Acta Physica Hungarica 65 (1), pp. 3–9 (1989)

ELECTRON BOMBARDMENT INDUCED CONDUCTIVITY IN CRYSTALLINE ANTHRACENE

M. SALEH

Department of Physics, Bahauddin Zakariya University
Multan, Pakistan

(Received 8 August 1986)

A study of the electron-bombardment induced conductivity at room temperature in crystalline anthracene was made using the drift method. The observed low gain (≈ 10) for the current induced by the electron beam is attributed to the short recombination lifetimes $\approx 10^{-8}$s and the low quantum efficiency ($\approx 4\%$) of pair production. These results are explained on the basis of a simple photoconductor model. The values for the drift mobilities normal to the 'ab' crystallographic plane viz., $\mu_e = 0.37$ and $\mu_h = 0.98$ cm^{2}s^{-1}V^{-1} agree well with other published values.

1. Introduction

A considerable number of discrepancies in the measurement of quantum yield under different modes of excitation has been reported by various investigators. Kepler and Merrifield [1] state that 10^{-8} carriers are produced per square centimetre for total photon flux of 10^{14} cm^2 in a $1\mu s$ pulse, from which one deduces a quantum efficiency of about $10^{-4}\%$, but no explanation is given of the method they used to calculate the number of excited carriers. Raman et al [2] estimate a quantum efficiency of the order of $10^{-2}\%$. Batt et al [3] have reported that the quantum yield for single-photon bulk generation of charge carriers remains relatively constant at about $10^{-2}\%$ for photons over the energy range from 4.2 eV to about 6 eV. Geacintov and Pope [4] using uv, found yields of the order 0.4% of energy absorbed. This yield is an order of magnitude greater than that reported for X-ray excitation [5], at least an order of magnitude greater than that obtained for intrinsic excitation with red light or near uv [6] both involving exciton–exciton processes and also for intrinsic excitation with uv [7,8] ascribed to band-to-band transitions. However, regardless of which value is correct, it is quite obvious that the quantum efficiency for carrier production is very low.

The work reported here is aimed at studying the electron bombardment induced conductivity in crystalline anthracene at room temperature using the drift method essentially pioneered by Spear [9,10], and to explain the observed low gain (induced current/bombarding current) on the basis of a simple photoconductor model.

2. Experimental

2.1 Anthracene crystals

Anthracene crystals were grown from the vapour phase, after the method of Sloan [11], under a vacuum of less than 6.7×10^{-4} Nm^{-2}, following intensive purification efforts, including liquid column chromatography, sublimation and zone refining [12]. The apparatus used for zone-refining was a Sloan–McGowan zone-refiner, manufactured to the pattern of the original refiner designed by Sloan especially for anthracene [13]. The crystal growth vessel was part of the zone-refining assembly, so that it was possible to exclude oxygen from the anthracene from the time it was introduced to the zone-refining steps [12].

All crystals for use were checked as single crystals by observing the extinction between cross polaroids under a polarizing microscope. Typical crystal thicknesses were between 200–250 μm and had surfaces of 1 cm × 1 cm, which were 'ab' planes.* The crystals were equipped with evaporated aluminium electrodes on two opposite faces and the subsequent mounting was carried out as described by Saleh [14].

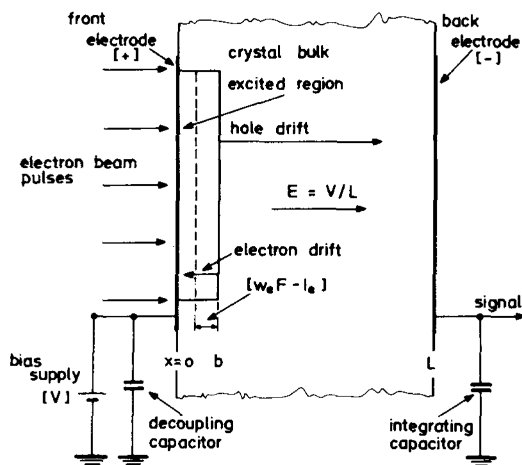

Fig. 1. Schematic arrangement for the measurement of transit time of positive carriers in an anthracene crystal

2.2. Basis of experiment

The experiment performed was essentially to irradiate the crystal specimen through a thin conducting electrode with a short pulse of electrons of energy between

*The orientation of the planes was kindly checked by Professor J. W. Jeffery of the Crystallography Department, Birkbeck College, University of London, London. U. K.

