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Electronic Conduction in Silver-Naphthalene-Silver Structures in Dark

by

U. BÜGET

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Electronic Conduction in Silver-Naphthalene-Silver Structures in Dark

U. BÜGET

Atomic Energy Commission, Ankara Nuclear Research Centre, Ankara–Turkey

ABSTRACT

To verify the theoretical model for electronic conduction in organic semiconductors proposed by Green in 1965, the dark current-voltage characteristics of silver-naphthalene-silver structures are measured and some theoretically predicted physical parameters determined at various temperatures.

INTRODUCTION

It has been known for some time that the carrier transport in some organic crystals like naphtalene and anthracene can be described with a band-theory model [1,2]. These materials are not intrinsic semiconductors, but they share one important experimental characteristic with them, the conductivity increases exponentially with temperature [3,4].

A theoretical model for electron injection into organic semiconductors in the dark has been proposed by Green [5] (for dark conductivity the question of which carrier predominates is not clear, however it is somewhat easier to visulize the injection of

1. Kepler R. G., 1962, Organic Semiconductors, Proc. Inter. Conf., Chicago 1961, pp. 1.

2. LeBlanc O. H., 1962, Organic Semiconductors, Proc. Inter. Conf., Chicago 1961, pp. 21.

3. Bornmann J. A., 1962, J. Chem. Phys. 36. 1961.

4. Riehl N. V., 1955, Zh. Fiz. Khim., 29, 959.

5. Green M.E., 1965, J. Phys. Chem. 69, 3510.

electrons). The author considers a semiconducting electrode in contact with a naphthalene crystal, provided that the electrode has its Fermi level very near to its conduction band. It is therefore believed that the same theory may be applied conveniently to metal-naphthalene contacts.

EXPERIMENTAL

The naphthalene crystals used in this experiment were sublimed twice in vacuum from the commercial grade of naphthalene, The silver was painted on both sides of the crystal as electrodes, dark current-voltage characteristics of the silver-naphthalene-silver structures were measured at various temperatures. A typical characteristic is illustrated in figure 1. The activation energy in naphthalene was also determined in this investigation, using the temperature dependence of dark conductivity, and found to be in the range of 1-1.3 e V for a large number of samples.

RESULT AND DISCUSSION

The naphthalene, as an organic crystal, may have a considerable number of surface states caused by impurities or irregularities. The electrons in the conduction band tend to fill up these states until the highest filled surface state coincides with the Fermi level of the bulk. A thin insulating layer is then formed in the vicinity of the surface. This insulating layer or barrier separates the silver from naphthalene, and gives a M - I - S (Metal-Insulator-Semiconductor) type of structure which has an energy band diagram as proposed by Green. Under the application of an external voltage, the electrons injected from the silver tunnel through the barrier to form a current in naphthalene. The density of inected electrons in naphthalene is [5],

