be diffuse as supposed for inorganic amorphous substances.[16] This effect may result in the smaller barrier height in the quaterrylene film.

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