

ELECTRICAL PROPERTIES OF ANTHRACENE FILMS

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ABSTRACT

Anthracene films have been fabricated on a glass substrate and their electrical properties have been measured as a function of film thickness, gamma-ray radiation doses, temperature, environmental pressure and electrode materials. Space-charge-limited phenomenon had been observed at intermediate fields. In all cases however, collision ionization begins before the trap-filled limit is reached. With increasing radiation dose, the energy distribution of traps becomes sharper, approaching the limit of traps with a discrete energy.

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CHAPTER I

INTRODUCTION.

Since organic semiconductor have more complex structure and much lower carrier mobilities, they have not been as extensively studied as inorganic semiconductors. Research on organic semiconductors, however, is very important from another point of view, because it would contribute to the understanding of biological processes. Moreover, by virtue of its photoconductive properties, every organic semiconductor has the potential of being utilized in scintillation counters.

Among the known organic semiconductors, anthracene possesses the simplest structure, a reasonable carrier mobility ($1 \text{ cm}^2/\text{v-sec}$), and it is much easier to purify the material and to grow an anthracene single crystals. It is partly for these reasons that it has been model compound in the studies of organic semiconductors.

The first published result on anthracene was due to Pecchettino (1906), who studied the photoconductivity in the visible and ultraviolet regions. Later investigations, from 1906 to about 1941, were also on photoconductivity and related topics. Since reasonably pure crystals and reliable experimental techniques were not available, there was not much research in anthracene during that period.

From 1941 to about 1958 more systematic studies on anthracene had been reported. In 1941, Szent-Gyorgi proposed that conduction in organic substances is due to transfer of π -electrons from molecule to molecule. Subsequently, experiments on conduction in anthracene had been

performed in the dark, under illumination, at different temperatures and under pressure, and the results related to the π -electron theory. The optical properties of anthracene had also been studied in that period.

In 1957 and 1958, Lipsett devised various methods for growing anthracene single crystals, and Kepler (1960) used various means of purifying these crystals. Around the same time, Kepler (1960) and LeBlanc (1960) succeeded independently in measuring the carrier mobility of anthracene using a pulse excitation technique, while Kallmann and Pope (1960) found that a saturated solution of iodine could be used as an ohmic contact for hole injection. With the discoveries of these more sophisticated methods of crystal growth and experimental techniques, it became possible to study anthracene on a level comparable to that on inorganic semiconductors. Recent investigations on anthracene (since 1960), centred on its band structure, its excitation bands and its space-charge-limited phenomena. Attempt has also been made to study the various transport coefficients by solving the Boltzmann equation.

So far the published literature shows that almost all the work done previously was on single crystal and experimental data on anthracene film was extremely rare (Suhrmann, 1953, 1937; Northrop and Simpson, 1956; Gheorghita-Oancea, 1961, 1963 and Fielding and Jarnagimo, 1967). It is therefore the purpose of this thesis to perform a systematic investigation on the charge carrier generation mechanism in film of anthracene.

In Chapter 2 will be given a brief survey of previous work on anthracene crystal, such as dark semiconductivity, the effect of electrode material, the effect of trapping, space-charge-limited current in organic semiconductor, photoconductivity of anthracene, and radiation effects in

anthracene. Some related models of insulating thin-film and anthracene thin-film will be given in Chapter 3. The experimental procedure, preparation of anthracene thin-film samples, thickness and conduction current measurement will be given in Chapter 4, and discussion of experimental results in Chapter 5. A conclusion and a proposed future research plan are given in the last Chapter.

CHAPTER 2

SURVEY OF PREVIOUS WORK ON ANTHRACENE CRYSTALS

By far the majority of previous work on anthracene were stressed on crystal, very little has been reported on thin-films.

Recently, Kommandeur (1961, 1965) and Gutmann and Lyons (1967) have given quite a detailed review on the properties of organic semi-conductors. In this Chapter only a brief survey on the work relevant to Present project is given, and with particular emphasis is on the work from 1965 to 1969, which have not been included in the review articles mentioned.

2-1. Dark Semiconductivity

Organic semiconductors have been extensively studied; both experimentally and theoretically for the last two decades. Although a great deal of experimental results have been reported by various investigators, there are still some discrepancies among their results. This sometimes makes it difficult to interpret the phenomena.

It has been clear for some time that the most experimental results on the dark current-temperature characteristics follows the Aurrenhis relation

$$\sigma = \sigma_0 \exp(-E_{act}/kT) \quad (2.1)$$

where σ is conductivity, k is Boltzmann constant, T is the absolute temperature, and E_{act} is activation energy, σ_0 is an emperical value ($\frac{mho}{cm}$). If the material is considered to be intrinsic, $E_{act} = \frac{E_g}{2}$, where E_g is the energy gap, then E_{act} can be interpreted as energy gap - a minimum energy

that an electrons have to have before they can contribute to conduction.

A typical dark conductivity vs temperature characteristics for anthracene is shown in Fig.2.1. The measured conduction current usually depends strongly on the particular experiment conditions as well as the history of the crystal being measured. From Fig. 2.1 the activation energy for conduction can be easily determined according to Equation (2.1). If anthracene is considered as an intrinsic semiconductor, the experimental values for E_{act} are in the range from 1.0 to 2.8 eV (Table 2.1) which are much smaller than the theoretically predicted values which are in the range from 3.5 to 4.0 eV. (Silver, 1965, Vaubel and Bacsseler). The values of resistivities so far reported vary by several order of magnitude (from 10^{14} to $10^{22} \Omega$ -cm) for anthracene. This indicates the importance of the purity of the crystal.

Eley (1967) has suggested that the following factors may be responsible for the dark conduction.

- (a) Electrons are thermally generated in the bulk of the material and transport by hopping over intermolecular barrier.
- (b) Electrons are thermally generated in the bulk of the material and tunnel through intermolecular barrier. In this case the barrier width must be narrow.
- (c) The band width is narrow.
- (d) Electrons and holes are injected from electrodes into the conductivity band. This process is most likely to happen in materials having high energy gap.

In the conduction processes these four mechanisms are present and it is possible that some processes are more dominant than the others under

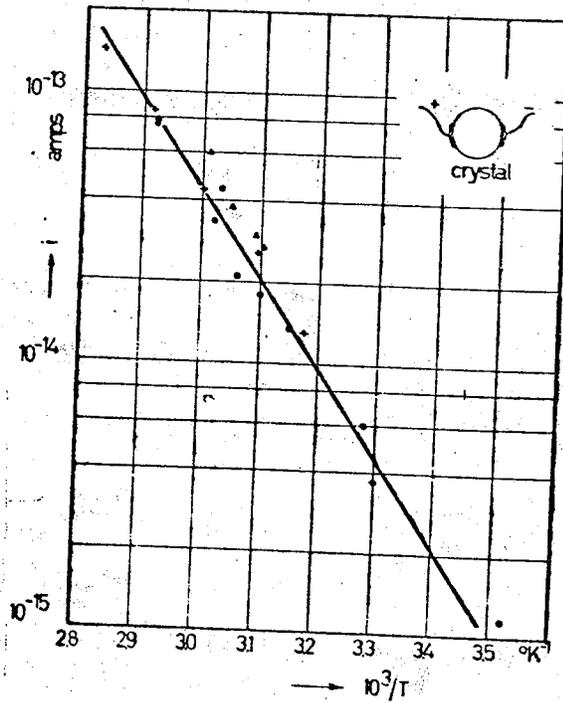


Fig.2.1. The dark conductivity of anthracene as a function of temperature. (Becker, Riehl and Baessler, 1966)

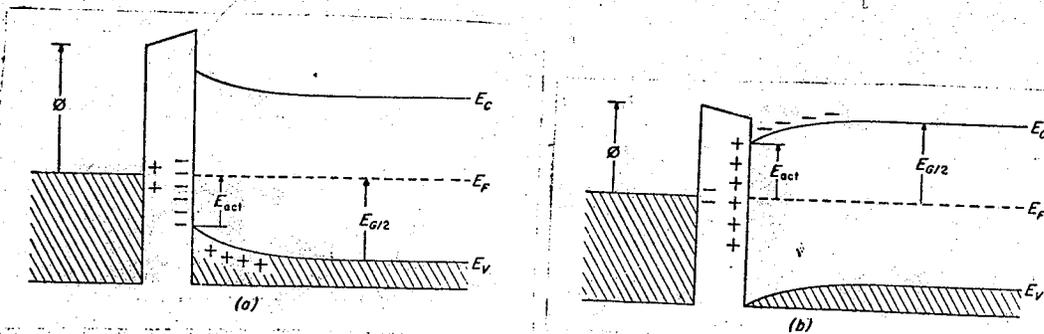


Fig.2.2. Ohmic contact. (a) Dark-injection contact for hole, (b) Dark-injection contact for electron. (After Eley, 1967).

TABLE 2.1 Summary of Previous Experimental Results for Anthracene Crystal

Method of producing samples	The form of Anthracene sample	Contacting electrode material	Temperature range °C	Activation energy (ev)	Resistivity (at 20°C)	Carrier mobility cm ² /volt/sec	Method of Measuring	Nature of carriers (+ hole - electron)	Reference
Sublimed	Compacted powder or pellet	pt		1.66	7×10^{15}				Eley (1953)
Sublimed	Single crystal in(ab) plane	Hg	80-200	1.66	1.35×10^{14}				Mette (1953)
	Single Crystal (ab)	Evap. A	20-60	1.5					Riehl (1955)
Sublimed	Deposited film	Hg.		1.5					Riehl (1955)
Sublimed	Sublimed film	Pb	30-70	1.94	10^{19}				Northrop (1956)
	Single crystal	Graphite	20-60	1.5	10^{14}				Riehl (1957)
Zone-refined	Single crystal	Ag paste	120-150	2.8 ± 0.2					Nakada (1957)
Reduction of anthraquinone	Single crystal ab plane	Evap. AI	50-150	2.7	10^{22}				Inokuchi(1956)

chromato-graphed sublimed	single crystal	Evap. Ag			$1 \text{ to } 3 \times 10^{17}$			+;PHC	Kommandeur(1958)
	Cast film	Conducting glass				50×10^{-3}	PHC and fluorescence	+;PHC	Northrop (1958)
	evaporated film and single crystal film	Conducting glass	25 - 90	1.95					Northrop (1959)
				1.95					
chromato-graphed sublimed	single crystal (ab)	surface cell Aquadag				= 2.13	PHC		Pigon (1959)
chromato-graphed	single crystal	Cu, A			1.5×10^{11}	2.13	PHC	+;PHC	Boroffka(1960)
chromato-graphed zone-refined	single crystal	Conducting glass	$-93 +_{0}^{30}$			= 0.4 = 0.3 = 1.3 = 2.0	Light pulse	+ and -	Kepler (1960)
Harshaw scintillation grade	single crystal	Ag in c-axis				=0.98±0.04 =0.54±0.03	PHC transient		LeBlanc (1960)
Chromato-graphed	single crystal	Evap. Ag	50-85	1.66					Bree (1961)
	single crystal	Electrolyte	25°		10^{15}	0.5	PHC	+;PHC	Pope (1961)

		dent of Contact (pulse method)		1.0			Heichenreid (1962)
sublimed redist- illed	single crystal	kI solution	20°C			0.43±0.05	+;injected electro- lytically Helfrich (1962)
sublimed	single crystal	Water	20-50	1.65			Helfrich (1962)
	single crystal compacted powder or pellet	in vacuo in O ₂		1.98±0.04			Plotnikov (1962)
zone re- fined chromato- graphed	melt	Ag	216-245	0.6 -0.8	10 ⁹		Pucher (1962)
zone re- fined chromato- graphed	single crystal	Ag	100-245	2.8			Pucher (1962)
	single crystal or powder			1.98±0.04			Plotnikov(1963)
chromato- graphed, zone re- fined	single crystal	Cu Ag	80-150	1.74±0.6	10 ¹⁸		Hasegawa(1964)
sublimed	compacted pwdr. or pellet	pt	160-217	2.92	10 ¹⁵		Mitskovich (1964)

	cast slab	O ₂			0.48	PHC transient	+;PHC transient	Raman (1964)
Zone-refined	single crystal	O ₂	20-130		0.85	PHC transient	+;PHC	Delacote (1965)
	single crystal	Ag	23-110	3.1				Sano (1965)
	single crystal	Ag		3.7				Silver (1965)
Zone refined	single crystal	Electrolytic			=0.8	space-charge limited		Helfrich (1966)
	(Harshaw) single crystal	Silver paste anode		0.65±0.05 ^{eV}	=0.4	current		Becker, Riehl, Baessler (1966)

TABLE 2.2 Materials used for injecting ohmic contacts to Anthracene

Injected Carrier	Contact Material	Reference
Hole	3mKI solution in water, saturated with iodine	Kallmann and Pope (1958), Mark and Helfrich (1962).
Hole	Ce^{4+}/Ce^{3+} 0.1 m in 2 m H_2SO_4	Kallmann and Pope (1960)
Hole	evaporated Ag, Ag paint	LeBlanc (1961)
Hole	$Ce_2(SO_4)_3$ and $Ce(SO_4)_2$	Adolph et al (1963)
Hole	Positive anthracene ions produced by interacting an anthracene and AIC ₃ in nitromethane	Helfrieich and Schneider (1965, 1966)
Hole Electron	evaporated gold sodium-potassium alloy	Mehl and Funk (1967)
Electron	Negative anthracene ions produced by interacting anthracene with sodium in tetrahydrofuran or ethylenediamine	Helfrich and Schneider (1965, 1966)

some given conditions.

2-2. The effect of electrode material

The electrode materials and the surface state in the contact which affect the potential barrier are very important in determining the electrical properties of a semiconducting system. Contacts can behave as ohmic contact, rectify contact, blocking contact or neutral contact depending on the work functions of the materials which form the contact and the surface states. The ohmic contact injects carriers into the solid, and the injected carrier may swap those originally present and may produce a completely different type of majority carrier conduction. The degree to which these inject carriers actually contribute to conductivity will depend on the efficiency of the ohmic contact; and in turn on the structure of the potential barrier at the interface between the electrode and the semiconductor. Electrons can normally penetrate the thin barrier by tunneling or gain sufficient thermal energy to surmount the barrier.

Dark-injecting contacts for electrons and hole are shown in Fig.2.2. The electrodes in these contacts can be considered as reservoirs of carriers. The band edge is bent downward at the contact when the work function of the electrode material is lower than that of semiconductor, and it is bent upward if the work function of the electrode is greater than that of the semiconductors. When an electric field is applied across the semiconductor, electrons will then be drawn into the interior of semiconductor and form space charges near the cathode which gives rise to a so called virtual cathode. The virtual cathode^{is} normally located a short distance from the real cathode. Within this short distance the electric field is zero due to the formation of space charges. Similarly a virtual anode would form for

hole injecting anode. Table 2.2 is a list of materials which have been used to form ohmic contacts to anthracene.

Electrolytic contacts have been used by Kallmann and Pope (1960) and Helfisch (1960, 1966). The electrolytes used are sodium in tetrahydrofuran or ethylenediamine for electron injection, and 3M KI solution in water saturated with iodine for hole injection. At the contact the conduction band or the valence band are bent into the vicinity of the Fermi-level of the solid, so that the Fermi-level of the electrolyte is roughly equal to the electron affinity (electron injection) or to the ionization energy (hole injection) of the anthracene.

However, there are many obvious disadvantages of using electrolytic contacts. Obviously it is difficult to use such contacts for solid-state electronic devices. It is therefore desirable to choose solid contacts. Mehl and Funk (1967) found that a sodium-potassium alloy makes an electron injecting contact to anthracene, and evaporated gold electrode a hole injecting contact. The simultaneous injection of electron from cathode and hole from anode leads to radiative recombination at room temperature.

2-3 Transport Mechanisms

Anthracene is a molecular crystal. The intermolecular interaction in these crystals is weak. The electrons, to a very large extent, are therefore localized, (The molecular orbitals which do overlap to an appreciable degree are the π -orbitals. Electrons in the π -orbitals are referred to as π -electrons), and they have to surmount a considerable potential barrier before they can move to an adjacent molecule. Consequently, in the absence of any influences which may generate carriers inside the crystal or in the absence of any external sources which may inject carriers

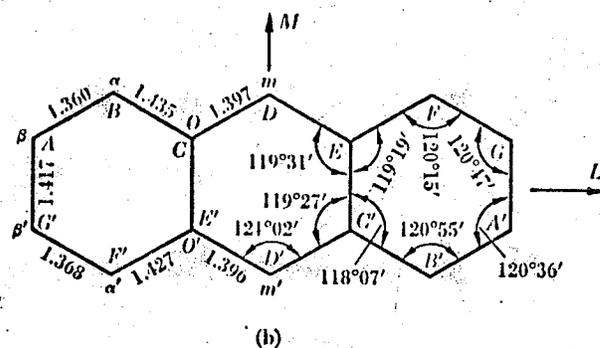
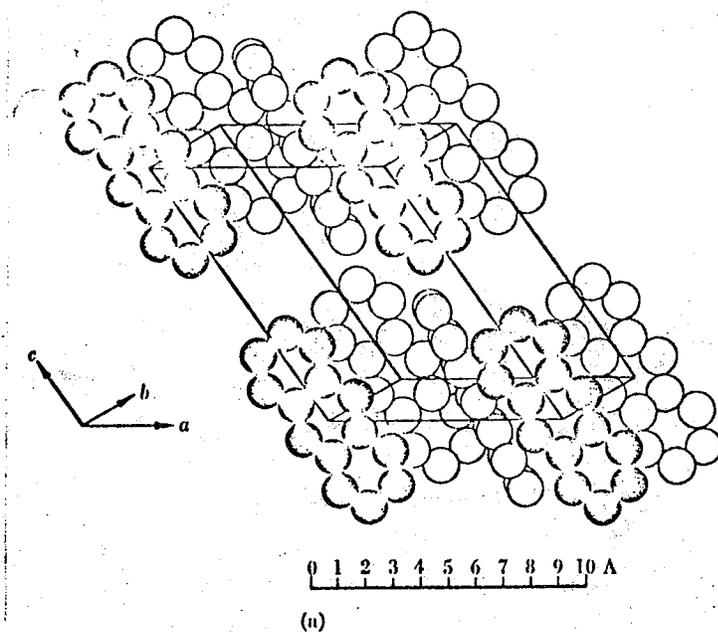


Fig. 2.3 Base centered monoclinic crystal structure for anthracene. (a) Molecular arrangement in the unit cell. (b) Carbon-Carbon distances and angles.

into the crystal electron; conduction is determined by the probability that a localized electrons (mainly π -electrons), assisted by thermal motion, can tunnel through the potential barrier to a neighbouring molecule. An alternative method for determining electronic conduction under the same conditions is by solving the Boltzmann equation if the band structure is known. Under the conditions specified above, (no carrier generation and carrier injection), the tunneling model is more intuitive and its approach is comparatively simple. It should be noted that when carriers are being generated or injected by external influences, the band theory is more expedient approach. The latter situation can be described as generation of electrons and holes or injection of carriers into the conduction band or valence band. The subsequent motion of these carriers can then be easily described by their mobilities, which are obtainable from the band theory model by a standard calculation.

In the following we shall discuss these two models separately.

2-3.1

2-3.1 Tunneling model and other related models

The structure of anthracene, among the organic crystals, was first determined by X-ray methods. The crystal structure of anthracene is depicted in Fig.2.3. It is based on a monoclinic unit cell with $a = 8.56\text{\AA}$, $b = 6.04\text{\AA}$, $c = 11.16\text{\AA}$ and $\beta = 124.7^\circ$ (Robertson, 1958). There are two molecules of anthracene per unit cell.

The barrier tunneling model was suggested by Eley and Parfitt (1955), and a simple mathematical treatment was given by Eley and Willis (1960). The tunneling mechanism as envisaged by Eley and Willis is illustrated in Fig.2.4, where three adjacent similar molecules are depicted (a) in the absence of an applied field V (volts-cm^{-1}) (b) after application

of V and after the excitation of an electron in the central molecule.