$$n \approx n_0 \frac{kT}{h} K \exp\left(-\frac{W}{kT}\right) \tag{1}$$

Here K is the tunnelling probability given by

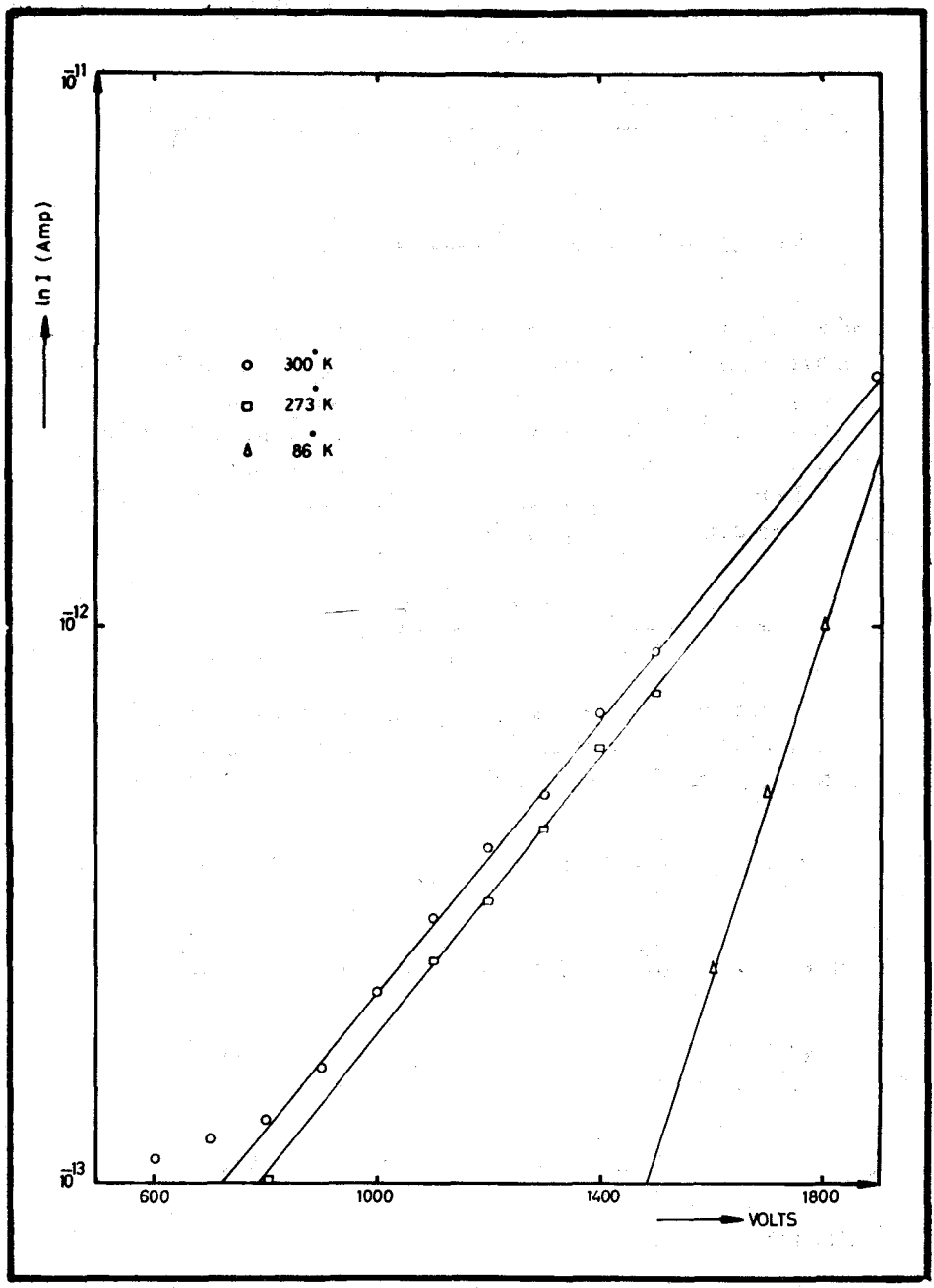

Figure 1 Current–voltage characteristics of silver–naphthalene–silver structure at various temperatures.

$$K \approx \exp\left\{-2\left(\frac{2m^*}{h^{*2}}\right)^{1/2}\frac{2}{3(Z-eV)}\left\{[A+(Z-eV)a]^{3/2}-A^{3/2}\right\}\right\} \quad (2)$$

$$A = \varnothing_m - W,\ Z = \frac{\varnothing_m - \varnothing_s}{a} \text{ end } h^* = \frac{h}{2\pi}$$

where $\varnothing_m$ and $\varnothing_s$ are the work functions of silver and naphthalene respectively, W activation energy, n_0 density of available electrons in silver, (a) barrier or tunnel thickness, m* effective mass of electron, h planck's constant, k Boltzmann constant, T absolute temperature, e electronic charge and V total applied voltage If the electron mobility is μ and the electric field in napthalene E_s then the current density is given by

$$J = \mu e n_0 \frac{kT}{h} K \exp\left(-\frac{W}{kT}\right) E_s \quad (3)$$

Denoting V_i and V_s as the voltages in the insulating layer and the bulk of the semiconductor, and ε_i and ε_s as the corresponding permittivities respectively, equation (3) becomes

$$j = \mu e n_0 \frac{kT}{h} K \exp\left(-\frac{W}{kT}\right) \theta V \quad (4)$$

where $\theta = \left[\frac{\varepsilon_s}{\varepsilon_i} a + d\right]^{-1}$, $V = V_i + V_s$ and $E_s = \frac{V_s}{d}$

d represents the thickness of the naphthalene crystal. The equation (4) can be written

$$\ln j = \ln\left(\mu e n_0 \frac{kT}{h}\theta\right) + \ln K - \frac{W}{kT} + \ln V \quad (5)$$