20 and 60 keV, and to record the transient charges induced on the opposite electrode for various applied electric field strengths in the crystal specimen (see Fig. 1). The bombarding electron pulses may be envisaged as generating electron-hole pairs in the region penetrated, and the subsequent drift of these carries as inducing charges on the electrodes. A bias field is essential not only to produce the drift, but also to prevent immediate recombination.

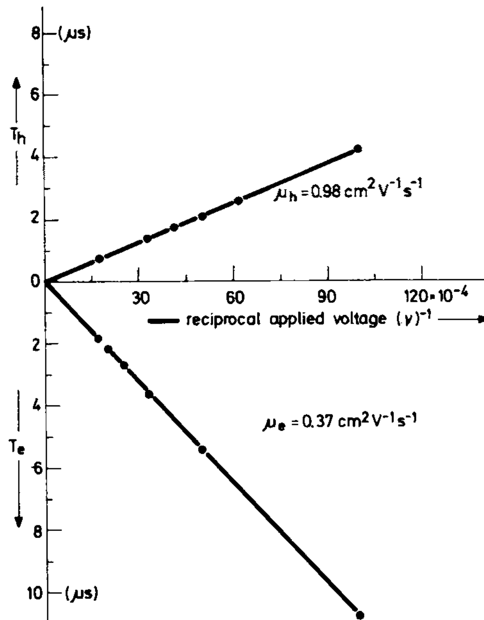

Fig. 2. **Electron and hole transit time vs reciprocal applied voltage at 293 K for specimen No.12.12, thickness 200 μm**

In the present experiments precautions were taken to avoid space charge effects such as those discussed by Saleh and Zafar [15]. The bombarding dose never exceeded 2.5×10^{-14} C (1.5×10^{7} electrons per cm^2), and the bias was regularly reversed as explained by Saleh and Zafar [15]. The induced conductivity transient may thus be treated analytically in terms of the drift of a sheet of charge across a parallel plate capacitor on which the field is uniform. When the back electrode is at a positive potential V with respect to the front electrode , the end of the ramp (the "knee") corresponds to the electron transit time; when the back electrode is negative, the knee marks the hole transit time. Provided the field is uniform, i.e., space charge is negligible, the carrier mobility is given by $\mu = L^2/TV$. T was always found inversely proportional to V, thus confirming the assumption of a uniform field as shown in Fig. 2.

3. Results and interpretation

Following the procedure described above, the values found for the electron and hole mobilities in anthracene single crystals at room temperature are $\mu_e = 0.37$ $cm^2s^{-1}V^{-1}$ and $\mu_h = 0.98$ $cm^2s^{-1}V^{-1}$, respectively (Fig. 2). These values agree well with those given by Kepler [16], Pogus [17], Sansal and Schott [18], and Saleh [12,19].

Figure 3 shows the electron and hole charge collected as function of bias field and primary electron energy for specimen No.12.12 (representative of a group of specimens). Curves for primary energies of 50, 55 and 60 keV are indistinguishable. The absence of saturation implies that in the bombarded region the recombination current far exceeds the drift current. A simple photoconductor model is used to explain these results.

It is assumed that (i) the excitation can be regarded as uniform in a layer o....x....b (Fig.1) where $b << L$, the crystal thickness; (ii) the longer of the carrier recombination lifetimes in this region is much shorter than the pulse duration so that a steady state may be assumed for the greater part of the pulse; there is no injection of space charge at the bombarded electrode (see Section 2.2).