After excitation of electron from the $(\frac{N}{2})$ level to the $(\frac{N}{2} + 1)$

level both the electron and hole can tunnel as shown in Fig.2.4. The total energy changes for the electron transfer process is given by

$$E = I_G - A_G - aeV - \left(\frac{e^2}{\epsilon r} \right) \quad (2.1)$$

where I_G and A_G are respectively the ionization energy and the electron affinity of the organic molecule; a is the barrier width, e is electronic charge and aeV is the energy change caused by a vertical displacement of a potential well relative to its neighbour. For the values of a of the order 5 to 10 \AA , the term, aeV , is very small unless V is very large. The term $\frac{e^2}{\epsilon r}$ represents the Coulombic interaction of the electrons separated by a distance r . The effective permittivity in the region surrounded the charges is large because of the polarization of surrounding π -electrons.

For $aeV \ll (V_0 - E)$, the bulk conductivity σ_0 is given by (Eley and Willis, 1960)

$$\sigma_0 = \frac{2(2\pi m_e kT)^{3/2}}{h^3} \cdot \frac{[(\frac{N}{2})+1] h(a+1)}{4L^2 m_e^*} \cdot 16 \left(\frac{E_w}{V_0} \right) \left[2m_e^* (V_0 - E_w) \right]^{1/2} \\ \cdot \left(\frac{ae}{h} \right) \exp \left[-2(2m(V_0 - E_w))^{1/2} \left(\frac{a}{h} \right) \right] \quad (2.3)$$

where

$V_0 - E_w$ is molecule electron affinity.

V_0 is the molecular ionization energy

L is the distance across the well

and the other parameters have the usual meaning.

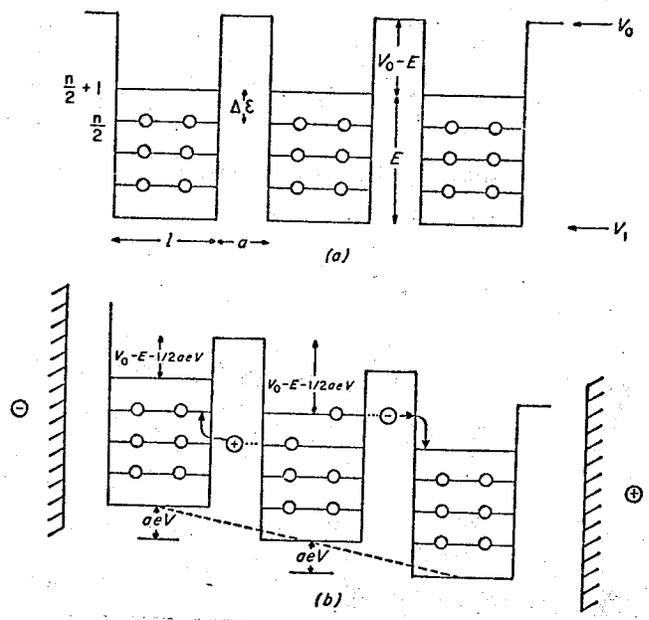


Fig.2.4 Potential box model (tunnel model) of organic semiconductor.(after Eley and Parfitt,1955).

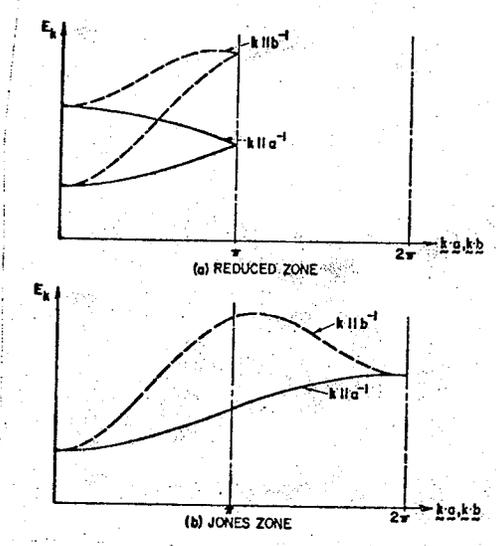


Fig. 2.5 Energy versus wave vector in reduced and Jones zone schemes for electrons in anthracene. (After LeBlanc, 1961).

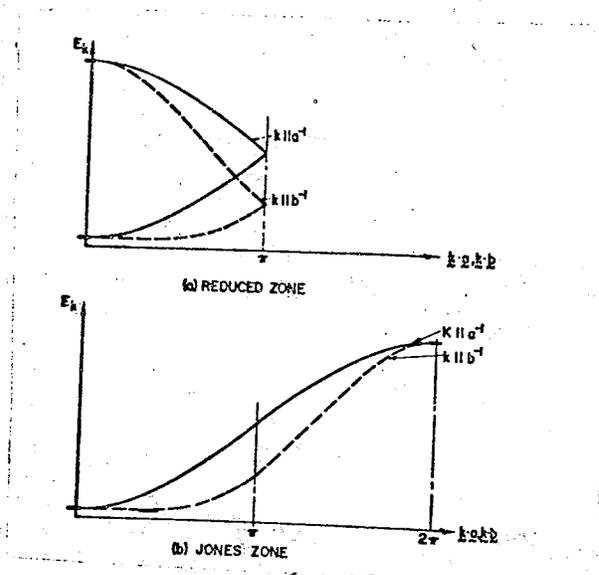


Fig.2.6 Energy versus wave vector in reduced and Jones zone schemes for holes in anthracene. (After LeBlanc, 1961).

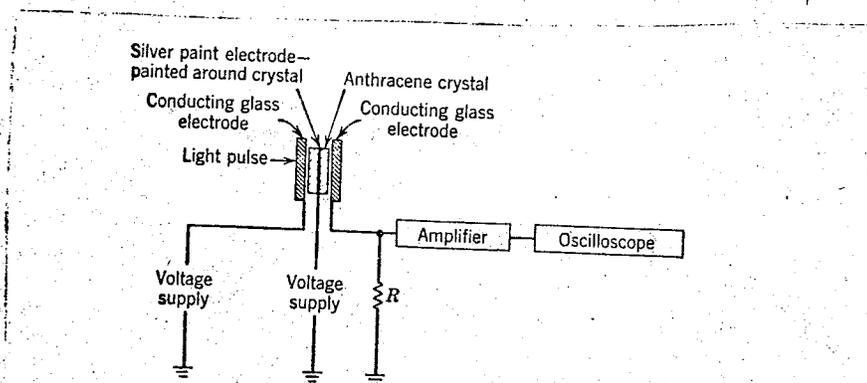


Fig. 2.7 Light pulse technique for measurement of the mobilities of electron and hole in anthracene. (After Kepler, 1960).

Keller and Rast (1962) used a similar model to estimate the mobility of the π -electron in anthracene. By choosing the values of 1.2eV for $V_0 - E_W$ (electron affinity), the value of 7.8^{eV} for V_0 (ionization energy of the molecular), the value of 2.5\AA for a and 8.5\AA for b , they calculated the electron mobility to be $0.8 \text{ cm}^2/\text{sec}/\text{volt}$ from Equation (2.3). The parameters I_G , A_G and a can be determined by the molecular wave functions but it is much easier to determine them by means of experimental methods.

Kears (1961) has proposed a similar model called "the reasonable transfer model". With this model no explicit expression is given for the potential wells and barriers, but it requires the knowledge of molecular wave functions and the time-dependent perturbation treatment.

2-3.2 Energy Band Model

Because of the small overlaps characteristic of anthracene, the motion of the excess charge carrier can be formulated in terms of the tight-binding approximation. The band structure of anthracene was first calculated by LeBlanc (1961) and later by Thaxton (1962) and Katz (1963) for the base-centered monoclinic unit cell as shown in Fig.2.3. The final result of their approach is

$$E_{\pm}(\vec{k}) = 2E_b \cos(\vec{k} \cdot \vec{b}) \pm 2E_d \left[\cos\left(\vec{k} \cdot \left[\frac{\vec{a} + \vec{b}}{2}\right]\right) + \cos\left(\vec{k} \cdot \left[\frac{\vec{a} \cdot \vec{b}}{2}\right]\right) \right] \\ \pm 2E_f \left[\cos\left(\vec{k} \cdot \left[\frac{\vec{a} + \vec{b}}{2} + \vec{c}\right]\right) + \cos\left(\vec{k} \cdot \left[\frac{\vec{a} - \vec{b}}{2} + \vec{c}\right]\right) \right] \quad (2.4)$$

where E_b , E_d and E_f are the intermolecular transfer integrals between the

molecule at the origin of the unit cell and those at relative vector position \bar{b} , $\frac{\bar{a} + \bar{b}}{2}$, and $\bar{c} + (\bar{a} + \bar{b}) / 2$ respectively. (See Fig.2.3).

Simplifications of the band structure are possible for certain direction of \bar{k} space. By considering $\bar{k} \cdot \bar{c} = 0$. (Fig. 2.5 and Fig. 2.6) E becomes

$$E(K_a, K_b, 0) = 2 E_b \cos(\bar{k} \cdot \bar{b}) + 4 E_a \cos\left(\frac{\bar{k} \cdot \bar{a}}{2}\right) \cos\left(\frac{\bar{k} \cdot \bar{b}}{2}\right) \quad (2.5)$$

$$-2\pi \leq \bar{k} \cdot \bar{a}, \bar{k} \cdot \bar{b} \leq 2\pi$$

in which E_p has been dropped as a consequence of the fact that Friedman (1964, 1965) has extended the band model to treat electrical and thermal transport phenomena for an anisotropy energy band, on the assumption that the relaxation time is constant.

The steady-state Boltzmann equation can be written as

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{diffusion}} + \left(\frac{\partial f}{\partial t}\right)_{\text{field}} + \left(\frac{\partial f}{\partial t}\right)_{\text{collision}} = 0 \quad (2.6)$$

$$-V_k \cdot \nabla_r f + \frac{e}{\hbar} \left[\bar{F} + \frac{1}{c} (\bar{V}_k \times \bar{H}) \right] \cdot \nabla_k f - \frac{f - f^{(B)}}{\tau} = 0 \quad (2.7)$$

where $f_k^{(B)}$ is the Boltzmann distribution function, \bar{F} and \bar{H} are the external electric and magnetic fields, $V_k = \frac{1}{\hbar} \nabla_k E_k$ is the velocity of an electron in block state \bar{k} , where E_k is given by Equation (2.4) or Equation (2.5) and τ is the relaxation time. The solutions of Equation (2.7) for given applied fields are straight forward. The order of magnitude, sign, and anisotropy of the electrical conductivity, Hall coefficient, magneto-conductivity, thermoelectric power, thermal conductivity determined from this transport equation are in good agreement with the experimental results (Friedmann, 1964, 1965).

2-3.3 Experimental work on drift and Hall mobilities

A. Drift mobilities

The drift mobilities of anthracene have been determined by the light pulse techniques (Kepler, 1966) (Fig.2.7), and by ohmic contact-pulsed voltage technique (Mark and Helfrich, 1962). Kepler's result shows that carrier drift is not isotropic. The drift mobilities of anthracene at room temperature are as follows (see Table 2.3)

Table 2.3 Anthracene drift mobilities at 25°C.

	Crystal (See Fig.2.3)	Mobility (cm ² /V-sec)	Reference
Holes	a	1.0	Kepler (1964)
	b	2.0	
	c	1.8	
Electron	a	1.7	Kepler (1964)
	b	1.0	
	c	0.4	

The temperature dependence has been extensively studied (see Fig.2.8). In those crystal the drift mobility is of the order of 1 cm²/v-sec. at room temperature and it varies as some inverse power of the absolute temperature. Some results are summarized in Table 2.4

Table 2.4 The temperature dependence of anthracene hole mobility

Crystal axis	Temperature dependence	Temperature range (°k)	Reference
a	T	77° - 293°	Kapler (1964)
c	T ⁻²	230° - 370°	Bogus (1965)
c	T ^{-1.7}	280° - 400°	Delacote (1964)

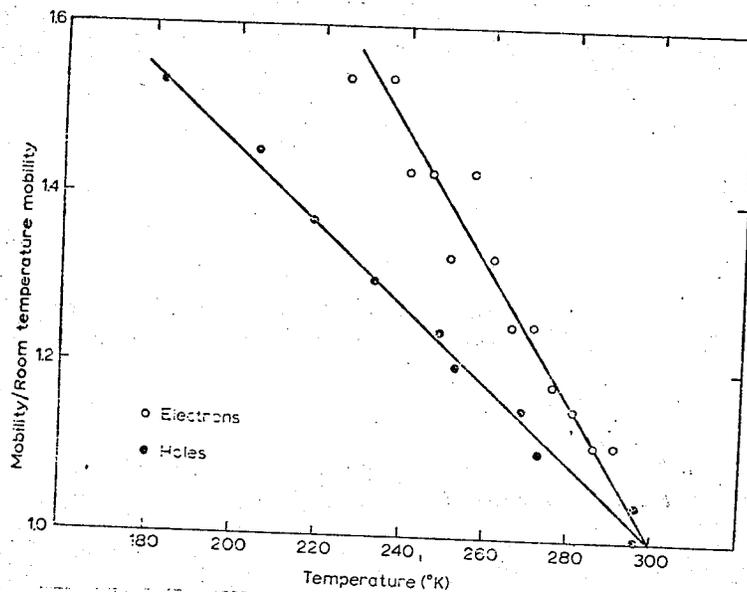


Fig.2.8. Temperature dependence of carrier mobilities.

(After Kepler, 1960)

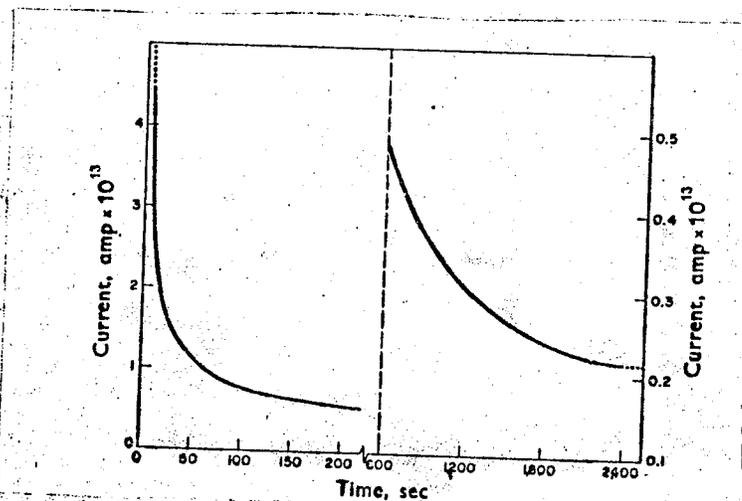


Fig. 2.9 Conduction current as a function of time for anthracene. (After Silver, 1958).

B. Hall mobilities

Dressner (1966) has observed a photo-Hall effect in anthracene which is anomalous. This is a two-carrier effect from which the individual hole and electron contributions unfortunately could not be determined. But Dressner was able to establish that the Hall mobilities at room temperatures for both carriers are at least $50 \text{ cm}^2/\text{v-sec}$. The ratio of Hall to drift mobilities is even larger than what would be expected from existing band structure calculations. (Freidmann, 1965, and LeBlanc 1963). Delacote and Schott (1966) devised a one carrier experiment in which both Hall and drift mobilities could be measured simultaneously. It was found that $\mu_d = 1.4 \text{ cm}^2/\text{v-sec}$ and Hall mobility $\mu_H = -35 \text{ cm}^2/\text{v-sec}$. LeBlanc (1963) predicted theoretically that the ratio of Hall to drift mobility should be approximately $-kT/\bar{W}$, where \bar{W} is the width of the energy band which is occupied by hole. The value for \bar{W} is deduced to be $6 \times 10^{-3} \text{ ev}$.

2.4 The Effect of Trapping

2.4.1 Slow-decay characteristics

The properties of anthracene are very sensitive to small impurity concentrations or localized defect states (traps and recombination centres). The presence of relatively deep traps will affect greatly the electronic conduction.

The effect of trapping of charge carriers in the bulk has been investigated by Kallmann and Rosenberg (1958) and Kallmann and Silver (1959), and it is sometimes referred to as the persistent internal polarization effect. Kallmann and Silver have shown that this effect is mainly due to a spatial distribution of trapped electrons. The lifetime of a trapped electron is large, it is usually several days.

Earlier measurements on anthracene single crystals have indicated that both the dark conductivity and photoconductivity are caused by space-charge limited currents in which the majority carrier are positive holes (Kallmann and Silver (1958), Pope (1958-1962), Helfrich (1962-1966)). Since positive holes are known to be the majority carriers, the most reasonable assumption is that the carriers being trapped are electrons.

As the minority carriers become trapped, a back electromotive force \mathcal{E}_b is rapidly built up, which approaches \mathcal{E}_a (applied electric field). Thus the effective field acting on the carriers is $\mathcal{E}_a - \mathcal{E}_b$, which in equilibrium attains a small values, resulting in a small limiting current. The distribution of trapped carriers as a function of the distance normal to the two electrodes, x , will be determined in part by the local field gradient $\left[\frac{d(\mathcal{E}_a - \mathcal{E}_b)}{dx} \right]_x$. Therefore in a region where this gradient is high, there is a greater probability that a carrier will be swept out when it becomes thermally detrapped; whereas when it is low, there is a greater possibility of retrapping.

The current decay phenomena always exists in electronic conduction measurement in anthracene. Depending on particular experimental conditions, the time taken to reach the steady state after the external field is applied is normally greater than half an hour. Fig.2.9 shows the measured current decays with time in anthracene crystal.

2-4.2 Trapping Processes

There are four conventional methods used to study trap distribution in anthracene.

1. Space-charge-limited current method.
2. doping impurity method

3. thermal stimulated current method
4. Optically stimulated current method.

There are two possible trapping mechanisms (a) lattice defects and (b) acceptors in the crystal which may be anthracene molecules or impurities molecules.

(1) Space-charge-limited current method

Steady-state space-charge limited currents (SCLC) in organic crystals have been observed by many investigators. The current-voltage characteristics follows the equations derived by Lampert (1956) for crystals with a shallow trap-level, and by Mark and Helfrich (1962) for crystals with trap distributed exponentially within the whole forbidden gap. Adolph et al (1963) reported that using $\text{Ce}_2(\text{SO}_4)_3$ as hole-injection electrodes then there is a discrete hole trapping level in anthracene, in addition to the exponential distribution suggested by Helfrich and Mark. On the basis of the current-voltage characteristics it is possible to determine the trap distribution by comparing the experimental results with the theoretical equations which are derived for different assumed trap distributions.

(2) Doping Impurities Method

The presence of chemical impurities in anthracene crystals has been shown to reduce charge carrier lifetimes by increasing the density of carrier trapping sites. Hoesterg and Leton (1963) have carried out a study on carrier trapping by intentionally adding impurities anthraquinone, anthrone and tetracene as dopants into anthracene. Anthraquinone and anthrone act as deep traps for holes and electrons. As little as 10 parts per million of either dopant reduces the carrier life time from the values greater than 2000 μ .sec in pure anthracene down to 10-100 μ sec.

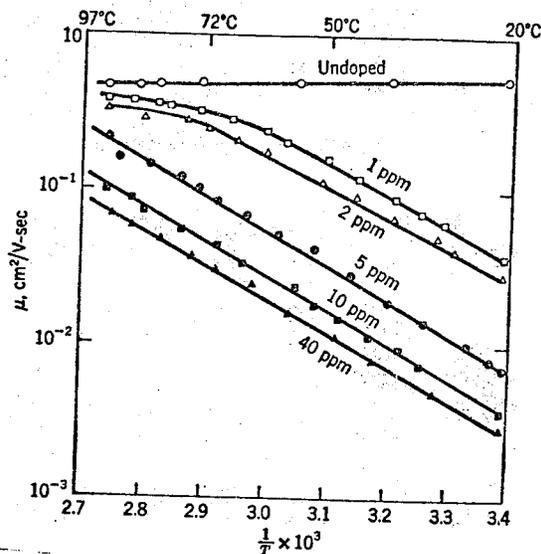


Fig.2.10 Hole drift mobilities in anthracene doped with tetracene, exhibiting the phenomena of Shallow trapping. (After Hoesterey and Letson, 1963).