Differentiating (4) with respect to V

$$\frac{d\ln J}{dV} = \frac{d\ln V}{dV} + \frac{d\ln K}{dV} \quad (6)$$

Experimentally it is possible to determine $\frac{d\ln J}{dV}$ and $\frac{d\ln V}{dV}$, and therefore $\frac{d\ln K}{dV}$. This is carried out by using the current-voltage characteristics of silver-naphthalene - silver structure shown in figure 1. The results are tabulated in Table 1.

On the other hand, from equation (2).

$$\frac{d\ln K}{dV} = -2\left(\frac{2m^*}{h^{*2}}\right)^{1/2}\left\{\frac{ea}{Z}(A+Za)^{1/2} - \frac{2e}{3Z^2}[(A+Za)^{3/2} - A^{3/2}]\right\} \quad (7)$$

According to previous publications [5,6], it is possible to choose Za $\approx$ 0.01 – 0.1 eV, a $\approx$ 20 – 60 A° and A $\approx$ 2.5 – 4 eV. Setting up a computer programme which takes values of Za, a and A in these ranges equation (7) is solved. This results in some 700 values for $\frac{d\ln K}{dV}$. The nearest three to those obtained experimentally are picked together with the corresponding parameters. These are all given in Table I.

TABLE I

$\left(\frac{d\ln K}{dV}\right)_{exp}$	$\left(\frac{d\ln K}{dV}\right)_{theo.}$	Za(eV)	A (eV)	a (A°)	T
$3.6 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	0.06	3.5	40	300 °K
$4.0 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	0.06	3.5	40	273 °K
$9.8 \cdot 10^{-3}$	$13.2 \cdot 10^{-3}$	0.02	2.5	50	86 °K

The temperature dependence of the adjustable parameters of Za and A can be explained as the change in $\varnothing_m$ and $\varnothing_s$ with temperature. The decrease in (a) with temperature, on the other hand, is consistent with the nature of the barrier layer discussed above. An increase in temperature cause s the ionization of sur-

6. L. E., 1957, J. Chem. Soc. 27. 5001.

face states, and therefore the barrier is expected to become smaller as the temperature rises.

The definition of $E_s = \frac{V_s}{d}$ in equation (4) is an approximation. E_s should be obtained from integration of Poisson equation. This gives a field of $E_s = \beta \frac{V_s}{d}$ where $\beta > 1$. In this condition, the measured values of $\frac{d\ln K}{dV}$ become β times larger giving a better agreement between the theoretical and experimental values of $\frac{d\ln K}{dV}$.

At $T = 300\,°K$, $A = \varnothing_m - W = 3.5$ and $Za = \varnothing_m - \varnothing_s = 0.06$ eV. For an activation energy of $W \approx 1.3$ eV, $\varnothing_m$ and $\varnothing_s$ are found to be about 4.8 eV and 4.74 eV respectively. If the resistivity of naphthalene is considered as about 10^{16} ohm. cm at room temperature and the electron mobility as $\mu \approx 1$ cm^2 / v. sec [1], the free electron density is calculated as about 10^3 cm^{-3} which corresponds to a Fermi level of $W_f \approx 0.94$ eV. Since $\varnothing_s = X_s + W_f$ then it is possible to estimate the electron affinity X_s as 3.8 eV.

ÖZET

1965 de Green tarafından teklif edilen organik yarı iletkenlerin elektronik iletkenliklerini çözümler teorik modeli doğrulamak için Gümüş - Naftalin - Gümüş yapısının voltaj karakteristikleri ölçüldü ve bazı önemli teorik parametreler deneysel olarak tayin edildi.

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