Let the direction of the applied bias field be as shown in Fig.1. Then during electron bombardment, the entire free electron population may be regarded as being displaced to the left by a distance (w_eF-l_e), where w_e is the electron recombination mean free path per unit field and l_e the diffusion length for electrons, provided $w_eF > l_e$. This displacement creates a layer in which recombination may be neglected and which represents the predominant source of free holes. To this degree of approximation the hole charge Q_0^+ crossing unit area of the plane at 'b' to the right during electron bombardment, and eventually collected at the back electrode, is

$$Q_0^+ = q_0 w_e(F - l_e/w_e), \tag{1}$$

where q_0 is the total charge of either sign excited by the bombarding beam per cm^3 per pulse. If the voltage V is reversed, electron charge Q_0^- per unit area is collected and, therefore,

$$Q_0^- = q_0 w_h(F - l_h/w_h), \tag{2}$$

where w_h and l_h are the hole recombination mean free path and diffusion length, respectively.

Applying Eq. (1) or (2) to Fig.3, it is found that the intercept on the F-axis is $F_h' = l_e/w_e$ or $F_e' = l_h/w_h$, giving

$$w_{e,h} = kT/e(F_{h,e}')^2. \tag{3}$$

This simple model fails when $F \leq F_{h,e}'$ as there is then no layer in which recombination may be neglected, and also when $F > (b + l_{h,e})/w_{h,e}$ in which case the electrons liberated by electron bombardment are exhausted from the entire bombarded region and Q_0^+ or Q_0^+ should saturate at the value q_0b. This could not be

observed at bias field up to 25 kV cm^{-1}. The crystal specimens break down at higher field strengths; this could be due to an intensive local field build up in the exhaustion region under these conditions.

Figure 3 shows that at constant bias field the charge drawn out of the bombarded region tends to saturate with primary electron energy; this is in confirmation with the idea that the charge originates from the end of this region. However, when the bombarding energy is reduced which in turn reduces the penetration depth 'b' a superlinear dependence of Q_0^+ or Q_0^- on F is obtained. A superlinear dependence of charge on field in anthracene excited by light has been reported by several investigators [2,7,20].

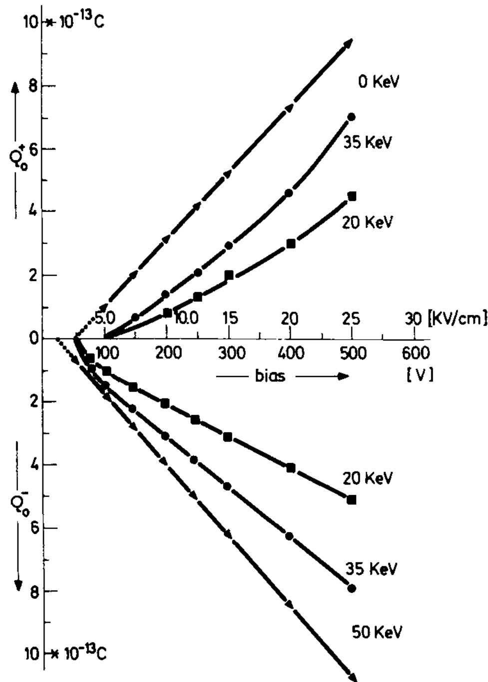

Fig. 3. **Field dependence of electron and hole induced charge at 293 K. Specimen No.12.12, thickness 200 μm, $Q_b = 2.5 \times 10^{-14}$C/pulse**

Therefore, applying this model to Fig. 3, the following approximate values are obtained,

$$w_h = 1.6 \times 10^{-8}\text{cm}^2 V^{-1}, \qquad w_e = 0.4 \times 10^{-8}\text{cm}^2 V^{-1},$$
$$\tau_h = 1.6 \times 10^{-8}\text{s}, \qquad \tau_e = 1.1 \times 10^{-8}\text{s}.$$