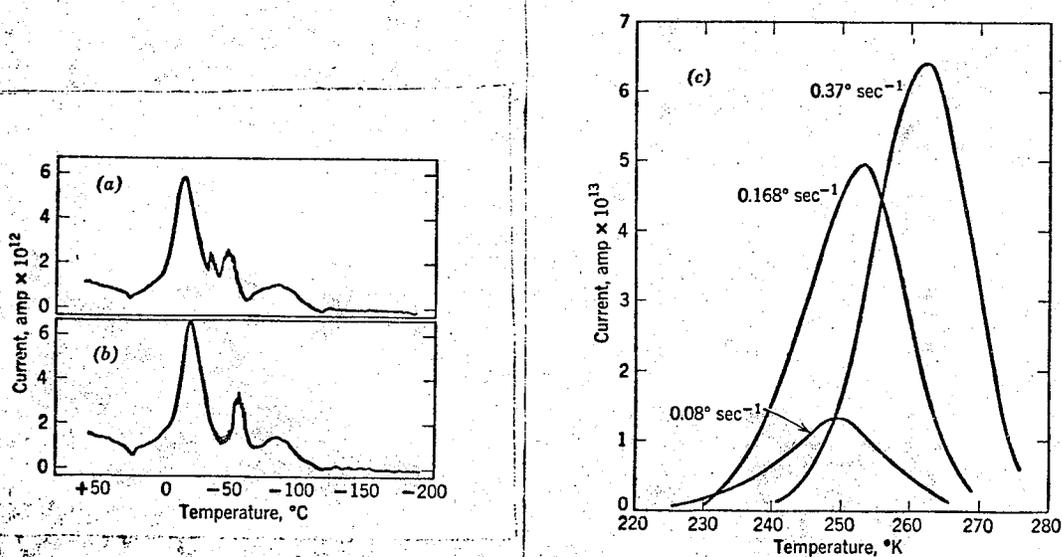


Fig.2.11 Conductivity glow cures for anthracene crystal. The cures in (a) and (b) are repeats at a heating rate of $0.7^{\circ} \text{C sec}^{-1}$, and a field of 3000 volt-cm. Diagram (c) shows the main peak for three different heating rates. (After Bryant, Bree, Fielding and Schneider, 1959).

Tetracene behaves differently for electrons and holes. Toward electrons it acts as a deep trap, while toward holes, on the other hand, tetracene acts as a shallow trap, i.e. the hole has a high probability of escaping the trap and being trapped again during one transient time. This leads to an effective-mobility, μ^* , lower than that in the pure crystal μ_0 according to the equation

$$\frac{\mu_0}{\mu^*} = 1 + \left(\frac{N_t}{N_c} \right) \exp \left(- \frac{E_t}{k_T} \right) \quad (2.8)$$

where N_t is the trap density

N_c is one-half the effective volume density-of-states in the hole band

E_t is the trap depth.

The experimental results are shown in Fig.2.10. Except at very high tetracene concentrations the results follow Equation (2-8) closely both in T and N_t dependencies. The trap depth is 0.43^{ev} , which is very close to the difference between ionization energy of anthracene and that of tetracene as expected.

(3) Thermally stimulated current method

More detailed information about the position and structure of the trapping levels from thermally stimulated currents. A typical glow curve obtained for anthracene (Bryant, Bree, Frelding and Schneider, 1959) is shown in Fig.2.11. Bree and Kydd (1964) and Kokado and Schneider (1964) also used thermally stimulated conductivity curves to study the trapping process in anthracene. Their experiments yield evidence for a discrete level at 0.75^{ev} , and no evidence of a continuous exponential distribution.

Weizz et al (1964) observed that some traps in anthracene crystals grown by the Bridgman-Stockbanger method which gives lifetimes of the order

of 100 sec can be removed by annealing at 120°C. It thus appears that the annealable traps are physical defects introduced during crystal growth. Because they are so easily removed, they suggested that these traps arise from individual molecules which are slightly misoriented in the lattice.

(4) Optical stimulated current method

Jansen, Helfrich and Riehl (1964) reported that the absorption peaks in the visible region as well as in the ultraviolet region can be photo-released from the energy transfer, it thus appears to be possible to excite carriers from traps. Kokado and Schneider (1964) also observed detrapping by long-wavelength light (in the visible and near infrared region) and an absorption peak near 0.76^{ev}. The laser-induced photocurrent reported by Hasegorwa and Schneider (1963, 1964) evidently occurs due to excitation of trapped carrier by triplet exciton. However, these subjects are beyond the scope of this thesis and therefore will not be discussed in further detail here.

2-5 Space-charge-limited current in organic semiconductor

The persistence of space charges within the organic crystal is well known, even when the solid as a whole is electrically neutral and carries no net charge. Electric charges may be generated either on the surface of a solid or in its bulk, and may give rise to surface charges or space charges or both. Thus, strong irradiation of a solid may cause the generation of charges only in a very thin surface layer and produces what is effectively a surface charge. In contradistinction, weakly absorbed radiation causes liberation of carriers throughout the bulk of solid and thus creates a space charge. In general, charges produced on the surface

will migrate into the bulk of the solid and form a space charge, unless they are caught by very deep surface traps.

Space charges near the electrodes, even if not produced by uniform illumination of the crystal are certainly present whenever a field is present, and they decay when the field is removed (Bree and Kydd, 1964). The evidence for the space charge present in the electrodes is that the reversal of the applied voltage causes a temporary diminution in current, which gradually returns to its original value. Space charges produced by illumination depend on the wavelength of the incident radiation, they give rise to a reverse current after the removal of the field, which results from the emptying of previously filled traps.

Another cause of space charge generation is likely to be due to inhomogeneous distribution of lattice defects in the imperfect organic solids. Since these defects are likely to act as trapping centres, they cause their vicinity to have a charge density different, even if not in its sign, from that of the other regions of the solid. A space charge then forms, surrounding the inhomogeneity. In order to maintain the electrical neutrality of the crystal as a whole even solids of low conductivity may contain a net electric charge. The radius of this space charge screen may be quite large and its effective scattering cross section calculated per impurity or defect, is very much larger than that of a coulombic centre carrying the same charge.

Space charge effects are of considerable importance to organic semiconductor. Apart from their intrinsic interest, they may profoundly falsify the resistance measurements because of the slow build-up of a space charge, particularly that due to an unsatisfactory and partially blocking contact. Space-charge-limited currents (SCLC) phenomena may be used for

organic solid state devices.

In the trap-free solids, the SCL current is proportional to the square of the applied voltage (Rose, 1955).

$$J \cong 10^{-13} \epsilon \mu_0 V^2 / d^3 \quad (2.10)$$

If only shallow traps are presented, at any one instant, only a fraction of the carriers injected from the contact will be free; the remainder will remain immobile within the traps. Assuming that an equilibrium between carriers remaining free and those in traps has been established, the fraction Θ of the total space charge which remains free may be expressed as (Rose, 1955)

$$\Theta = \left(\frac{N_c}{N_t} \right) \exp \left(- \frac{E_t}{kT} \right) \quad (2.11)$$

Where N_c is the number of carriers injected into the conduction band per cm^3 , i.e. the concentration of free carrier. N_t represents the concentration of shallow trapping levels, which are all assumed to be of equal energy and situated E_t eV below the conduction band. (See Fig.2.12). Defining an effective mobility μ as

$$\mu = \mu_0 \Theta \quad (2.12)$$

where μ_0 stands for the free carrier mobility, the current in the presence of shallow traps becomes (Rose, 1955)

$$\begin{aligned} J &\cong 10^{-13} \Theta \mu_0 \epsilon V^2 / d^3 \\ &= 10^{-13} \left[\left(\frac{N_c}{N_t} \right) \exp \left(- \frac{E_t}{kT} \right) \right] \left(\mu_0 \epsilon V^2 / d^3 \right) \end{aligned} \quad (2.13)$$

It can be seen that the presence of traps causes the concentration of carriers in the conduction band to drop sharply.

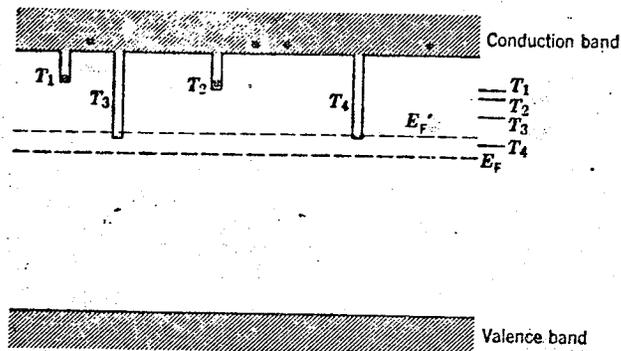


Fig. 2.12 Energy level diagram of a semiconductor with traps. The shallow traps T_1 and T_2 are occupied, while the deep traps T_3 and T_4 are empty. As carriers are injected from the contact, the Fermi-level will be shifted from its equilibrium position to new position.

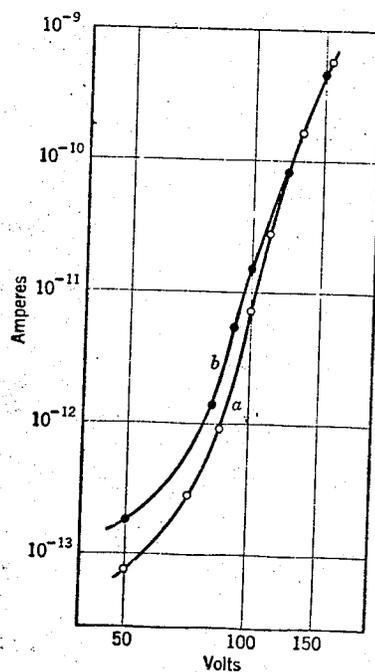


Fig. 2.13 Current versus voltage characteristics for the anthracene crystal of thickness of 134 microns. Curve a was obtained immediately after a constant voltage of 99 volts had been applied for one week. Curve b was obtained 20 hours after curve a. (After Helfrich and Mark, 1963).

The transition voltage V_{TFL} (TFL stands for trap filled limited) can be defined as the voltage at which the Fermi-level lines up with trapping level. The concentration of traps can then be expressed in terms of V_{TFL} (Rose, 1955) as

$$N_t = 10^{-12} V_{TFL} \epsilon / 4\pi e d^2 \quad (2.14)$$

where ϵ is permittivity and d is thickness.

If instead of talking the trapping levels to be discrete, we assume an exponential distribution of trapping states per unit energy interval, $h(E)$, such as

$$h(E) = \left(\frac{H}{kT_c} \right) \exp \left(- \frac{E}{kT_c} \right) \quad (2.15)$$

where E is now the energy in eV measured from the top of the valence band, H stands for the total trap concentration and T_c ($T_c > T$) is a characteristic temperature of the trap distribution.

The current-voltage characteristics obtained by Mark and Helfrich (1962) is shown in Fig. 2.13

On the following assumptions

- (i) The band model is applied to describe the current carrier in the crystal
- (ii) Diffusion of the excess current in the crystal is negligible
- (iii) one of the electrodes forms an "ohmic contact" which is capable of injecting the carriers into the crystal at a sufficient rate.
- (iv) only hole currents are considered and also hole mobility is field independent.
- (v) the Boltzmann statistics are applied to the free carriers in the band, and Fermi-Dirac Statistics to the trapped ones. The density of current J due to an external field applied to the crystal may be evaluated by solving the continuity equation

$$J = \mu p_f(x) F(x) \quad (2.16)$$

and the Poisson's equation

$$\frac{dF(x)}{dx} = \frac{\rho_o(x)}{\epsilon} \quad (2.17)$$

where the functions $\rho(x)$ and $F(x)$ are defined by equations.

$$\rho_o(x) = en(x) \quad (2.18)$$

$$F(x) = \frac{d\psi(x)}{dx} \quad (2.19)$$

where μ is the mobility of the current carrier, $n(x)$ is the particle density, $\rho_o(x)$ is the total charge density, $\rho_f(x)$ is the charge density of free carriers in the band, $F(x)$ is the electric field strength and $\psi(x)$ is the electrostatic potential, e is electronic charge, ϵ is permittivity, x is linear distance variable ($x = 0$ at the injecting electrode, $x = d$ (thickness of the crystal) at the collecting electrode.)

The solution of these equations depends on the particular form of the function $F(x)$. At low injection rates the crystal is free of space charge; and the electric conduction is ohmic. If the density of injected carriers exceeds that of carriers thermally generated in the bulk, a space charge builds-up in the crystal, the effect of which depends on the trapping process. The charge density of free carriers in the band is given by

$$\rho_f(x) = (eN_v) \exp(-E_f(x)/KT) \quad (2.20)$$

where $E_f(x)$ is called quasi steady state Fermi-level, N_v is the effective density of states in the valence band which has the value $2.4 \times 10^{19} \text{ cm}^{-3}$ for anthracene at room temperature. Assuming that the total positive space-charge $\rho_o(x)$ at the distance x from the anode has filled all the traps to a quasi Fermi-level for holes $E_f(x)$, then we have

$$\begin{aligned}
 p_o(x) &= e \int_{E_f(x)}^{\infty} \frac{H}{kT_c} e^{-E/kT_c} dE \\
 &= (eH) \exp \left(- \frac{E_f}{kT_c} \right)
 \end{aligned} \tag{2.21}$$

From equation 2.20. and 2.21 we obtain the relation between the total space charge density

$$\begin{aligned}
 [p_o]^{T_c/T} &= \left[(eH) \exp \left(- \frac{E_f}{kT_c} \right) \right]^{T_c/T} \\
 &= e^{T_c/T} H^{T_c/T} \exp \left(- \frac{E_f}{kT} \right)
 \end{aligned} \tag{2.22a}$$

setting $\lambda = \frac{T_c}{T}$, we can write

$$p_o(x) = N_v e^{-\lambda} H^{-\lambda} [p_o(x)]^{\lambda} \tag{2.22b}$$

From equation (2.16) the current becomes

$$J = \mu N_v e^{-\lambda} H^{-\lambda} [p_o(x)]^{\lambda} F(x) \tag{2.23}$$

Therefore

$$p_o(x) = H e^{(\lambda-1)/\lambda} \left(\frac{J}{\mu N_v} \right)^{1/\lambda} [F(x)]^{-1/\lambda} \tag{2.24}$$

Substitution of Equation (2.24) into (2.17) gives

$$\begin{aligned}
 \frac{dF}{dx} &= \frac{H}{\epsilon} \left(\frac{J}{\mu N_v} \right)^{1/\lambda} \cdot e^{\lambda/\lambda} \cdot [F(x)]^{-1/\lambda} \\
 &= D [F(x)]^{-1/\lambda}
 \end{aligned} \tag{2.25}$$

Using the boundary condition $F(0) = 0$, Equation (2.25) can be solved as

follows

$$\int [F(x)]^{1/\lambda} dF(x) = D dx$$

Integrating both sides gives

$$F(x) = \left(\frac{\ell+1}{\ell} D \right)^{\ell/\ell+1} x^{\ell/\ell+1} \quad (2.26)$$

Thus

$$\begin{aligned} V &= \int_0^d F(x) dx = \int_0^d \left(\frac{\ell+1}{\ell} D \right)^{\ell/\ell+1} x^{\ell/\ell+1} dx \\ &= \left(\frac{\ell+1}{\ell} D \right)^{\ell/\ell+1} \cdot \left(\frac{\ell+1}{2\ell+1} \right) d^{2\ell+1/\ell+1} \end{aligned} \quad (2.27)$$

and

$$D^\ell = \left(\frac{\ell}{\ell+1} \right)^\ell \left(\frac{2\ell+1}{2\ell+1} \right)^{\ell+1} \frac{V^{\ell+1}}{d^{2\ell+1}} \quad (2.28)$$

Hence we obtain

$$J = N_V \mu e^{-\ell} (\epsilon/H)^\ell D^\ell \quad (2.29)$$

From equations (2.28) and (2.29) we can get the current-voltage characteristics with exponential trap distribution

$$J = N_V \mu e^{-\ell} \left(\frac{\epsilon \ell}{H(\ell+1)} \right)^\ell \left(\frac{2\ell+1}{\ell+1} \right)^{\ell+1} \frac{V^{\ell+1}}{d^{2\ell+1}} \quad (2.30)$$

In the particular case, when traps are either absent or completely filled, all injected carriers participate in the conduction process, then

$f_F(x) = f_O(x)$, and the current density follows Mott-Gurney law for one-carrier injection.

$$J_M = \frac{q}{8} \mu \epsilon \frac{V^2}{d^3} \quad (2.31)$$

By setting J equal to J_M we obtain the transition voltage V_{TFI} for the current to transfer from trap limited to trap-free space-charge-limited

current. From equation (2.30) and (2.31) we obtain the V_{TFL} as follows.

$$V_{\text{TFL}} = \frac{ed^2}{\epsilon} \left[\frac{q}{8} \frac{H^{\lambda}}{N_v} \left(\frac{\lambda+1}{\lambda} \right)^{\lambda} \left(\frac{\lambda+1}{2\lambda+1} \right)^{\lambda+1} \right]^{\frac{1}{\lambda-1}} \quad (2.32)$$

which can be reduced to Lampert's formula (1956) if we set $\lambda \rightarrow \infty$. This is for the case when the traps are uniformly distributed and current-voltage curve become infinitely steep. We thus have

$$\lim_{\lambda \rightarrow \infty} V_{\text{TFL}} = \frac{ed^2 H}{\epsilon} \quad (2.33)$$

The total trap concentration can now be obtained in two ways. Solutions of equation (2.29) yields

$$H = \frac{\epsilon \lambda}{\lambda+1} \left[\frac{N_v \mu}{J e^{\lambda-1}} \left(\frac{2\lambda+1}{\lambda+1} \right)^{\lambda+1} \frac{V^{\lambda+1}}{d^{2\lambda+1}} \right]^{\frac{1}{\lambda}} \quad (2.34)$$

Alternatively, if the transition voltage V_{TFL} can be measured we obtain H from Equation (2.32).

$$H = \frac{\lambda}{\lambda+1} \left(\frac{\epsilon V_{\text{TFL}}}{ed^2} \right)^{\frac{\lambda-1}{\lambda}} \left[\frac{8}{9} N_v \left(\frac{2\lambda+1}{\lambda+1} \right)^{\lambda+1} \right]^{\frac{1}{\lambda}} \quad (2.35)$$

which is independent of μ and J . Finally, the quasi Fermi-level for holes, can be obtained by differentiating Equation (2.26) and substituting it into Equation (2.21). Thus

$$E_f(x) = kT_c \ln \left[\frac{(\lambda+1)^2}{\lambda(2\lambda+1)} \frac{\epsilon H d^2}{\epsilon V} \left(\frac{x}{d} \right)^{\lambda+1} \right] \quad (2.36)$$

Recently, the double injection of space-charge-limited current have also been observed in anthracene. The behaviour of the SCL transition current have been further discussed by Helfrich and Schneider (1966),

Delacote, et al (1964), and Silver, et al (1962).

2-6 Photoconductivity of Anthracene

When anthracene is illuminated its conductivity will increase many times higher than its dark conductivity. The phenomena of photoconduction in anthracene have been studied extensively for many years. The present section is mainly organized in the sequence of the questions that might occur in a photoconductivity experiment; how do the carriers generate? how do they move? how do they become trapped? and how do they recombine?

In most inorganic semiconductor photocarrier generation is a simple process, the absorbed photon excites an electron and hole pair directly. But in organic crystals generation is more complex. The photoconduction excitation spectrum generally is identical to the crystal absorption spectrum (See Fig.2.14).

The absorption spectra of organic molecular crystals can be entirely understood in terms of Frenkel exciton (Kittel, 1968). This implies that the first step in photocarrier generation involves the creation of non-conducting excitons.

The excitons create carriers via secondary processes, which are known as (1) A single exciton processes in which one exciton yields one carrier, either an electron or a hole. This is observed predominantly near the crystal surface. (2) A double-exciton process in which two excitons annihilate to yield an electron-hole pair. This is observed in the crystal bulk.

The direct process of photon absorption to create an electron and a hole, each in its lowest energy state, is difficult to observe experimentally simply because the various exciton transitions in these low dielectric constant molecular crystals steal all the intensity from the "band to band" transition. However, it is obvious that a photon of very high energy, e.g. X-rays, can cause ionization of the crystal, although the electron and the hole may not be in their lowest possible energy state immediately after creation.

If a beam of light of energy of the order of several eV (ultra or visible regions) strikes an anthracene molecule inside the crystal, an electron will be excited to one of the upper energy levels of molecule, specifically to the first excited "singlet" state which is 3.15^{eV} above the ground level, or to the excited "triplet" state which is 1.83^{eV} above the ground level. The vacancy in the ground level of molecule left by the excited electron can be regarded as hole. On the average the electron will remain in the excited state about 10^{-4} seconds before recombining with the hole in the ground state. It has been found that during the interval of this 10^{-4} seconds the excitation (a hole-electron pair) can be transferred as a unit, from one molecule to its neighbour (in some cases to a molecule some distance away from its neighbour). There can be as many as 10,000 transfers taking place before the excitation disappears. This excitation, or hole-electron pair on the same molecule is called singlet exciton or triplet exciton; and it diffuses through the crystal like a particle, with exception that it transfers energy and not matter.

In the course of its diffusion the exciton may strike the inner surface of the crystal, but the exciting light is so highly absorbed that practically all the excitons are created very close to the illuminated

surface. When the exciton strikes the surface, several things may happen. If there is an electrode at the surface, the exciton can react with the electrode in such a way that the electron of the crystal enters the electrode and the hole in the molecule diffuses away from the surface under the influence of the external electric field.

The exciton can create charge carriers even if no electrode is in contact with crystal. When an exciton strikes an impurity such as oxygen at the surface of the crystal, the electron is taken up by the oxygen molecule and the hole is then free to move. Another example of carrier generation which does not involve the surface of the crystal is that when two excitons meet on the same molecule at the same time they will annihilate each other. The energy given off in this case is the sum of the two energies of the two excitons, and it is usually so large that the molecule at the site of the collision may be ionized. Thus the excitons can produce charge carriers, either by utilizing the additional potential energy of an electrode or an impurity or by mutual annihilation of two excitons.

Some impurities inside the anthracene would also form a different type of exciton which is called charge transfer exciton (Wannier exciton) ($\sim 2.9\text{eV}$). In this type of exciton, the electron and hole are located separately in the host and foreign molecules. The charge-transfer exciton also plays very important role in charge carrier generation mechanisms. A simple model of charge transfer exciton suggested by Silver and Sharma (1967) is based on the following assumptions.

- (i) Carriers are generated by direct optical absorption (auto-ionization of the excitons is included for completeness)
- (ii) Carriers are trapped during the process of recombination in

in charge-transfer exciton states.

- (iii) The charge-transfer excitons may decay or be thermally dissociated (detrapping), charge transfer excitons may also be produced directly from autoionization levels.

The concentration of charge carriers is governed by the following two rate equations

$$\frac{dn_c(x,t)}{dt} = \alpha I(x,t) + \phi \gamma I(x,t) + h n_{CT}(x,t) - R n_c^2(x,t) \quad (2.37)$$

and

$$\frac{dn_{CT}(x,t)}{dt} = R n_c^2(x,t) + \delta \gamma I(x,t) - h n_{CT}(x,t) - \beta n_{CT}(x,t) \quad (2.38)$$

where n_c is the density of free carriers, n_{CT} is the density of charge-transfer excitons (Wannier excitons) α is the absorption coefficient for the band-to-band transition, ϕ is probability of auto-ionization, γ is the absorption coefficients of the non-conducting level, δ is the probability for generation of a charge-transfer exciton directly from the nonconducting level, β^{-1} is the lifetime of the charge transfer exciton, $h = \nu \exp(-E_{CT}/k_{CT})$ is the probability per second for thermal dissociation of the electron trapped in a charge-transfer exciton state and $I(x,t) \cong I_0(t) \exp(-(r+d)x)$ is the light intensity.

2-6.1 The Mechanisms of Photocarrier Generation

The difficulty of determining the mechanism of photocarrier generation can be seen from the following list of all known processes which

have been summarized by Gutmann and Lyons (1967) and will be discussed in the following.

One quantum processes

A. Exciton-Surface Processes

1. Collision of an exciton with a surface, especially when suitable gas is absorbed.
2. Collision of an exciton with a dissociation centre which traps one of the carriers.
3. A process involving a triplet exciton rather than a singlet.
4. A collision of an exciton with an impurity host molecular-pair.
5. Liberation of a trapped carrier by a photon or an exciton.

B. Direct Processes

1. Excitation across an energy gap in the pure crystal to form an electron and a hole.
2. Spontaneous ionization of an exciton.
3. Thermal ionization of an exciton.
4. Field ionization of an exciton.

C. Double-quantum processes

1. Photon plus a singlet exciton.
2. Photon plus triplet exciton.
3. Two photons.
4. Collision of two singlet excitons.
5. Collision of two triplet excitons.
6. Collision of singlet and triplet excitons.
7. Collision of two ion pair excitons, probably triplet.

In some cases it is likely that more than one process may occur simultaneously.

These three important processes will be discussed in the following.

A. Exciton-surface processes

The older experimental evidence for this mechanism (exciton-surface process) has been reviewed by Kepler (1964) and Kommandeur (1965). It is the carrier generation process that predominates in most photoconductivity experiments, i.e. where photoconduction is produced by light intensity absorbed in the lowest singlet band.

The importance of reactions of excitons at the crystal surface for the photoconduction of anthracene was first stated by Lyons (1955). He worked with a surface type of cell in which the light is incident on the surface between the electrodes. The excitation spectrum of the photocurrent is similar to the absorption spectrum (maxima and minima at the same wavenumber in either spectrum). This can be explained in terms of generation of charge carriers in reactions of excitons at the surface of the crystal. This qualitative picture has been shown by Eremento and Medveder (1962) and Steketee and de Jonge (1962) to be in excellent quantitative agreement with experimental results for steady photocurrents in anthracene. Assuming the illuminated surface to be planar and letting the distance from the surface be x , the differential equation for the exciton density, $n(x)$, at steady state is

$$0 = \epsilon_x I_0 \exp(-\epsilon_x x) - n(x)/\tau + D \frac{d^2 n}{dx^2} \quad (2.39)$$

Here ϵ_x is the extinction coefficient, I_0 the incident photon flux,

τ the fluorescence lifetime, and D the exciton diffusion constant with

boundary conditions $n(0) = n(\infty) = 0$, the exciton at the surface $x = 0$ is

$$D \left(\frac{du}{dx} \right)_0 = I_0 (1 + \frac{1}{\epsilon_x \lambda})^{-1} \quad (2.40)$$

where

$$\lambda = (D\tau)^{1/2} \quad (2.41)$$

is the exciton diffusion length.

According to the assumed mechanism the photocarrier generation rate, and hence the steady-state photocurrent, should be proportional to the exciton flux at the surface. Therefore, plots of the reciprocal of the current versus the reciprocal of the extinction coefficient should yield straight lines. Values of the exciton diffusion length can be calculated from the slopes of these plots; these vary from crystal to crystal according to Steketee and de Jonge, who reported the values of the exciton diffusion length to be 700 - 2,000 Å.

Because an exciton can react to give a hole or an electron only at the crystal surface the higher the extinction coefficient the closer to surface the exciton is created, therefore the higher the probability that it will diffuse to the surface before it decays by fluorescence. Unequal numbers of holes and electrons are created for a given photon flux, indicating that the surface state or impurity with which the exciton reacts to produce a hole is different from that with which it reacts to produce an electron.

B. Direct process

A direct process is one in which the absorbed photons directly create free electron-hole pairs without intermediate steps involving excitons.

The photocarrier generation mechanism should be distinguishable experimentally from the single exciton surface mechanism by the following properties: (a) The photocurrent spectral response should not be identical to the absorption spectrum. (b) The yields per photon of electrons and holes should be equal (c) The yields should be insensitive to surface preparation and to the ambient atmosphere. (d) The yields should not be temperature activated.

Castro and Hornig (1965) performed an experiment showing a direct photocarrier generation process. They studied quantum yields in anthracene using the pulse method. In the region of the first singlet absorption band, 3950 Å, they observed only the exciton-surface process. At shorter wavelengths, 2500 to 3000 Å, the generation mechanism was distinctly different. So they tentatively identified the photon energy at maximum photocarrier yield 4.4^{ev} , as the band-gap energy of anthracene. But it is likely that the direct process of Castro and Hornig (1965) is one in which the carriers are created with excess kinetic energy of some unknown amount; the true band-gap energy is less than 4.4^{ev} by just this amount.

Silver (1967) has undertaken a quantitative reinterpretation of the data of Castro and Hornig (1965) by considering the effects of the large electron-hole capture radius. He found excellent agreement between the theoretical and experimental spectral dependence by assuming the minimum energy necessary to create a ground-state hole and a plane-wave electron to be 4.0^{ev} . This value now represents the best current estimate of the smallest photon energy required for direct carrier generation in anthracene.

C. Double quantum processes

Intrinsic photocarrier generation by the mutual annihilation of two singlet excitons was proposed some years ago by Northrop and Simpson

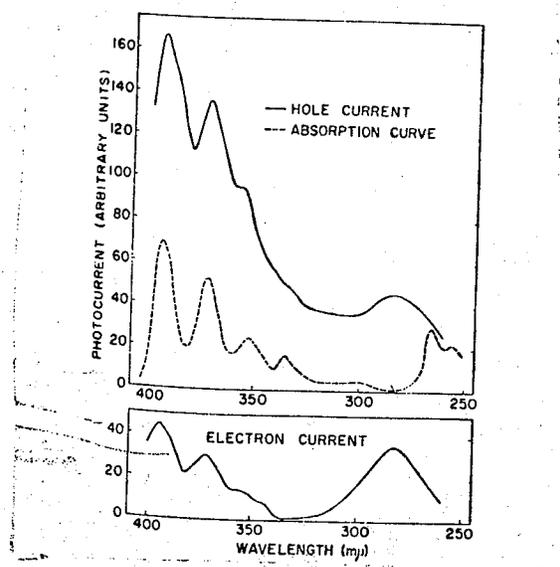


Fig. 2.14 Spectral dependence of dc photocurrent in anthracene. Note: the arbitrary photocurrent units are the same for both the hole and electron curves. (After Chaiken and Kearns, 1966).

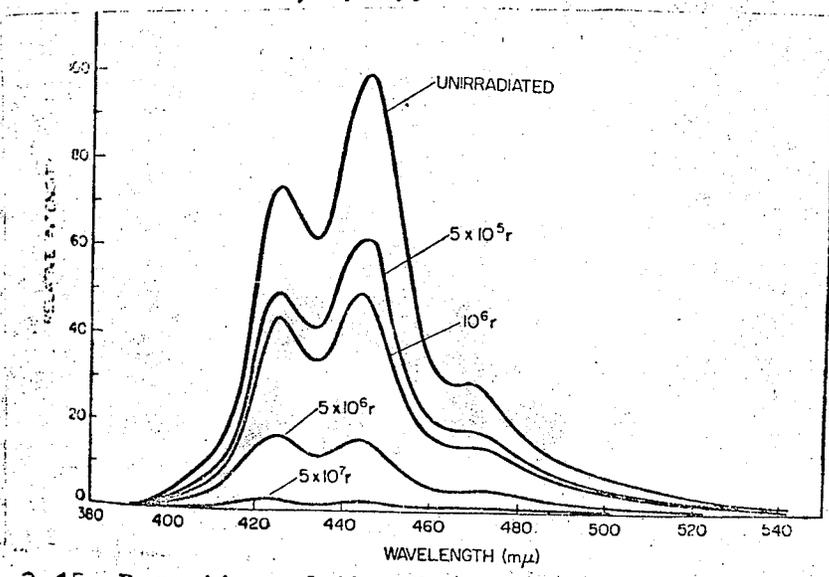


Fig.2.15 Degradation of the fluorescence spectral intensity due to various of Co gamma-radiation for anthracene crystal (After Sharm, 1961).

(1958) to explain their data on surface photoconduction in anthracene. Burshtein (1963) interpreted much of the old work before 1961 on steady state photocurrents. Choi and Rice (1963) pursued the possibility of exciton-exciton generation in an elegant theoretical paper, and their work led directly to the experimental observation of this phenomenon by Silver, Olness, Swicrod and Jarnagin (1963). The reaction considered was the following: In an initial state the crystal contains two singlet excitons and in a final state the excitons have annihilated one another to yield a hole in the lowest hole band and electron in a highly excited level. Suppose two singlet excitons in anthracene have more than sufficient energy to create an electron-hole pair. If both carriers were to be created in their lowest energy band than many lattice phonon would have to be created as well to take up the excess energy. Kearns (1963) extended the theory of Choi and Rice to triplet-triplet and singlet-triplet exciton annihilations. In anthracene the triplet-singlet process was predicted to predominate over singlet-singlet process for steady-state photocurrent, and vice versa for pulsed photocurrents. Silver et al (1963) in their ingenious double light-pulse experiment found only the singlet-singlet process as predicted.

2.7 Radiation Effects in Anthracene

The common radiations may be divided into four types (i) Heavy charged particles such as protons, heavy ions, α -particles and mesons (ii) Light charge particles such as electrons (β -rays) (iii) Neutral particles such as neutrons, (iv) Electromagnetic radiations such as γ -rays and x-rays.

In this section, we shall confine our discussion to the effects of radiation in anthracene. The radiation damage was observed by Birks and

Black (1951) in anthracene crystals bombarded by α -particles. Schulman, Etzel and Allard (1957) have observed the degradation of the photoluminescence efficiency of anthracene crystal under γ -rays (Co^{60}) and electron radiation over the dose range 3×10^5 to 2×10^{18} rep. The relative photoluminescence efficiency I/I_0 with Co^{60} γ -ray dose D in rep is given by

$$I/I_0 = \frac{1}{1 + AD} \quad (2.42)$$

where $A = 8.5 \times 10^{-7}$ rep $^{-1}$ for anthracene. This corresponds to a value of 1.4×10^8 erg-cm $^{-1}$ for $E_{1/2}$ where $E_{1/2}$ is half value of initial energy which is in agreement with α -irradiation value obtained by Black (1953).

No recovery has been observed in anthracene stored for long periods in the dark (photochemical changes can occur in sunlight) or heated for several hours (Birks and Black, 1951; Black, 1953; Schulmann et al, 1957), but Attix (1959) reported a slight recovery when heating for an hour at 100°C. The γ -ray irradiations in air, vacuum or helium produce similar degradation effects indicating that the radiation damage is not due to oxidation.

Irradiation with intense ultraviolet light also produces a deterioration of fluorescence efficiency in anthracene (Black, 1953) indicating that there may be some relation between the radiochemical and photochemical changes. These probably result in the formation of new molecular species, such as dimers. Photodimerization of anthracene in solution is a well known process, which causes fluorescence quenching. Schulmann et al (1957) have observed new luminescence emission bands in anthracene produced by prolonged γ -irradiation.

Detailed studies of the changes in the fluorescence spectra of anthracene crystals under Co^{60} γ -irradiation have been made by Sharn (1961). His results on the degradation of the anthracene fluorescence spectrum are given in Fig. 2.15. Although the results are generally similar to that described by Equation (2.42), there are some differences between the radiation dose for different peaks in the fluorescence spectrum. This can be explained in terms of excitons and quenching centres of different energies. An alternative explanation would be to attribute the differences to the absorption and luminescence spectra of the damaged molecules. Spectrometric studies of irradiated crystal usually give useful information about damaged molecular species.

Clark, Northrop and Simpson (1962) have studied radiation damage in thin evaporated films of anthracene, and of anthracene doped with various concentration of naphthacene, under irradiation by Po^{210} α -particles and H^3 β -particles. They showed that the quenching due to radiation damage has an identical effect on the α -particle and β -particles scintillation efficiencies and on the photofluorescence efficiency. This confirms that the permanent radiation affects the secondary scintillation processes (energy transfer) only, and is not relevant to the primary scintillation processes (ionization quenching).

CHAPTER 3

ORGANIC SEMICONDUCTOR THIN FILMS

The most important difference between a crystal and a thin film is that in a thin film, the idea of a periodic structure can rarely be applied. Most films are polycrystalline or amorphous, and even if a film is single-crystalline, the surface and size effects play an important role in the determination of its properties. Because of the smallness of film thickness, it is often necessary to consider the electrodes as an integral part of the whole film when discussing its electrical properties.

Since anthracene has a very low conductivity, anthracene thin film can be considered as an insulating thin film. Thus before discussing the properties of anthracene thin films, it is desirable to give a brief review of some existing physical models and carrier transport processes of insulating films.

3-1 Models of Insulating Thin Films.

(a) Fowler-Nordheim field or tunnel emission model.

It is possible to induce field emission into any insulator without causing intrinsic breakdown. Consider very thin insulating film placed between two metal electrodes as shown in Fig. 3.1. If the insulating film is sufficiently thin, (≈ 10 to 100 \AA), tunneling current flows between the two metals in both directions as shown in Fig. 3.1(a). When a field is applied between the two metals, more electrons will tunnel from the negative electrode than from the reverse direction, because the field modifies the barrier width. The net tunneling current is proportional to

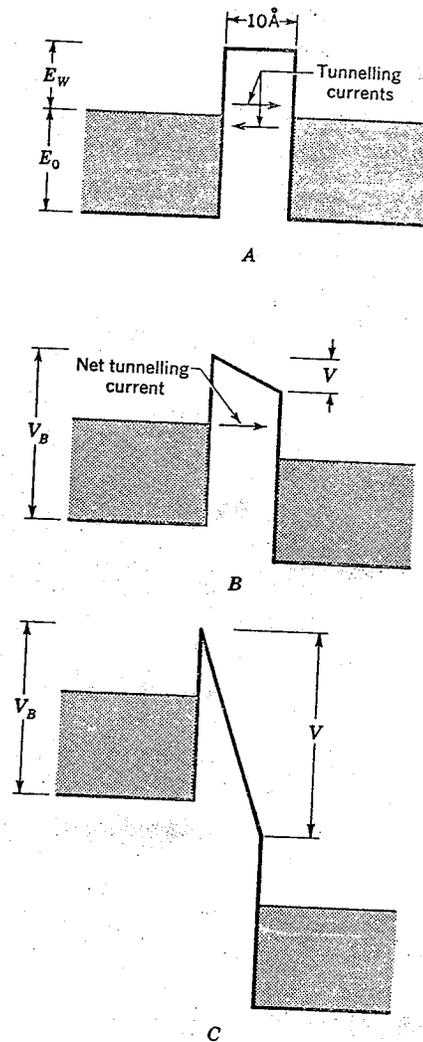


Fig. 3.1. Tunneling currents through an insulating film between two metals for (a) no applied potential; (b) small applied potential; (c) large applied potential.

the tunneling probability. For small applied field, the film appears to have a constant resistance although the film itself may have a much higher resistance. When the applied voltage is greater than V_B (see Fig.3.1(c)), sufficient states are available in the positive metal and width of the barrier becomes smaller. The current tunneling through a triangular barrier shown in Fig.3.1(c) is given by the well known Fowler-Nordheim field emission Equation (Fowler and Nordheim, 1928).

$$J = \left(\frac{e^3}{8\pi h \phi_B} \right) \mathcal{E}^2 \exp \left[- \frac{4K \phi_B^{3/2}}{3e \mathcal{E}} \right] \quad (3.1)$$

or

$$J = A_F \mathcal{E}^2 \exp(-b/\mathcal{E}) \quad (3.2)$$

where

$$K^2 = \frac{8\pi^2 m^*}{h^2}$$

$$A_F = e^3 / 8\pi h \phi_B$$

$$b = 6.8 \times 10^9 \phi_B^{3/2}$$

$$\mathcal{E} = V/d$$

and ϕ_B is the barrier height \mathcal{E} is the applied electric field, m^* is the effective mass, V is the applied voltage and d is the insulator thickness.

(b) Schottky and Poole-Frenkel emission models

For a thick film (The Fowler-Nordheim model applies only to a very thin film), the current flowing through it increases exponentially with the square root of the applied field. This type of current-voltage characteristics is usually ascribed to Schottky emission mechanism.