$\tau_{h,e}$ are the recombination lifetimes; $\tau_{h,e} = w_{h,e}/\mu_{h,e}$ where $\mu_{h,e}$ are the drift mobilities. Also from the slope of the straight lines in Fig. 3 and with the known value of $w_{h,e}, q_0$ can be calculated. Therefore, the quantum efficiency of pair production is given by the relation:

$$\eta = (q_0/Q_b) \cdot E_{h,e}/(\overline{dE_b/dx}),$$

where Q_b is the charge deposited by the electron beam through 1 cm^2 of surface to form a free carrier pair, and $(\overline{dE_b/dx})$ the average rate of energy lost by a bombarding electron per cm path. Substituting $E_{h,e}$ =5 eV [20], $(\overline{dE_b/dx}) = 2 \times 10^7$ eV cm^{-1} [21], in the above equation, quantum efficiency η of pair production of the order of 4% is obtained and, therefore, an estimate of the current gain 'G' which is expected in such thin anthracene crystals can be calculated by the formula:

$$G = \eta \left[(\overline{dE_b/dx})/E_{h,e}\right] (w_h + w_e)F.$$

Taking half the value for (dE_b/dx) to allow for incomplete excitation and F = 10 kV cm^{-1}, $G \approx 16$ which is of the order observed.

4. Conclusions

The field dependence of the collected charge and the small gain (≈ 10) for the current induced by the electron beam is, therefore, attributed to the short recombination lifetimes of $\approx 10^{-8}$ and a quantum efficiency for carrier pair production of $\approx 4\%$. The values found for the drift mobilities normal to the 'ab' crystallographic plane viz., $\mu_e = 0.37$ and $\mu_h = 0.98$ cm^{2}s^{-1}V^{-1} agree well with other published values.

Acknowledgement

The author wishes to thank the Chairman, Department of Physics, Birkbeck College, University of London, London for providing him with the facilities for conducting the experimental work. The author also acknowledges the Central Research Fund of the University of London for the provision of a zone melter.

References

1. R.G. Kepler and R.E. Merrifield, J. Chem. Phys., *40*, 1173, 1964.
2. R. Raman, L. Azarraga and S.P. McGlynn, J. Chem. Phys., *41*, 2516, 1964.
3. R.H. Batt, C.L. Braun and J.F. Horning, Appl. Opt. Suppl., *3*, 20, 1969.
4. N. Geacintov and M. Pope, J. Chem. Phys., *54*, 3884, 1966.
5. R.G. Kepler, and F.N Coppage, Phys. Rev., *151*, 610, 1966.
6. H. Bauser, Naturwiss., *54*, 505, 1967.

7. G. Castro and J.F. Horning, J. Chem. Phys., *42*, 1459, 1965.
8. R.F. Chaiken and D.R. Kearns, J. Chem. Phys., *45*, 3966, 1966.
9. W.E. Spear, Proc. Phys. Soc., *B70*, 669, 1957.
10. W.E. Spear, J. Non-Cryst. Solids, *1*, 197, 1969.
11. G.J Sloan, Molec. Cryst., *2*, 323, 1967.
12. M. Saleh, Japanese Journal of Applied Phys., *17*, No. 6. (June), 1978.
13. G.J. Sloan and N.H. McGown, Rev. Sci. Instr., *34*, 60, 1963.
14. M. Saleh and M.S. Zafar, Acta Phys. Hung., *45*, 233, 1978.
15. M. Saleh and M.S. Zafar, Acta Phys. Hung., *60*, 161, 1986.
16. R.G. Kepler, Organic Semiconductors, p.1. The Macmillan Co., New York, 1962.
17. C. Bogus, Z. Physik, *207*, 281, 1967.
18. B. Sansal and M. Schott, Solid State Commun., *8*, 1499, 1970.
19. M. Saleh, J. Phys. C: Solid State Phys., *9*, 4165, 1976.
20. I. Nakada and Y. Ishihara, J. Phys. Soc. (Japan), *19*, 695, 1964.
21. W. Ehrenberg and D.E.N. King, Proc. Phys. Soc. (London), *81*, 751, 1963.