The Schottky emission refers to the emission of the electrons from the metal electrode into the conduction band of the insulating film over an imaginary force of interfacial barrier, which is lowered by the electric field. The current density due to Schottky emission into an insulating film is given by (Simmon, 1969)

$$J = \frac{4\pi m^* e k^2}{h^3} T^2 \exp \left[-q \left(\Phi_B - \left(\frac{q \epsilon}{4\pi \epsilon_i} \right)^{1/2} \right) / kT \right] \quad (3.3)$$

or

$$J = A^* T^2 \exp \left[S_s \epsilon^{1/2} - \Phi_B / kT \right] \quad (3.4)$$

where

Φ_B = the interfacial barrier height

ϵ_i = insulator dynamic permittivity

A^* = effective Richardson constant.

and

$$S_s = \left(\frac{q^3}{4\pi \epsilon_i} \right)^{1/2} / kT \quad (3.5)$$

The Schottky emission process is electrode-controlled.

Another conduction mechanism which results in an equation of similar form is the Poole-Frenkel effect. The Poole-Frenkel emission is due to field-enhanced thermal excitation of trapped electron into the conduction band. For trap states with coulomb potentials, the expression is virtually identical to the Schottky emission. The current density equation is then given by

$$J = G_0 \epsilon \exp \left[S_{PF} \epsilon^{1/2} - \chi / kT \right] \quad (3.6)$$

where G_0 is a function of density of trapping centers

χ is the barrier height, and

$$\begin{aligned} \delta_{PF} &= 2 \delta_s = 2 \left(\frac{q^3}{4\pi\epsilon_i} \right)^{1/2} / kT \\ &= (q/\pi\epsilon_i)^{1/2} / kT \end{aligned} \quad (3.7)$$

The barrier height, however, is the depth of the trap potential well, and the quantity δ_{PF} is larger than that for the case of Schottky emission by a factor 2, since the barrier lowering is twice as large due to the immobility of the positive charge. Poole-Frenkel process, in contrast to the Schottky model, is bulk controlled.

(c) Frohlich - O'Dwyer Model

O'Dwyer (1966) has recently calculated the voltage-current characteristics of insulating films for film thickness of a few hundred to a few thousand Angstroms with the help of a dielectric model originally proposed by Frohlich (1947). His calculation is based on a field-dependent conductivity, which is caused by thermal and field-excitation of deeply trapped electrons into shallow traps and into the conduction band, (see Fig.3.2), and an emission process from the cathode of either Fowler-Nordheim or Schottky type. O'Dwyer has employed some reasonably typical data to calculate the voltage-current characteristics, taking into account the space charge effect.

In terms of the bulk properties of the dielectric, O'Dwyer has derived the space-charge density (O'Dwyer, 1966) as

$$n = n_0 \left[\left(\frac{J}{q_0 \epsilon} \right) \exp \left(-\beta \frac{\epsilon^2}{\epsilon^* z} \right) - 1 \right] \quad (3.8)$$

where n_0 is the space-charge-free electron density over all traps and conduction level, σ_0 is the zero-field conductivity, ϵ^* is the breakdown field of the dielectric, J is the current density and β is the ratio of the depth of the deep traps to energy range of the shallow traps, ($\beta = \frac{W}{eV}$). By combining Equation (3.8) and Poisson's equation, and separating the variables, O'Dwyer obtained the expression for the barrier height.

$$\chi = \left(\frac{\epsilon}{n_0 e} \right) \int_{\epsilon_c}^{\epsilon} \left[\left(\frac{j}{\sigma_0 F} \right) \exp(-\beta \epsilon^2 / \epsilon^{*2}) - 1 \right]^{-1} d\epsilon \quad (3.9)$$

where ϵ_c is the electric field at the cathode. The current density relation is then given (O'Dwyer, 1966) by

$$J = \sigma_0 \epsilon \exp \left[\beta \left(\frac{\epsilon^2}{\epsilon^{*2}} \right) \right] \quad (3.10)$$

The characteristics is not a linear relation between $\log J$ and $\epsilon^{1/2}$ (so called Schottky Plot), but rather $\log J$ is approximately proportional to ϵ^2 .

(d) O'Dwyer's Double ejection model

O'Dwyer (1968) also proposed another model for steady-state current flow at high fields in a dielectric material with blocking contacts. His model was based on the assumption that finite collision ionization mechanism exists in dielectric material, and that the ionization process produces charge carriers at a rate exceeding that of recombination. This charge carrier generation can be either Fowler-Nordheim emission type or Schottky emission type.

Using the current continuity equation and Poisson's equation, and defining a collision ionization function as

$$\sigma_i = (d_n n + d_p p) \exp\left(-\frac{F}{\xi}\right) \quad (3.11)$$

and

$$\frac{dn}{dp} = \frac{\mu_n}{\mu_p} \quad (3.12)$$

O'Dwyer obtained the following equation

$$\frac{\partial^2 \xi}{\partial x^2} = \left(\frac{2q}{\epsilon}\right) \sigma_i \left(\frac{1}{\mu_n} + \frac{1}{\mu_p}\right) \quad (3.13)$$

where F is constant high field strength (e.g. 5×10^5 V/cm), ξ is electric field strength, d_n and d_p are constants with the dimension of inverse time (sec^{-1}). Substitution of Equations (3.11) and (3.12) into Equation (3.13) yields

$$\frac{\partial^2 \xi}{\partial x^2} = \left(\frac{A}{\xi}\right) \exp\left(-\frac{F}{\xi}\right) \quad (3.14)$$

where

$$A = \left(\frac{2d_n}{\epsilon \mu_n}\right) \sigma_i \left(\frac{1}{\mu_n} + \frac{1}{\mu_p}\right) \quad (3.15)$$

Introducing the following dimensionless quantities

Normalized distance

$$X = A^{1/2} x / F^{3/2}$$

Normalized field

$$E = \xi / F \quad (3.16)$$

Normalized current

$$\Gamma = \int_0^{\infty} E^{-1} \exp\left(-\frac{1}{E}\right) dx$$

From Equation (3.14), (3.15) and (3.16), the current can be expressed as

$$J = \left(\frac{d_n}{\mu_n} \right) \left(\frac{F \epsilon}{2} \right) \left(\frac{1}{\mu_n} + \frac{1}{\mu_p} \right)^{-1} \Gamma^2 \quad (3.17)$$

the distances between two electrodes as

$$x = \left(\mu_n H / d_n \right) \left(\frac{x}{\Gamma} \right) \quad (3.18)$$

and the mean field strength

$$\Sigma = \frac{V}{x} = \frac{F}{x} \int_0^x E dx \quad (3.19)$$

(e) Space-charge-limited Current (SCLC) Model

The above four models apply to dielectric films with non-ohmic contacts. But for dielectric films with ohmic contacts, the current is then determined by the space charge inside the films. Sumann (1968) was the first to make measurements of space-charge limited current (SCLC) in evaporated thin films of organic semiconductor (Copper phathocyanine). He measured the dark current as a function of temperature, thickness and ambient gas. Applying a simple band model, he explained most of the relevant features of experimental SCLC results and, calculated the trap depth, trap distribution, mobility and position of **Fermi**-level. Sumann's samples were produced in a vacuum of 10^{-5} torr. Ohmic contacts were made by evaporating gold on to the surface of organic semiconductor films. The structure of gold/CuPhth thin-film/gold causes injection of carriers, but until the density of injected hole become comparable with the density in thermal equilibrium \bar{P} , the current density follows ohm's law

$$J = \bar{p} \mu e_0 V/d \quad (3.20)$$

The density of holes in thermal equilibrium is given by

$$\bar{p} = N_V \exp (E_{F_0} / kT) \quad (3.21)$$

where μ is the mobility in $\text{cm}^2/\text{v-sec}$

e_0 is the electronic charge

V is the applied voltage

d is the thickness of the film

and E_{F_0} is the equilibrium Fermi-level measured from the valence band edge.

By examining the behaviour of the current-voltage characteristic under injection conditions, the distribution of the total free carrier density in quasi-thermal equilibrium can be expressed as

$$P = p_i + \bar{p} = N_V \exp (E_F / kT) \quad (3.22)$$

where E_F is the steady-state Fermi-level, and

p_i is the injected-carrier density

To include trapping effects, Sumann assumed that the trapping states were distributed in energy as a Gaussian distribution.

$$P_t(E) = P_0 \exp (E / kT_c) \quad (3.23)$$

where P_0 is the density of defects near the edge of the valence band per unit energy and T_c is a parameter which describes how fast the defects fall off with energy E .

The density of filled traps (which lie above the Fermi-level) is

$$P_t = kT_c P_0 \exp \left(\frac{E_F}{kT_c} \right) \quad (3.24)$$

The quasi-Fermi level for an exponential distribution of traps given by Equation (3.23) can be determined by equating the total injected charges

to the charges in traps which are in thermal equilibrium with the free carriers normally present below V_x (before injection), and the carriers which have been injected then trapped above V_x ; where V_x is defined as the voltage at which the total current is approximately twice what would flow in the absence of injection. P_t is usually greater than P_0 implying that most of the injected charges goes into trap.

Since

$$\begin{aligned} Q &= \frac{\epsilon_i V_x}{d \epsilon_0} + \frac{\epsilon_i V}{d \epsilon_0} \\ &= d \int_{-\infty}^{E_{F_0}} P_t(E) dE + d \int_{E_F}^{E_{F_0}} P_t(E) dE \\ &= d \int_{-\infty}^{E_{F_0}} P_0 \exp \left(\frac{E}{kT_c} \right) dE + d \int_{E_F}^{E_0} P_0 \exp \left(\frac{E}{kT_c} \right) dE \\ &= P_0 d \cdot kT_c \exp \left(\frac{E_F}{kT_c} \right) = \frac{\epsilon_i}{d \epsilon_0} (V_x + V) \end{aligned} \quad (3.25)$$

therefore we have

$$E_F = kT_c \ln \left[\frac{\epsilon_i}{P_0 kT_c \epsilon_0 d^2} (V_x + V) \right] \quad (3.26)$$

Defining

$$V_m = \frac{kT_c P_0 \epsilon_0 d^2}{\epsilon_i} \quad (3.27)$$

where ϵ_i is the permittivity. Then Equation (3.26) becomes

$$E_F = kT_c \log \left[(V + V_x) / V_m \right] \quad (3.28)$$

when V is small compared to V_x , the injected charge is negligible. Then we can write

$$\begin{aligned} E_F &= E_{F0} = kT_c \cdot \log \left(\frac{V_x}{V_m} \right) \\ &= kT_c \cdot \log \left(\bar{P}t / kT_c P_0 \right) \end{aligned} \quad (3.29)$$

The current relationship can be found by examining the ratio

$$\frac{P}{\bar{P}} = \exp \left[\frac{(E_F - E_{F0})}{kT} \right] \quad (3.30)$$

Thus we obtain

$$J = P \mu e_0 \frac{V}{d} = \bar{P} \mu e_0 \exp \left[\frac{(E_F - E_{F0})}{kT} \right] \quad (3.31)$$

Substituting the E_F and E_{F0} from Equation (3.28) and (3.29) into Equation (3.32) we obtain

$$\begin{aligned} \frac{E_F - E_{F0}}{kT} &= \frac{T_c}{T} \left[\log \left(\frac{V + V_x}{V_m} \right) - \log \frac{V_x}{V_m} \right] \\ &= \frac{T_c}{T} \left[\log \frac{V + V_x}{V_m} \right] = \log \left(\frac{V + V_x}{V_m} \right)^{T_c/T} \end{aligned} \quad (3.32)$$

setting

$$\frac{T_c}{T} = \ell \quad (3.33)$$

Equation (3.32) becomes

$$J = \bar{P} \mu e_0 \left(\frac{V + V_x}{V_x} \right)^\ell \frac{V}{d} \quad (3.34)$$

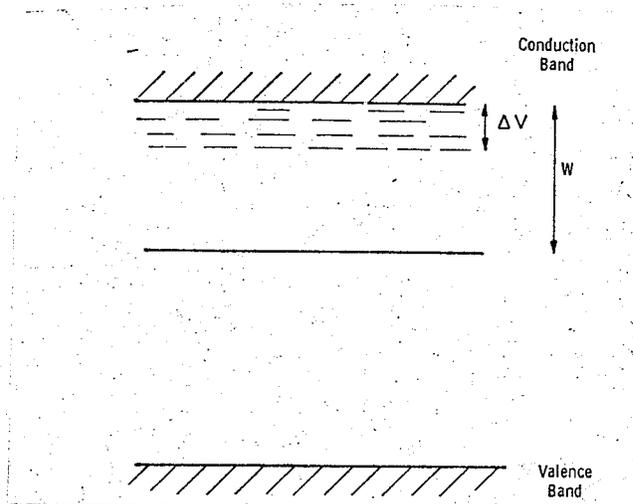


Fig. 3.2 Electronic energy level diagram of idealized Frohlich-O'Dwyer model.

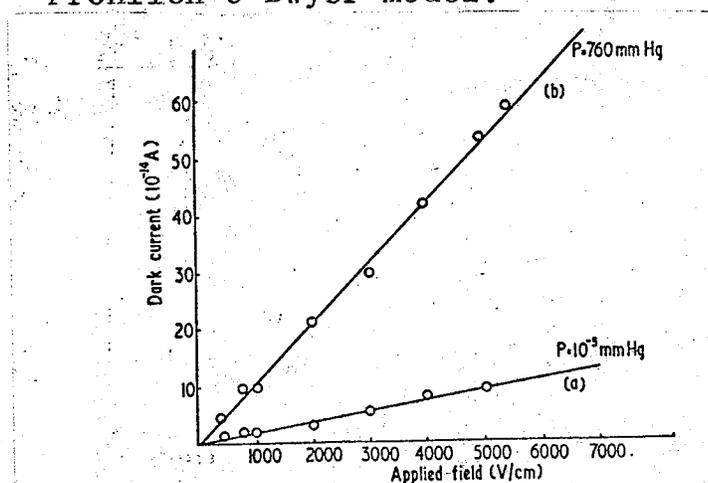


Fig. 3.3 Current-voltage curves for anthracene films under different oxygen pressures. The films remain ohmic even at high oxygen pressures, though, again the current is greatly reduced at lower pressure. (After Gheorghita-Oancea, 1961)

At sufficiently high voltages that is $V > V_x$, Equation (3.34)

becomes

$$J = N_v \mu e_0 \left(\frac{\epsilon}{kT_c P_0 e_0} \right)^{\rho} \frac{V^{\rho+1}}{d^{2\rho+1}} \quad (3.35)$$

Equation (3.35) shows also the explicit dependence of the current on the film thickness. This equation is very similar to the Mark and Helfrich's steady-state SCLC equation (See Sec.2-4).

$$J \propto \frac{V^{\rho+1}}{d^{2\rho+1}} \quad (3.36)$$

Electrical conduction phenomena in thin films of some organic polymers have also been investigated by Caserta, Rispoli and Serra (1969). They found that the current-voltage characteristics of polymethylmetacrilate (PMMA), polyvinylformal (PVF), and polyethylene-terephthalate (PET) films display a space-charge-limited current (SCLC) and a uniform distribution of traps within the energy gap.

3-2 Anthracene thin-film

Northrop and Simpson (1956) investigated the evaporated films of anthracene, using lead as contact electrode material. They found that the conductivity of anthracene thin film becomes non-ohmic at fields in excess about 3000 V/cm, and resistivity at room temperature is about $5 \times 10^{14} \Omega\text{-cm}$, and it follows the usual semiconduction relation

$$\sigma = \sigma_0 \exp(-E/kT)$$

For anthracene, $\sigma_0 = 2 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$, $E = 1.93 \text{ eV}$.

Gheorghita-Oancer (1962) observed the linear dependence of

conductivity on anthracene thin film at a field up to 7 kV/cm as shown in Fig.3.3. They also showed that the observed results are strongly affected by the ambient gases and hydrostatic pressure of pressure of 10^{-5} mm Hg .

Lohanick, Cook and O'Dwyer reported that conduction in anthracene thin-film governed by both electrode injection and electric processes in the bulk. Using double ejection model, they suggested that electron and holes of equal mobility μ , produce ionization at a rate of $\alpha \exp\left(-\frac{F}{\epsilon}\right)$ per second. This causes space charges, and the current is carried by the electron and holes in the effective field produced by all the charges. Using the following value for F , α , and μ in Equation (3.11)

$$\begin{aligned} F &= 2.5 \times 10^5 \text{ V/cm} \\ \alpha &= 40 \text{ sec}^{-1} \\ \mu &= 3 \times 10^{-7} \text{ cm}^2/\text{v-sec} \end{aligned}$$

they calculated the mobility of electrons to be $1 \text{ cm}^2/\text{v-sec}$. The low value of the mobility as compared to the true carrier mobility of anthracene is attributed to the difference in the trapping effects.

CHAPTER 4

EXPERIMENTAL PROCEDURES

4-1 Preparation of Anthracene Thin-Films

In this section the fabrication anthracene films by means of thermal evaporation in high vacuum system is described in detail.

Thin film specimens were fabricated by evaporating onto glass substrate (Corning type-cover glass 22 mm sq. 0.2 mm. thick), the anthracene material of scintillation grade obtained from Harshaw) in a 10^{-6} torr vacuum coater (NRC Model 3114). Other substrates such as pyrex flat (Northrop 1956), **NaCl** single crystals mica, gypsum, molten quartz and colloidal paste deposit on the surface have been used to investigate the effect of the substrate on anthracene deposition. (Gheorghita-Oancea, 1964). Glass substrates were used because they are easy to handle and have been widely used by other investigators.

Because of the high vapor pressure of anthracene it is necessary to cool the substrate to at least -40°C (Northrop, 1956), or to liquid nitrogen temperature (Fielding, 1967; Lohanick, 1968). The temperature used for the present work was about -60°C , and the pressure was about $1-2 \times 10^{-6}$ torr during evaporation.

Electrode materials used were Ag, Au and Pb and they were deposited on both sides of the films under a vacuum of 10^{-6} torr. This sandwich-like cell is shown in Fig.4.1. Silver paint was also used as electrode material, but the silver-painted electrode was not satisfactory at low temperatures. Therefore all electrodes used were vacuum-deposited electrodes. Electrical

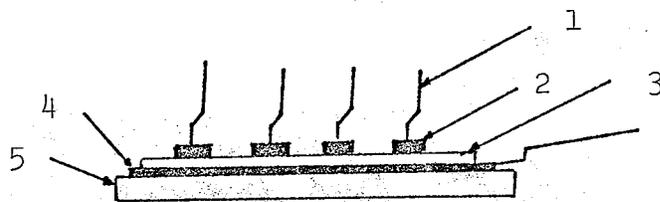


Fig.4.1 Anthracene film specimen

1. Electric connection
2. Upper silver electrode
3. Anthracene thin film
4. Bottom silver electrode
5. Glass substrate

connection was made by soldering clean fine copper wires to the electrodes. Since anthracene has a low melting point, a low melting solder, indium, was used.

4-2 Thin-Film Thickness Measurements

In general, it is desirable to have films with a uniform thickness, over a fairly large area. This can be realized by using appropriate evaporating sources. Evaporation sources generally used are the point sources and the small area sources. The former ideally consists of a small sphere from which material evaporated uniformly in all directions. The small area source is a small, planar surface from which the material evaporates only to one side within an angle θ between the normal to the evaporating surface and direction of evaporation (Fig.4.2). On a planar substrate which is placed directly above the source the film thickness for a point source, (Holland, 1963) is given by

$$t = \left(\frac{m}{4\pi\rho} \right) \left(\frac{\cos\theta}{r^2} \right) = \frac{m}{4\pi\rho} \cdot \frac{h}{r^3} \quad (4.1)$$

and for small area source

$$\begin{aligned} t &= \left(\frac{m}{\pi\rho} \right) \left(\cos\varphi \cos\theta / r^2 \right) \\ &= \left(\frac{m}{\pi\rho} \right) \left(\cos^2\theta / r^2 \right) = \left(\frac{m}{\pi\rho} \right) \left(\frac{h^2}{r^4} \right) \end{aligned} \quad (4.2)$$

where ρ is the density of the evaporant (g/cm^3), t is the thickness of the film condensed per unit time, h is the vertical distance between the source and the plane of the substrate (normal to the substrate surface), r is the distance. The distance between the source and point under consideration and θ is the angle between h and r .

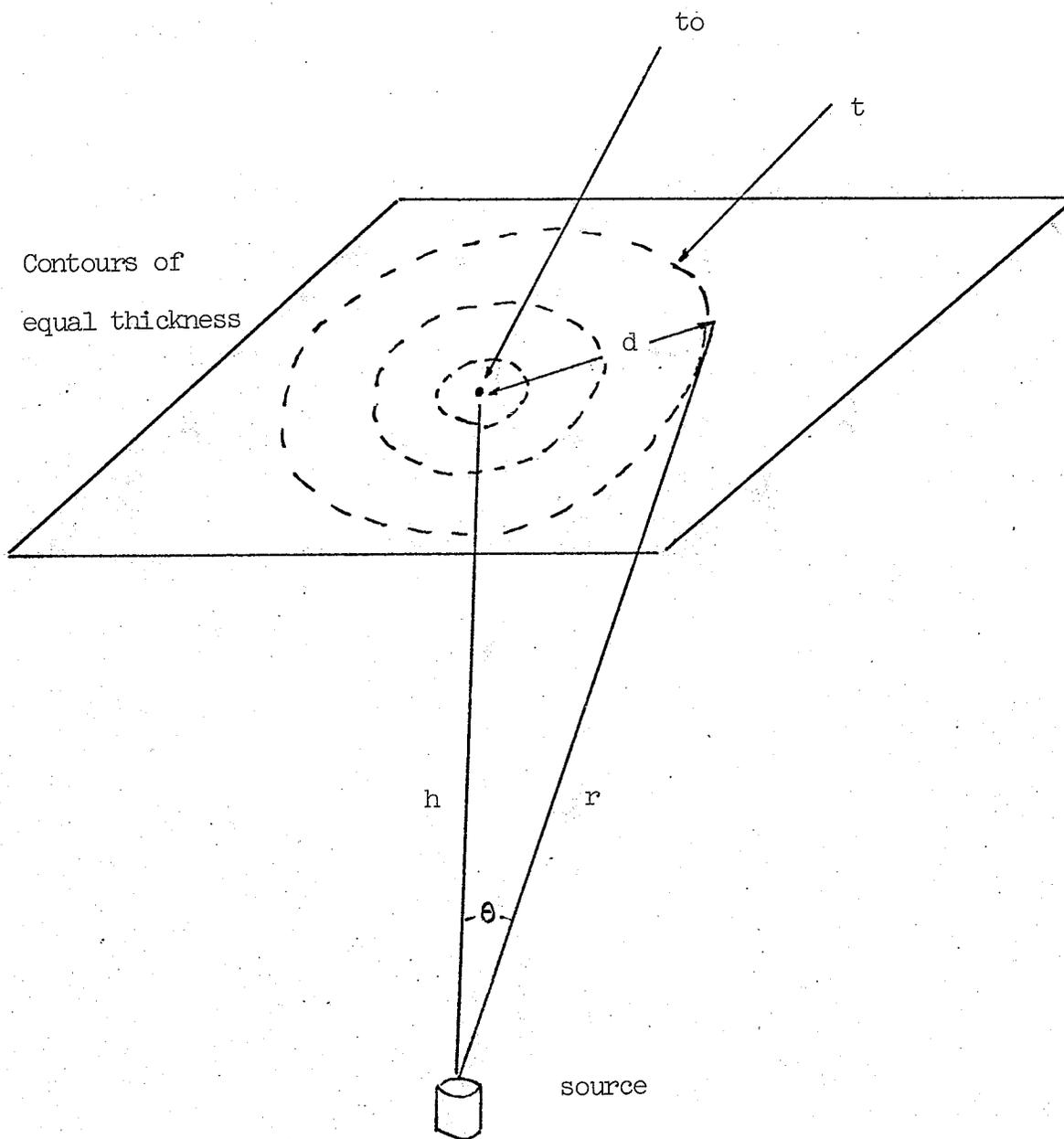


Fig.4.2 Evaporation source in vacuum system

It is clear that, in both cases, the film thickness will have its maximum directly above the source and decreases as d increases. Contour of equal thickness will be circles of radius d . The decrease of thickness with increase of d is more rapid for the small area source than for point source. It is obvious then that the film thickness is more uniform for greater h . Thus the distance between source and substrate should be as large as possible.

Suitably shaped molybdenum boats served as point source or small area source were used. For depositing metal, a point source was used, while for depositing anthracene a small area source was used since the anthracene crystals jumped about during evaporation.

Three techniques are generally used to measure film thickness; (1) Microbalance weighing method, (2) Multiple beam interferometric technique and (3) thickness crystal monitor technique. Only the first two techniques were used to measure the thickness of anthracene films.

(1) Microbalance weighing method.

The small mass changes of the substrate before and after film deposition were measured by a microbalance on the assumption that the film thickness is uniform. The film thickness is given by

$$t = (W_{\text{after}} - W_{\text{before}}) / (\rho \times A) \quad (4.3)$$

where ρ is the density of the substance of the film. For anthracene

$\rho = 1.25$ (at room temperature) and A is the area of the film.

(2) Multiple beam interferometric technique

This is one of the most elegant methods for thickness measurements.

Multiple beam method depends on the production of Fizeau fringes by a wedge formed from the material of refractive index μ . Each fringe is a contour line of equal wedge thickness. For n th order interferences of light with wavelength λ , the thickness of film can be calculated from the relation

$n\lambda = 2\mu d \cos \phi$ (where ϕ is the angle between the incident beam on the wedge and the line normal to the reference flat surface).

Variation A - Scope - Interferometer, model 940-4000 was used for thickness measurement. This interferometer provides an absolute measurement of microscopic vertical surface variations in the range from 30 Å to 20,000 Å. Accuracy is normally ± 30 Å. This instrument employs a sodium vapor lamp ($\lambda_2 = 2946$ Å).

(3) Thickness crystal monitor technique

The crystal thickness monitor has the advantage of being capable of measuring the film thickness during deposition. A quartz crystal has a well defined resonant frequency which depends on its cut and geometric dimensions. If a film is deposited on this crystal, this resonant frequency will change according to the film thickness. The monitor therefore consists of a crystal placed adjacent to a substrate onto which film is deposited and the electrical equipment necessary for measuring the change of resonant frequency.

4-3 Measurements of current-voltage characteristics

Since anthracene is a material of very high resistivity the Keithley model 210 Electrometer with input impedance up to 10^{14} ohms was used for current measurements. Prior to measurement the instrument was switched on for one hour until the zero drift of the instrument was less

than $1\mu\text{V}$ per hour, this was found to be very important to reduce the errors due to drifting. For most experiments the specimen was mounted or clipped on brass cell which was then placed in the screen room and all connection leads were shielded and kept as short as possible. Arrangement for current-voltage measurements is shown in Fig.4.3.

In low temperatures, the test cell was made a vacuum of 10^{-4} torr to avoid the condensation of moisture from air. The specimen was cooled by passing through liquid nitrogen to the metal block on which the thin film specimen was placed. It was found that silver paste electrode were peeled off at very low temperatures therefore, for low temperature measurement only evaporated silver or gold were used as electrodes.

The radiation source was a cobalt 60 gamma cell with a half lifetime of 5.27 years and an average dose rate of 1.6×10^6 rads per hour, determined by ferrous sulphate dosimetry method. A correction factor was applied for the calculation of radiation dose when the specimens were irradiated at dates differing more than one month.

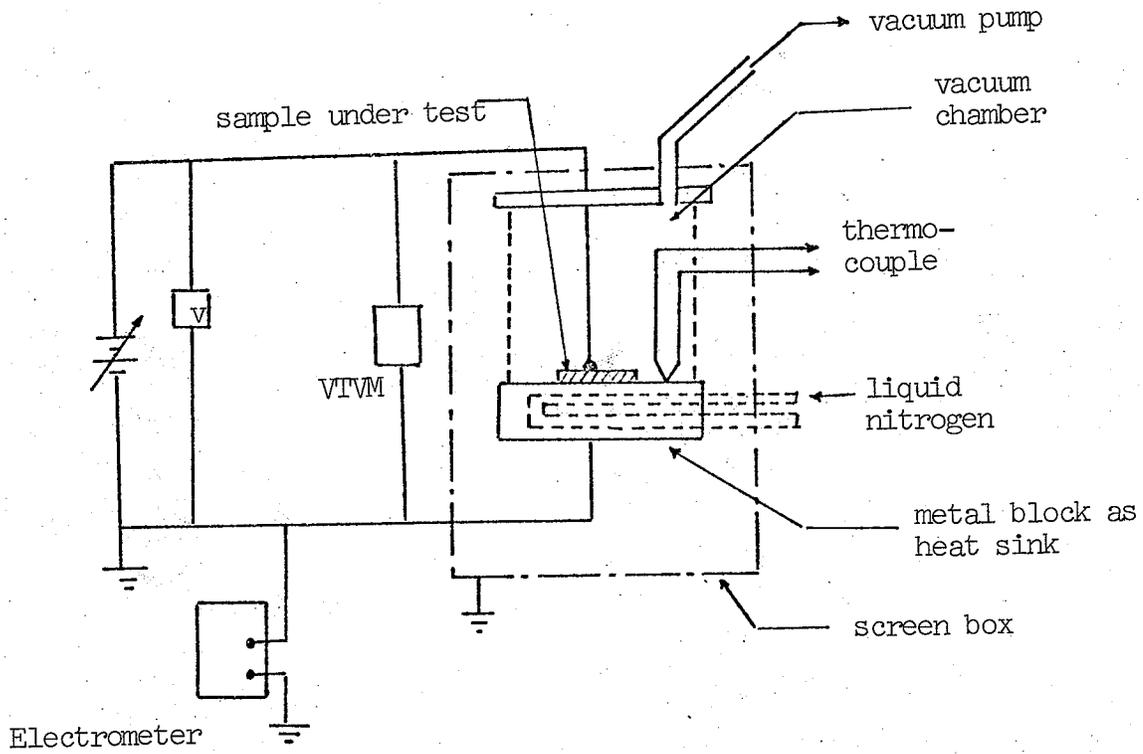


Fig.4.3 Arrangement for I - V characteristics measurements.

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

Using the experimental set up described in Sec. 4-3, the current (I) - voltage (V) characteristics of anthracene thin films had been measured for various film thickness, temperatures, environmental pressure, electrode materials and after being exposed to different gamma-ray radiation doses.

Fig. 5.1 shows a typical steady state I - V curve. Based on the relationship $I \propto V^n$, three regions can be distinguished.

(i) From zero field to about $2.5 \times 10^{3v}/\text{cm}$, $n = 1$. This is the ohmic region. At these field strengths, the current carriers come from the bulk of the film by thermal generation, the field being too small for the number of injected carriers to be significant. Furthermore, since at low fields the carrier energy due to field-directed drift is much smaller than that due to thermal agitation, the tunneling probability through the barrier between the electrode and the film is essentially determined by the average thermal energy of the carriers. These facts explain why I varies linearly with V. In thin films, a relatively small applied voltage gives rise to a considerably high electric field. Thus on a I - V curve the ohmic region is barely detectable.

(ii) From about $2.5 \times 10^{3v}/\text{cm}$ to about $8 \times 10^{4v}/\text{cm}$, it is more appropriate to consider carrier injection to be more important than carrier generation by thermal motion. Since n is about 3 in this region we can assume with some confidence that the current is space-charge-limited (SCL). For crystals the SCL I - V relationship for crystal with discrete traps

in the band gap is given by

$$J = 10^{-13} \left[\left(\frac{N_c}{N_t} \right) \exp\left(-\frac{E_t}{kT}\right) \right] \cdot \mu_0 \epsilon V^2 / d^3 \quad (5.1)$$

and that with an exponential distribution of traps in the energy band gap is

$$J = N_v \mu e^{-l} \left(\frac{\epsilon l}{H(l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{d^{2l+1}} \quad (5.2)$$

These two equations have been given in Sec. 2-5.

(iii) From about $8 \times 10^{4v}/\text{cm}$ to about $4 \times 10^{3v}/\text{cm}$, n is greater than that in region (ii). We attribute this greater rate of increase I with increase in V to ionization produced by carrier collision as described in Chapter 3. A model had been proposed by O'Dwyer to take into account the collision ionization in dielectric thin films at high fields. Unfortunately, this model contains many parameters which are not known even for anthracene crystal and consequently no explicit form of $I - V$ characteristics can be obtained. We would therefore have to be contented with qualitative discussion and our analysis, in some respect, would be rather inconclusive in this region.

It is worthy to note that there is no region in which I is proportional to V^2 indicating that the current is space-charge-limited with deep traps. It is possible that collision ionization begins before the trap-filled limit is reached and this may explain why beyond region (ii) n in $I \propto V^n$ is greater than 3. At fields above about $4 \times 10^{5v}/\text{cm}$, the film breaks down. Just prior to breakdown, current instability had been observed. This is in qualitative agreement with O'Dwyer's theory (O'Dwyer, 1969). Breakdown phenomena, however, is not within the scope of this thesis.

In the light of the experimental $I - V$ curves for various film

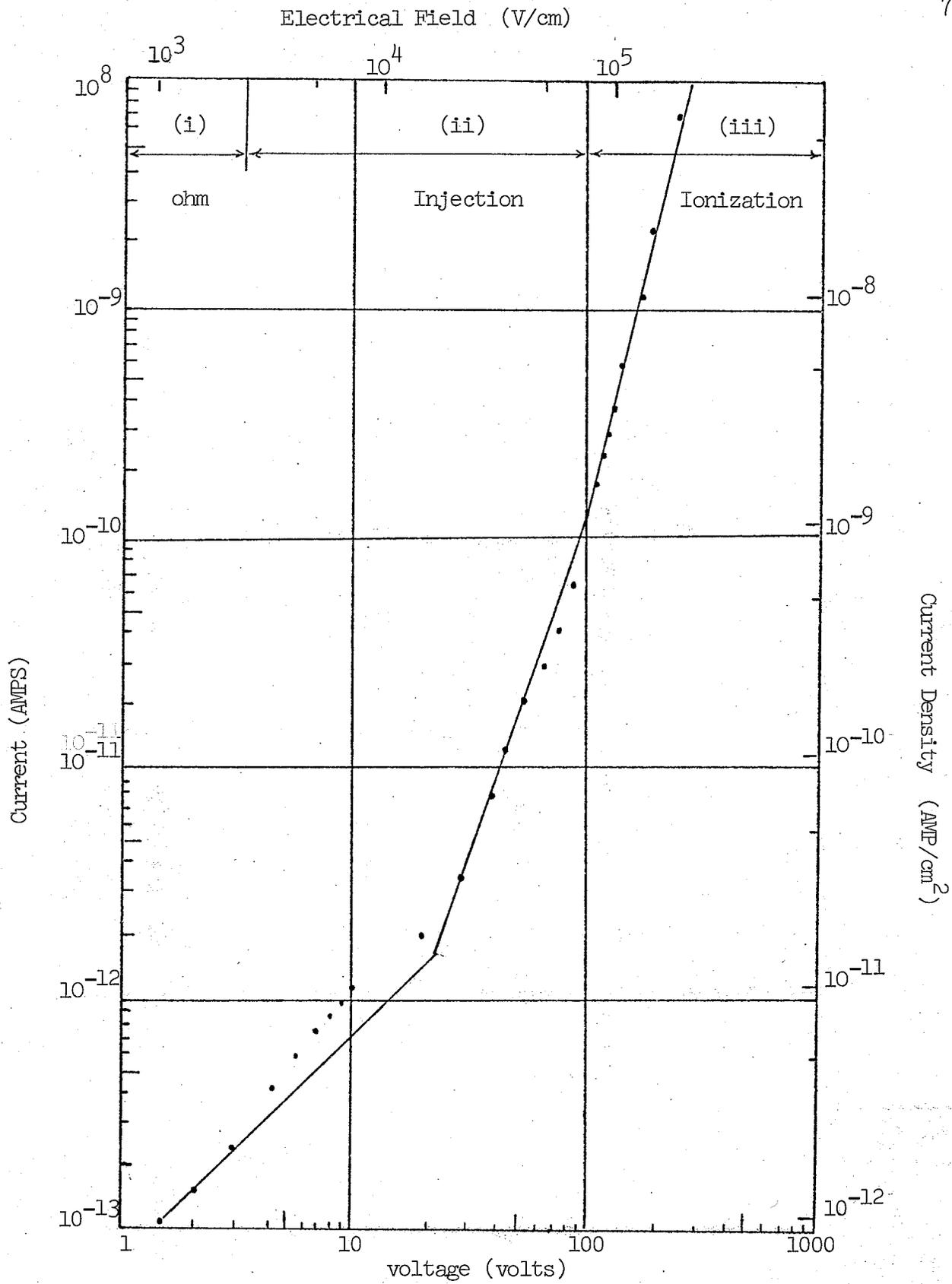


Fig.5.1 Typical current-voltage characteristics of anthracene thin film (Thickness = 11.5 μ)

thickness, we shall show that in region (ii) the current is space-charge-limited with traps. We shall analyse the experimental results using Equations (5.1) and (5.2).

5-1 The effect of Film Thickness

Fig. 5.2 shows a plot of $\log I$ as a function of $\log V$ for various film thickness.

In region (ii), the slope n of the curves are all nearly equal to 3. In Fig. 5.3 is shown $\log I$ as a function of film thickness d at constant voltage and constant field ($E = V/d$). If Equation (5.2) holds, the value of the slope in Fig. 5.3 should be given by $m = 2(n-1) + 1 = 5$. The measured value of m is 4.9. This is an evidence of the fact that the current in this region is space-charge-limited with traps and that the trap distribution is approximately exponential. Referring to Equation (5.2) we can calculate $\frac{T_c}{T}$ when $T = 300^\circ\text{K}$. For the films used for this investigation the value of T_c is 600°K . This is close to the value of T_c of anthracene crystals reported by Schadt and William (1969).

The slopes n and m are also calculated in region (iii). They are found to deviate from the relation $m = 2(n-1) + 1$. We can conclude, therefore that the current in region (iii) is not dominated by the space-charge-limited mechanism.

5-2 The Effect of γ -ray Radiation

Fig. 5.4 shows a plot of $\log I$ as a function of $\log V$ for different radiation doses. The radiation source is Co^{60} . The measurements were made after each irradiation and not during irradiation. In general,

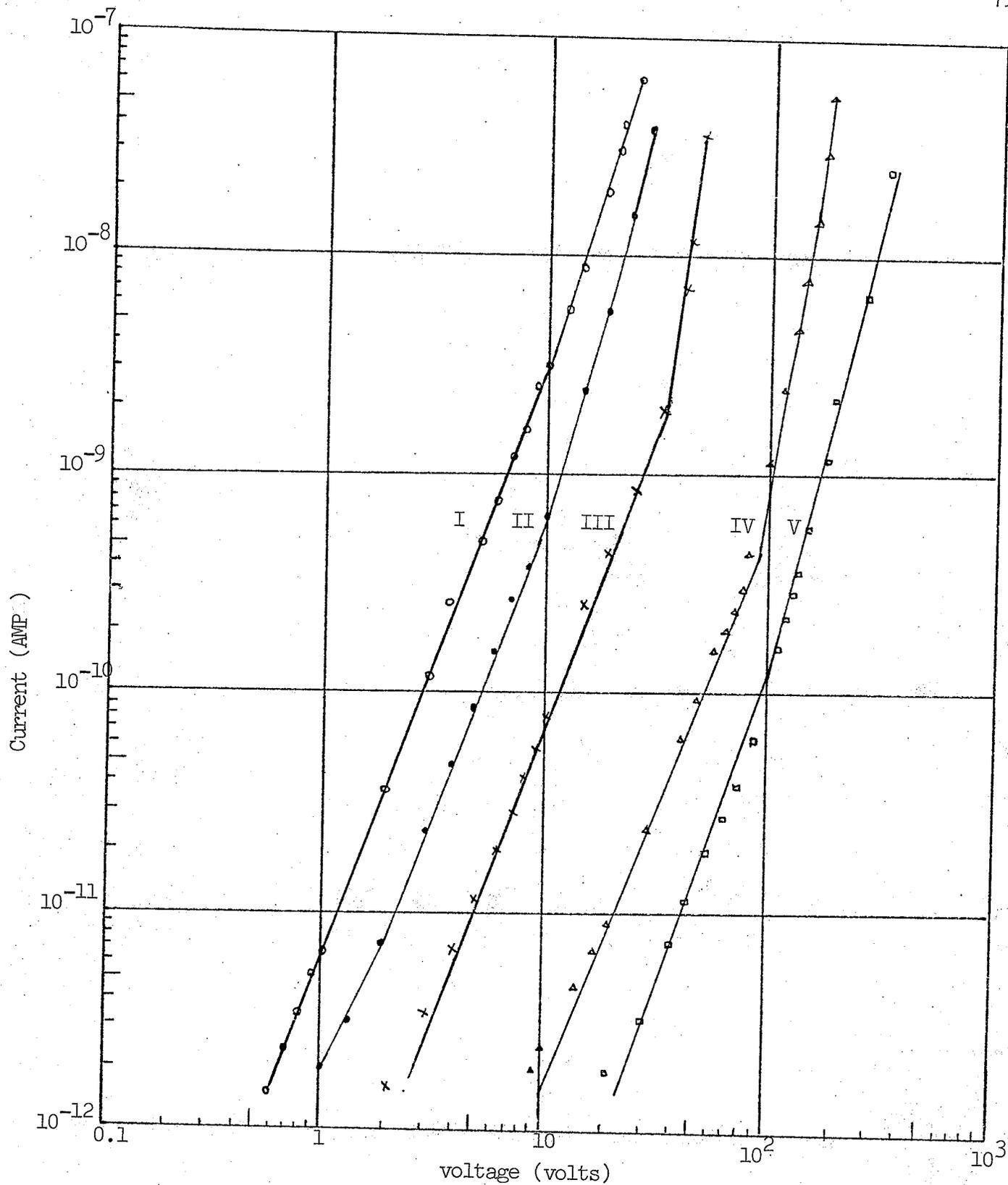


Fig.5.2 The film thickness dependence of the current-voltage characteristics of anthracene films.

- (I) thickness is 1.62 μ ,
 (II) thickness is 2.49 μ ,
 (III) thickness is 3.9 μ and
 (IV) thickness is 8.8 μ and =
 (V) thickness is 11.5 μ

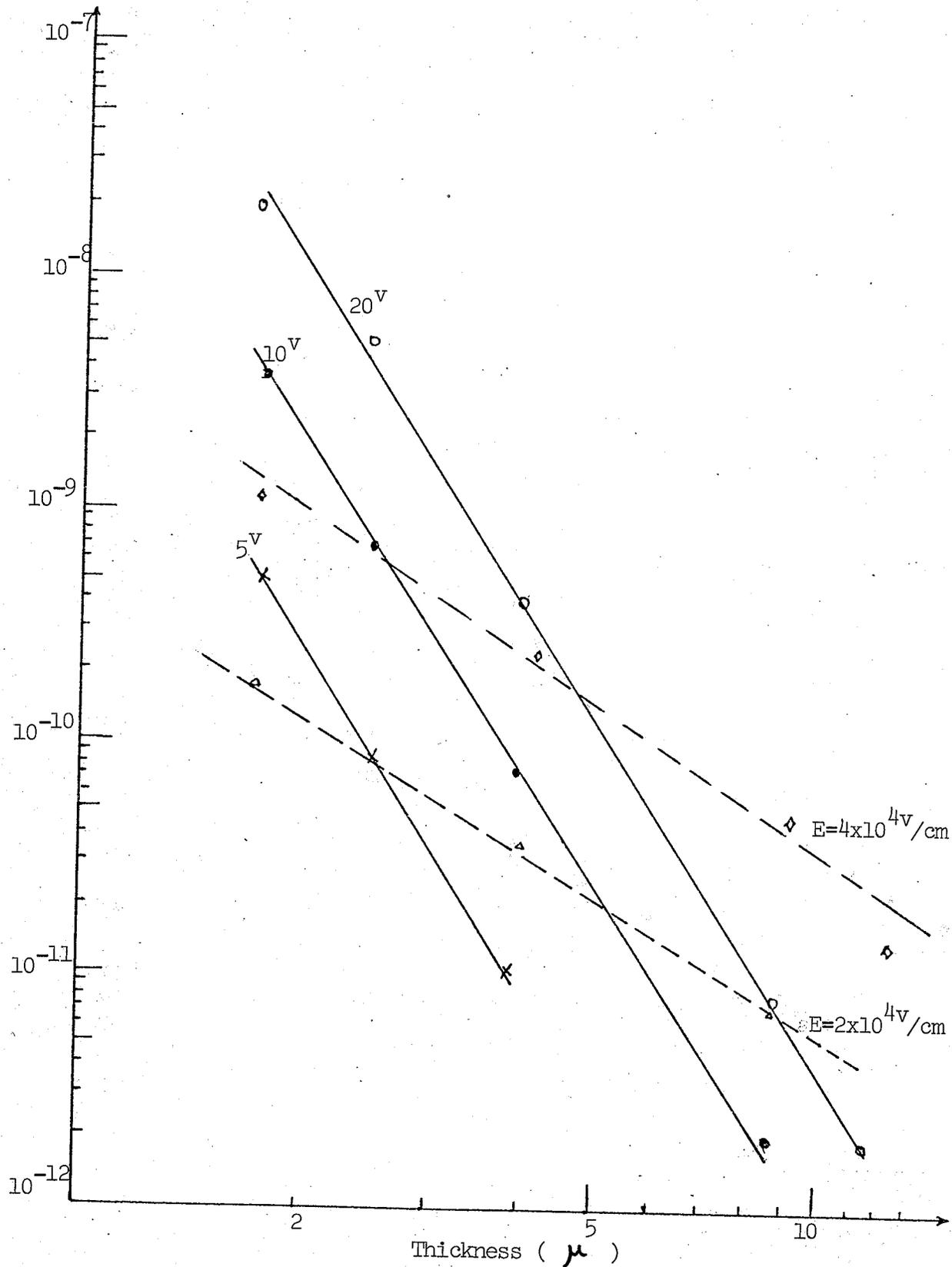


Fig.5.3 The current as a function of the anthracene films thickness at constant voltage and constant electrical field.

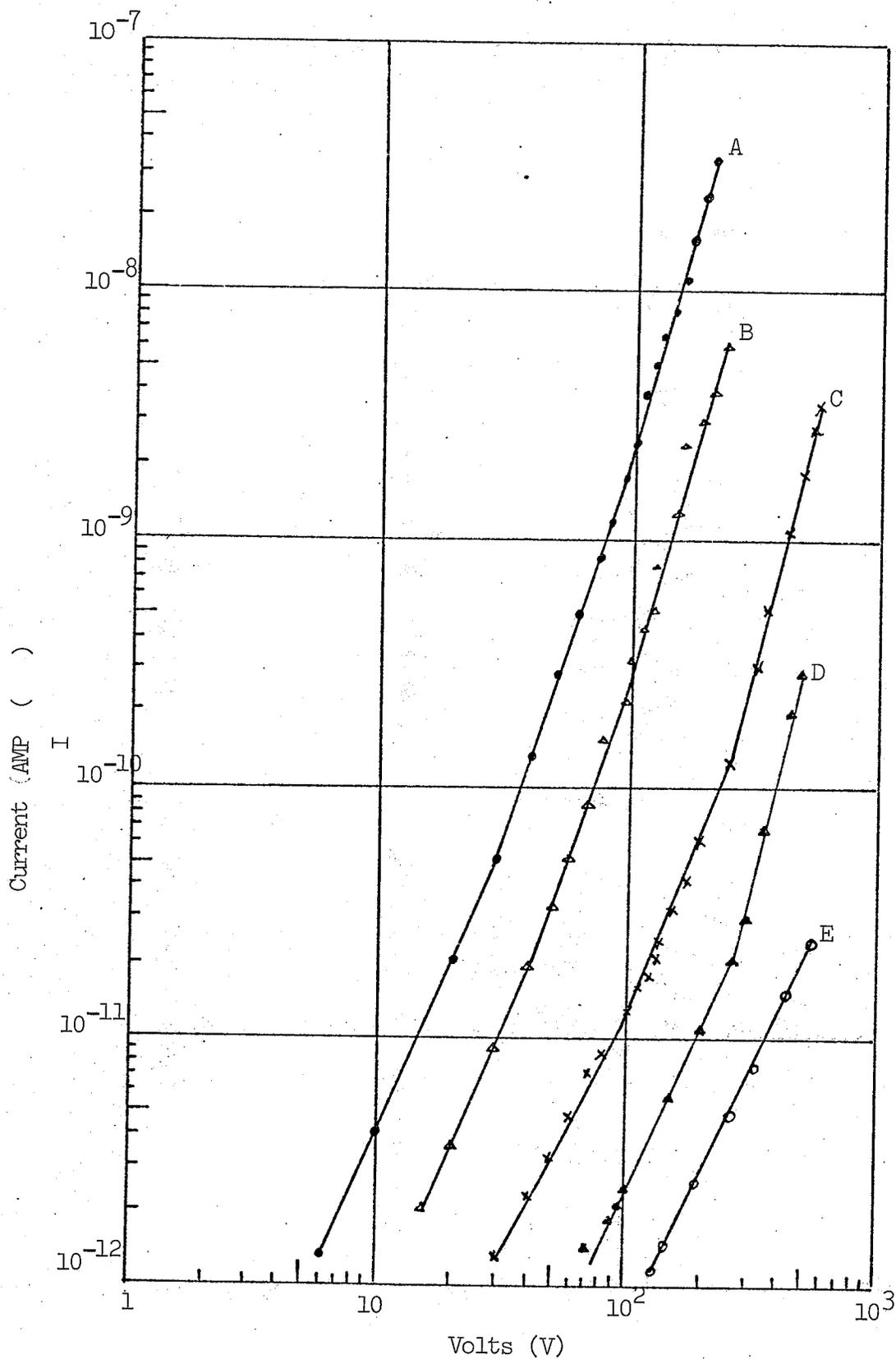


Fig.5.4 The effect of γ -ray radiation on the current-voltage characteristics of anthracene films. Film thickness = 7.46μ

(a) Before radiation	(b) 1.75×10^6 rads
(c) 5.85×10^6 rads	(d) 2.8×10^7 rads
(e) Greater than 5.58×10^7 rads	

the current at a given applied voltage decreases with increasing dose (Fig.5.5). This can be explained by the fact that with increasing dose more carrier-trapping states are created. In region (ii), the slope n is seen to decrease with increasing dose. This has been plotted explicitly in Fig.(5.6(a)) n decrease from about 3 before irradiation to very near 2 at a radiation dose greater than 5.58×10^7 rads. Now n is $\frac{T_c}{T} + 1$, so that a decrease of n means decrease of T_c , which in turn means a sharper energy distribution of traps. In the limit of $n = 2$, the energy distribution of traps become discrete. The other two possible cases in which $n = 2$ are; (i) when the film is trap-free and (ii) after the trap-free-limit has been reached. These cases can be ruled out because the number of traps increases with increasing radiation dose. We can conclude therefore that the increase in γ -ray irradiation which gives out essentially monoenergetic radiation would produce more and more traps of single energy level until the traps distribution at this particular energy level dominates over traps of other energy levels. This process is illustrated in Fig. 5.6(b).

5-3 Variation with electrode material, environmental pressure and temperature

(i) Electrode Material

Fig. 5.7 shows a plot of $\log I$ as a function of $\log V$ with Au as anode and Pb as cathode (labelled Au(t) in Fig. 5.7) and An as cathode and Pb as anode (labelled Au(-) in Fig.5.7). It can be seen that the two curves have almost identical shape but at a given voltage, the current with Au(+) as anode is larger than that with Au(-) as cathode. It has been described in Sec.2-2 that in anthracene crystals the Au(+) electrodes inject holes while the Au(-) electrode injects electrons and that the rate

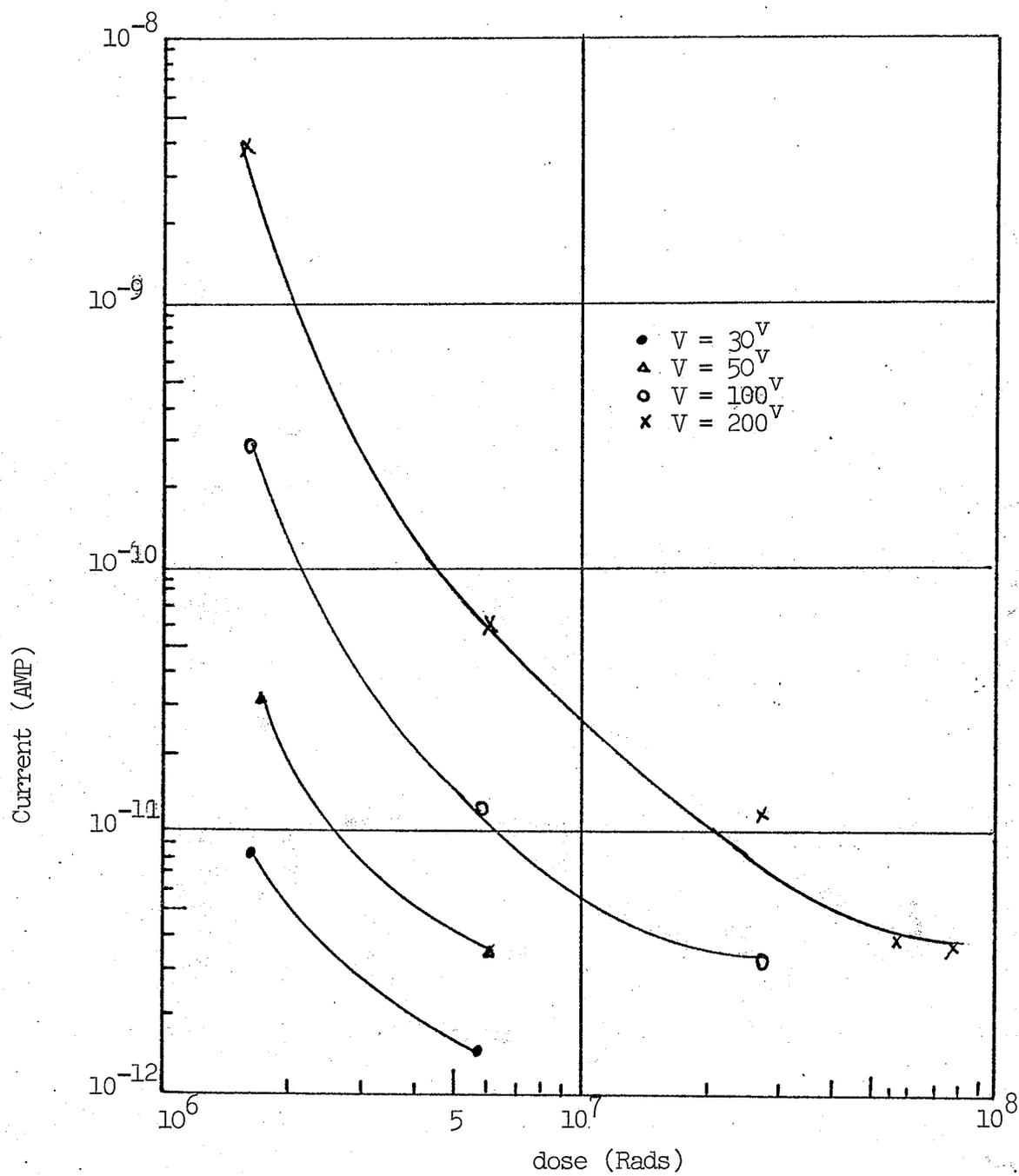


Fig.5.5 The current as a function of γ -ray radiation dose
(Thickness = 7.46μ)

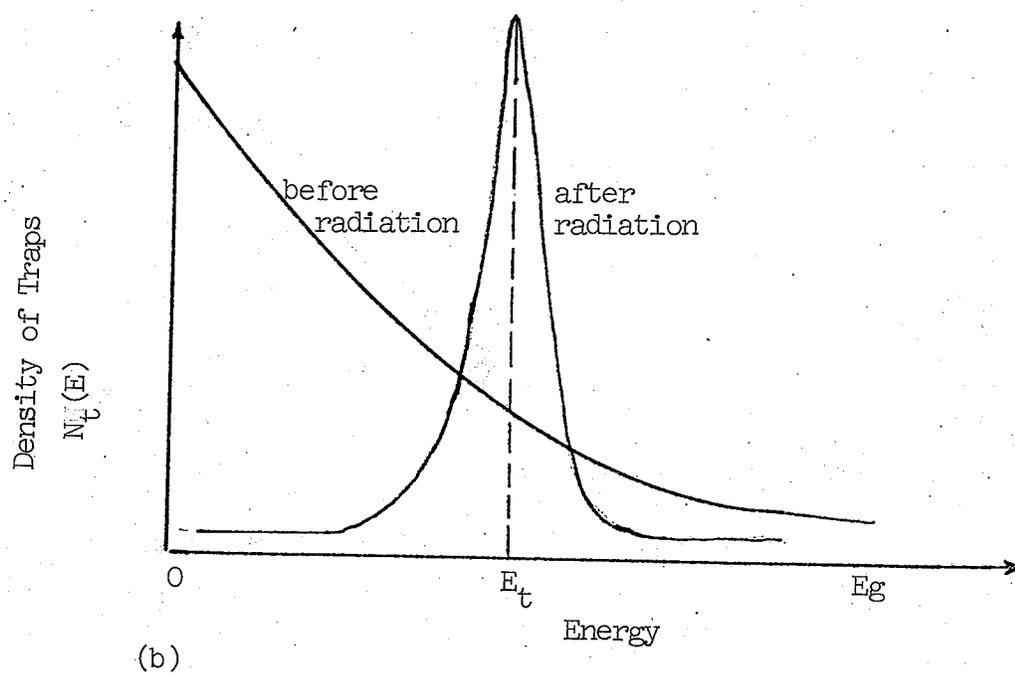
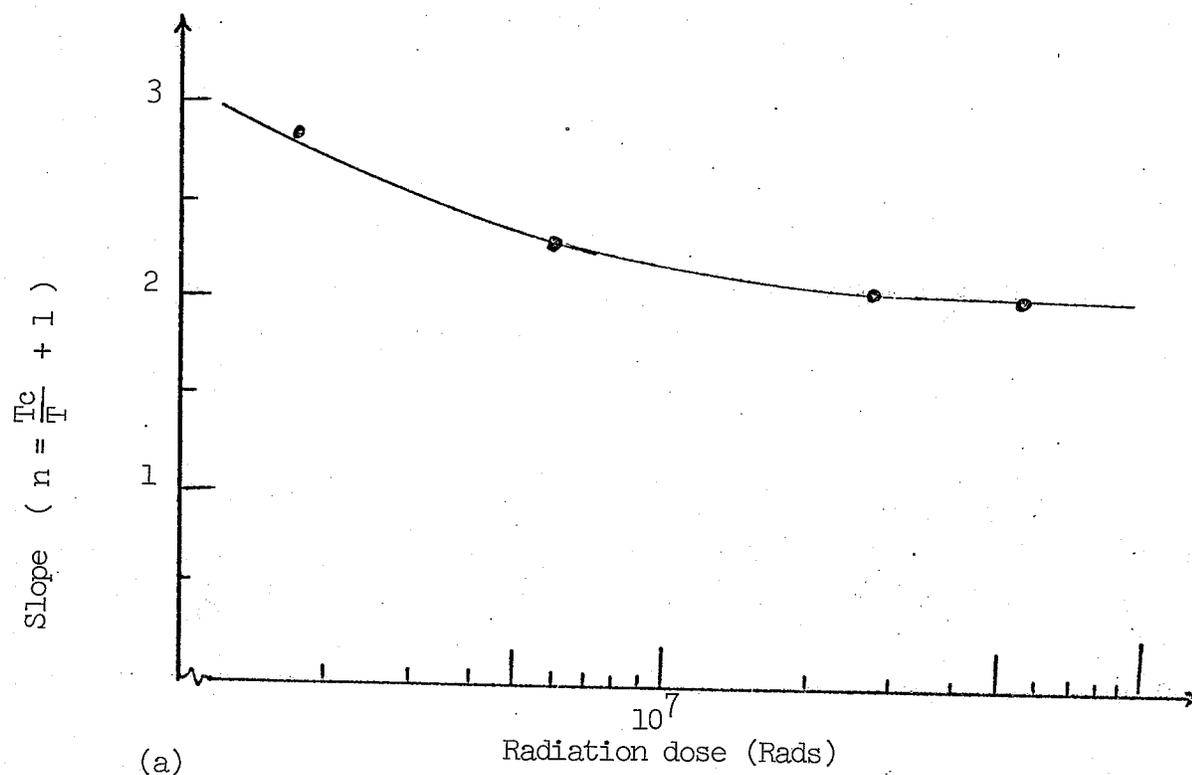


Fig.5.6 (a) Variation of slope n with the radiation dose
(derived from Fig.5.4)

(b) Illustrating the effect of radiation on the
energy distribution of traps

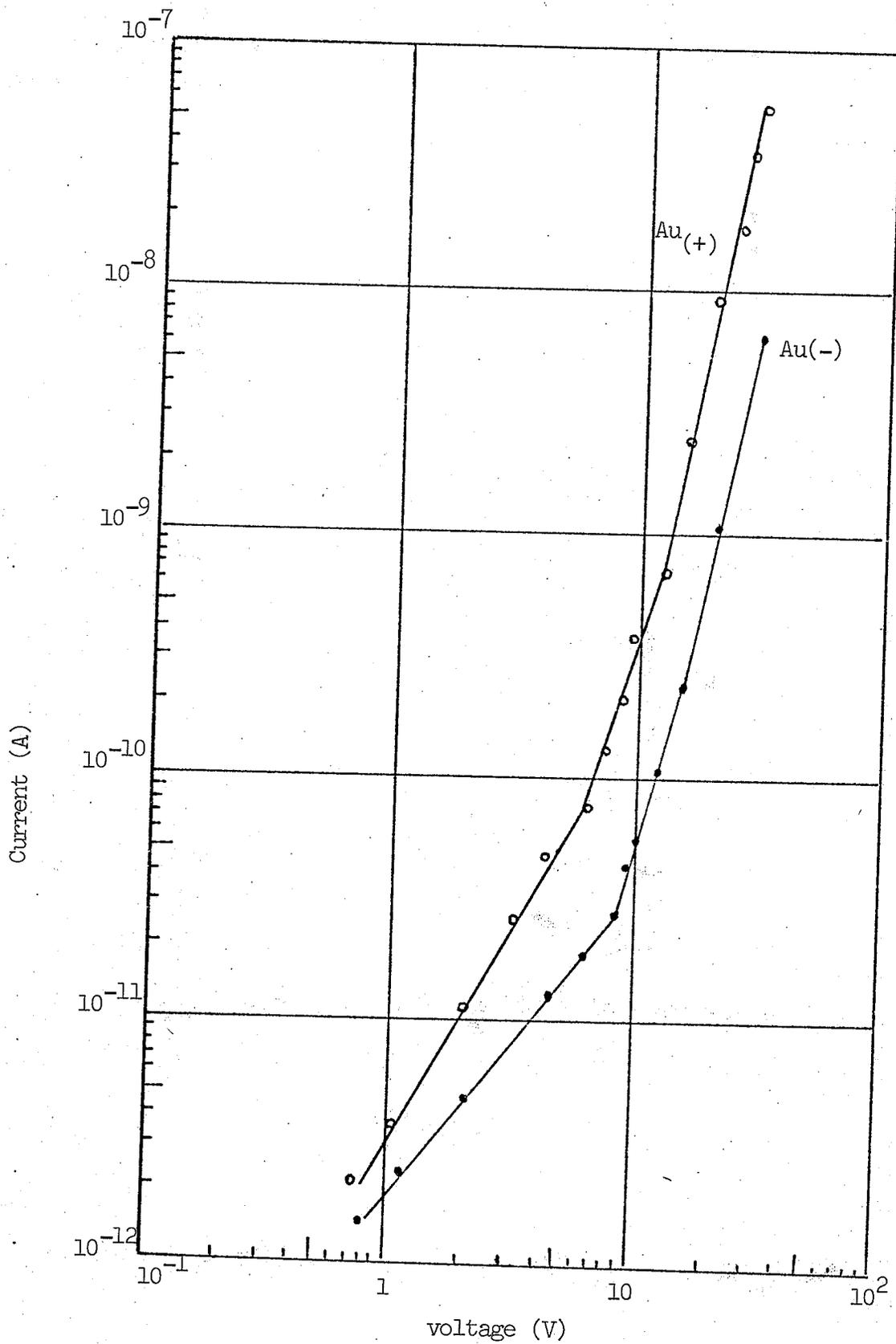


Fig.5.7 The effect of electrode materials on the current-voltage characteristics of anthracene films, for Au - Anthracene - Pb systems.
 (a) when Au^+ is positive - hole injection
 (b) when Au^- is negative - electron injection

of hole injection is larger than the rate of electron injection. The present experimental data indicates that the same is true in anthracene thin films.

(ii) Environmental pressure

Fig. 5.8 shows a plot of $\log I$ as a function of $\log V$ with the environmental pressure of one atmosphere (760 mm Hg.) and 10^{-3} mm Hg. The current at low pressure increases at a smaller rate with voltage than the corresponding rate at atmosphere pressure. This tendency is in agreement with that observed by Gheorghita-Oancea (1961). The change in $I - V$ due to change in environmental conditions had been attributed to a change in the properties of surface states. The present experimental results, which is measured on a film sandwiched between the electrodes, cannot be attributed to the same cause unless it is assumed that the portion of film which is not embedded between the electrodes has a significant effect on the current.

(iii) Temperature

Fig. 5.9 shows a plot of $\log I$ as a function of $\log V$ at temperature 293°K and 77°K . The measurements are made by placing the film in an evacuated chamber to avoid condensation of moisture at low temperature. The film used in this measurement is the same as the film used in Sec.5-3 (ii), and the pressure in the evacuated chamber is the same pressure attained in the low pressure curve Fig. 5.9. Thus one can see that curve marked 293°K in Fig. 5.9 is identical with curve marked 10^{-3} mm Hg. in Fig. 5.8.

In region (ii), the slope at 293°K is **2.1** and the slope at 77°K is 2.5. If an exponential distribution of traps is assumed, the value of

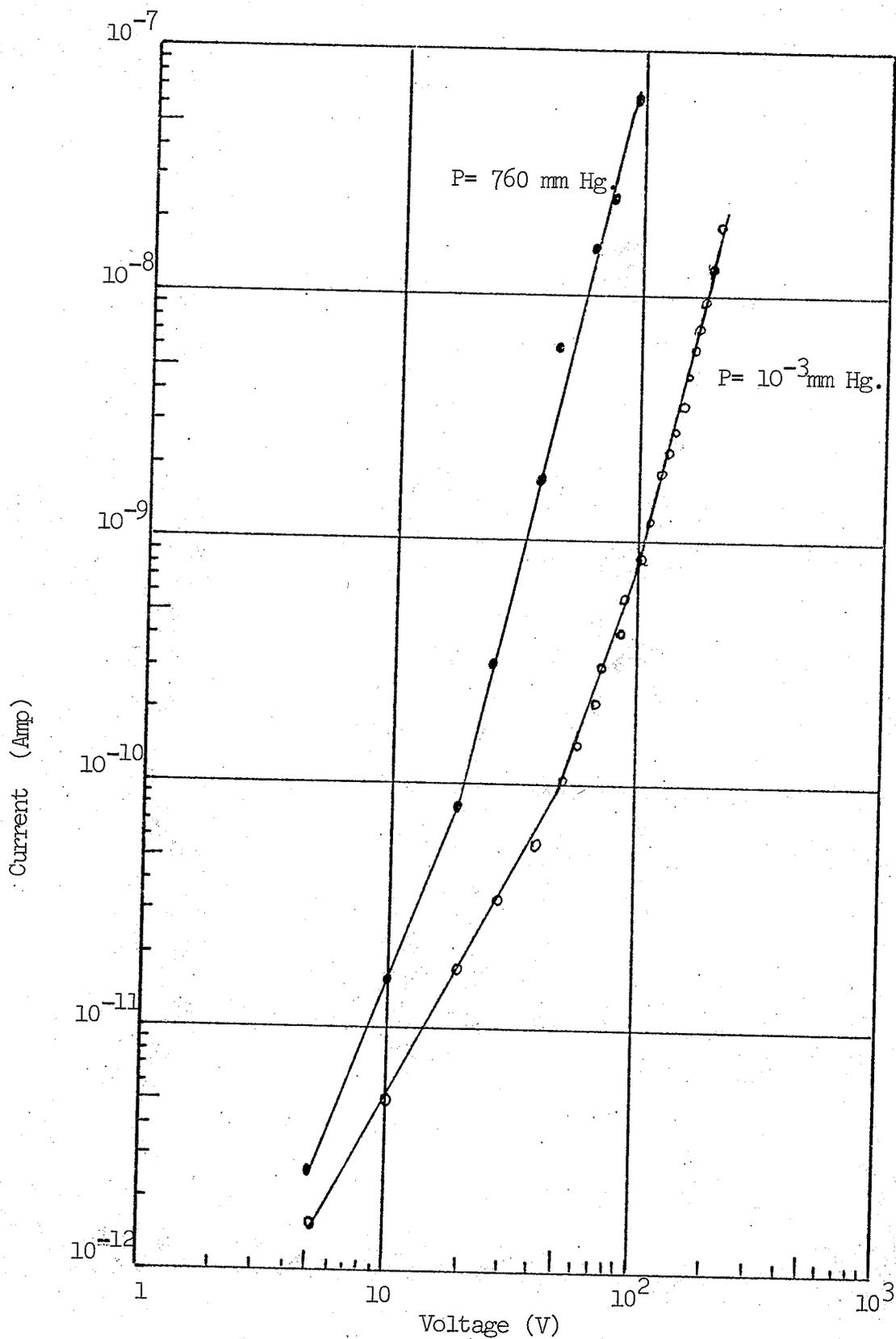


Fig.5.8 The effect of environment pressure on current voltage characteristics of anthracene films
(a) Pressure 760 mm Hg. (b) Pressure 10^{-3} mm Hg.

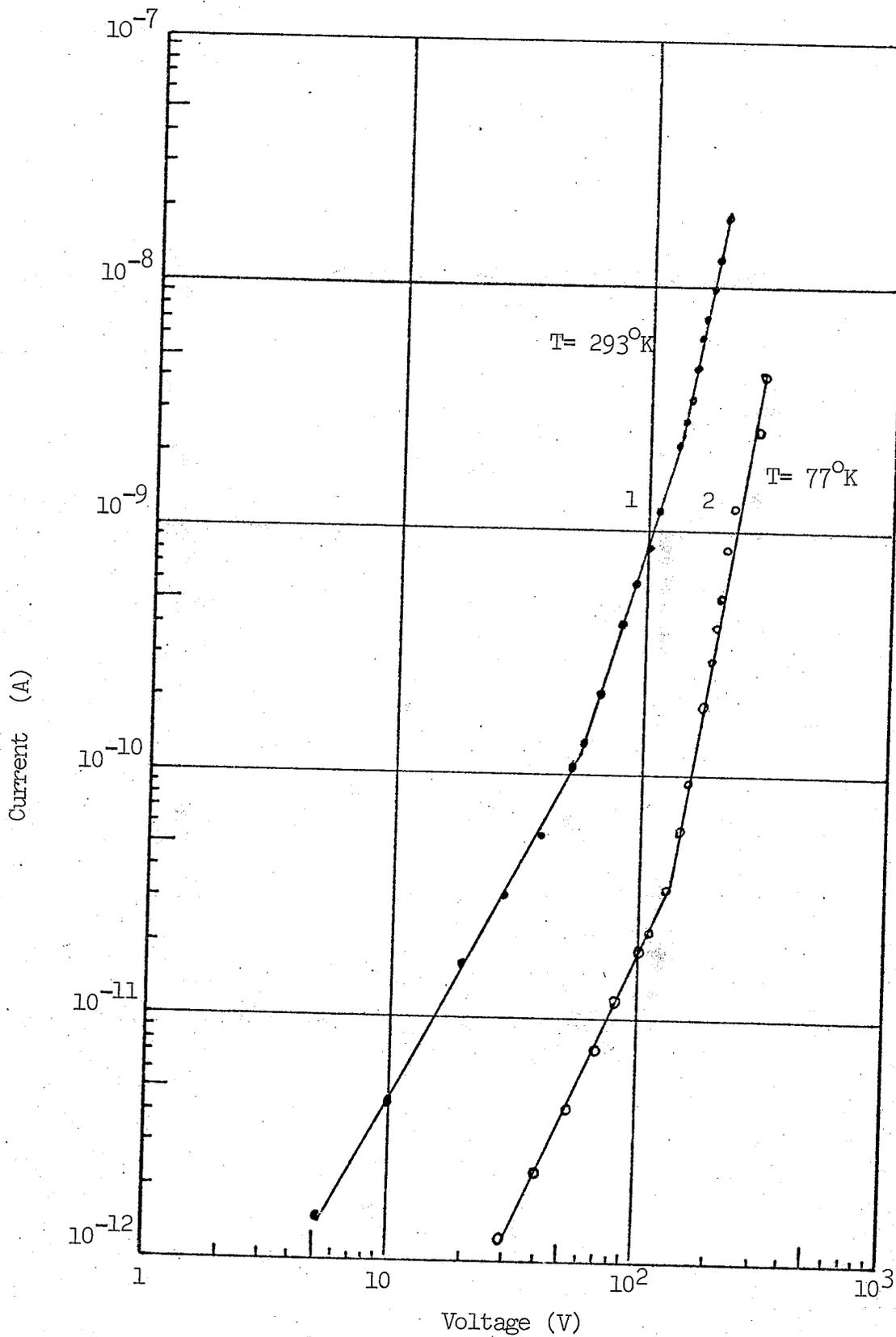


Fig.5.9. The effect of temperature on the current-voltage characteristics of anthracene films
 (a) $T = 293^{\circ}\text{K}$ (b) $T = 77^{\circ}\text{K}$ pressure 10^{-3} mm Hg.

of the slope at 77°K should be about 5.4. On the other hand, although the slope at 293°K is very close to 2, the distribution of traps cannot be considered to be discrete otherwise the slope at 77°K would have to be identical with the slope at 293°K . In view of our results in Sec. 5-3(ii) at low environment pressure, it is not unreasonable to ascribe this apparent discrepancy to the effect of surface states.

5-4 The current-time characteristics

It has been observed in anthracene crystals that it takes many minutes for the current to reach a steady state value. We have observed the same phenomena in anthracene thin films. In Fig. 5.10 is shown a typical current-time characteristic curve immediately after the application of a d.c. voltage. It usually took more than 45 minutes for the current to reach a steady state.

This phenomenon has been attributed to the trapping of minority carriers which produces a back emf (Bree, Reucroft and Schneider, 1960). The time required by the current to reach a steady state value represents the characteristic time constant of the trapping process. A similar phenomenon has also been observed in alkali halides crystals (Kao, Whitham and Calderwood, 1970). This was interpreted in terms of the decay polarisation currents produced by the relaxation of complexes consisting of ions bound by crystal defects. Thus it is reasonable to assume that the decay of current immediately after application of voltage observed in anthracene thin films is due to the relaxation of current-carrier capture processes. We cannot, however, calculate the time characteristic of the relaxation because the mechanisms of these capture processes have not yet been identified.

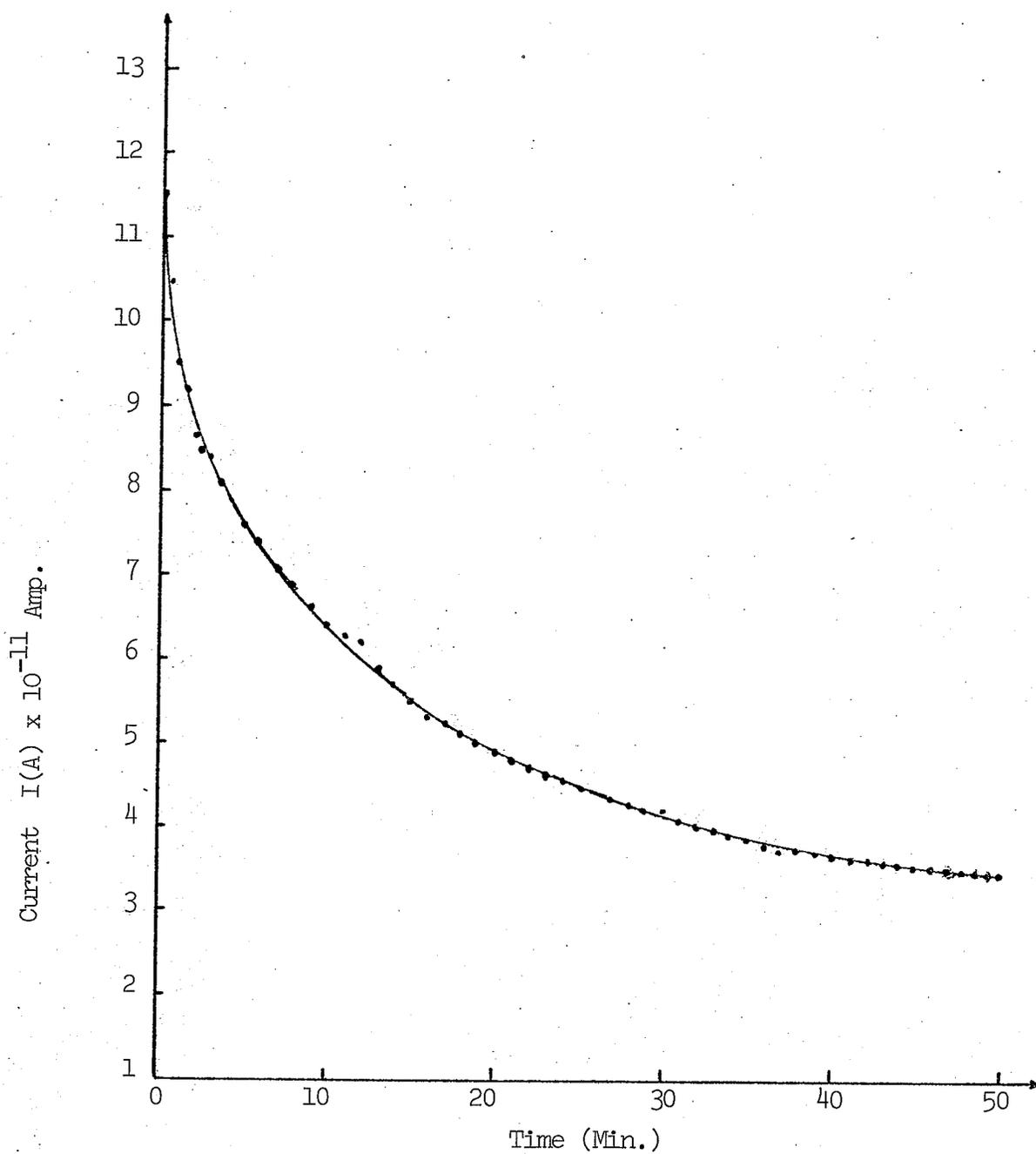


Fig.5.10 Typical current-time characteristics of anthracene film.
applied voltage - 30 volts, film thickness - 5.1μ .

CHAPTER 6

CONCLUSIONS

On the basis of the above experimental facts, some conclusions are tentatively drawn as follows

- (1) (1) At medium fields the current is space charge limited with traps, the distribution function of traps being exponential in the energy gap.
- (2) The γ -ray irradiation tends to produce traps of discrete energy level. For large dose this density of traps in this level is predominant.
- (3) At high field, a collision ionization process may start before the trap-filled limit is reached.
- (4) The $I - V$ characteristics are dependent on temperature, environment pressure and electrode materials.
- (5) Current decays very slowly to a steady value after the application of an applied field.

Although the mobilities of carriers in organic semiconductors are generally very low, it is quite easy to produce carriers in these materials. Therefore these materials have a high potentiality for solid-state devices. Furthermore, these materials are normally very sensitive to light and readily produce light under an electric field. It is highly possible that these materials activated with suitable impurities, an efficient electroluminescence may be produced. From application point of view, these

materials cannot be said to be less important than the inorganic semi-conductors. However, the properties of these materials are not yet fully explored, more research work is definitely required in order to obtain a good understanding of various electronic processes in these materials.

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