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Study of carrier transport in molecularly doped polymers by interrupted time-of-flight measurements

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Abstract. Interrupted hole transit experiments were carried out on dispersions of DEH, BD, and DBH in polycarbonate, using electron beam excitation. The sweep field was switched off for intervals Δt between 10 ms and 10 s. On re-applying the field after more than 30 ms, the transit current initially rose to a value lower than that before interruption, but then gradually increased until holes began to arrive at the collecting electrode. The observations of a current plateau in uninterrupted transits, and of almost constant total charge collected irrespective of Δt, suggest negligible deep trapping. The results seem incompatible with monoenergetic polaron transport, but can be understood on the basis of the Gaussian disorder model. When the field is switched off, the hole population 'cools', slowly sinking into tail states. When the field is restored it is more quickly 're-heated' towards its original field-enhanced mean energy.

1. Introduction

Most modern xerographic photoreceptors are organic and consist of a thin photogeneration layer overlaid by a transport layer about 20 μm thick, which is transparent to light. The transport layer is normally a molecularly doped polymer (MDP). It is generally agreed that hole or electron transport in these materials occurs via hopping between the donor or acceptor molecules embedded in the inert polymer matrix (Borsenberger and Weiss 1994). Consequently, in doped polymers where the energy of the transport levels for holes is high owing to the low ionization energy of the donor molecules, carrier trapping caused by impurities is expected to be negligible. However, fatigue and a build-up of residual potential are commonly observed, and suggest that some of the transiting carriers do become trapped during the xerographic discharge process (Okuda *et al* 1982, Kanemitsu *et al* 1990, Pacansky *et al* 1991).

Photoreceptors exposed to long xerographic cycling cannot be discharged below a characteristic level. This level ($\sim$100 V) is related to the complete filling of traps by charged carriers within the photoreceptor, and is described by the saturated residual potential V_{RS}. In theory, bulk trapping leads to a quadratic dependence of V_{RS} while interfacial trapping leads to a linear dependence of V_{RS} on sample thickness L (Abkowitz and Enk 1982). Hence, the functional dependence of $V_{RS}(L)$ can indicate the presence and location of traps in the photoreceptor. With this in mind, double layer photoreceptors were prepared with charge transport layers (CTL) of 33% TTA (tri-*p*-tolylamine) doped polycarbonate in various thicknesses, but using thin ($\sim$ 100 Å) identical photogeneration layers (PGL) of vacuum-evaporated dibromo-anthanthrone (Németh-Buhin 1996). In TTA, $V_{RS}(L)$ follows a linear relationship which clearly indicates the absence of carrier trapping in the transport layer. Hence the observed residual potential is either caused by charge trapped in the PGL,

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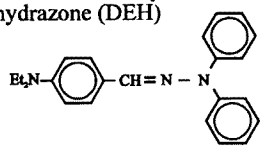
or is the result of injection limitation at the PGL/CTL interface. Although these are two physically different processes, both lead to a linear behaviour of $V_{RS}(L)$ owing to the very small thickness of the generation layer. Based on xerographic evidence, interface trapping in layered organic photoreceptors has also been reported by Kanemitsu and co-workers (Kanemitsu and Imamura 1990, Kanemitsu *et al* 1990).

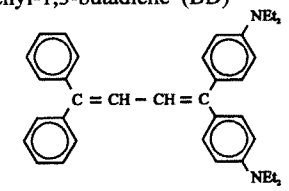
However, xerographic measurements are not always able to distinguish clearly between a linear and a quadratic L-dependence of V_{RS}. For example, our results on DEH-doped polycarbonate are inconclusive, V_{RS} rising supralinearly with L above 15μm (Németh-Buhin 1996).

It is possible to investigate transport layers on their own by using a metal/MDP/metal sandwich structure and carrier injection by electron beam excitation (Spear 1957). Hole transit current signals thus recorded in DEH as well as the other polymers studied (BD, DBH, see figure 1) at room temperature generally exhibit an initial spike decaying to a plateau which is followed by a slowly decaying tail (figure 2). The initial decay is interpreted as reflecting the thermalization of the injected hot carriers into their transport states (Movaghar *et al* 1986). The plateau indicates thermal equilibrium in the drifting carrier population, and its very existence means that the capture time into any deep bulk traps present greatly exceeds the transit time. In BD, we were able to observe plateaus extending to two hours (Németh-Buhin 1996), suggesting a trap density $< 10^{14}$ cm^{-3}. One may conclude that, in the MDPs studied, deep traps play no role in the transport. In order to clarify the ambiguity between the residual potential measurements and the above observations, we decided to explore an alternative approach to the trapping problem.

p-diethylaminobenzaldehyde-diphenylhydrazone (DEH)



1,1-bis(4-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (BD)



p-dibenzylamino-2-methylbenz-aldehyde-diphenylhydrazone (DBH)

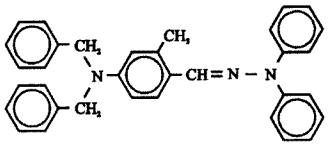


Figure 1. Chemical structures of the donor transport molecules studied.

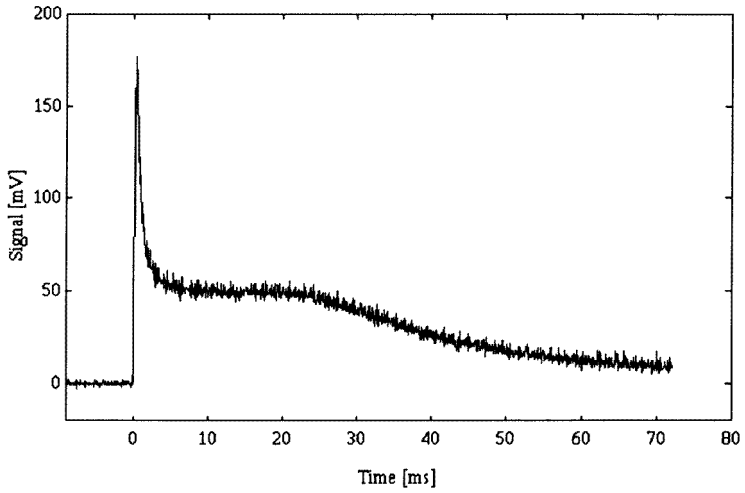


Figure 2. Uninterrupted hole transit signal obtained by electron beam excitation in 30% DBH-doped polycarbonate at room temperature and $F = 250$ kV cm^{-1}. Electron beam energy $= 5$ keV, dose $= 5$ pC and $CV = 10$ nC.

2. Interrupted time-of-flight method

Gibbons and Spear (1966) first suggested that, by removing the electric field during the transit and reapplying it after some waiting time Δt, deep trapping can be studied at zero field over extended periods well beyond normal transit times. This technique is known as the interrupted field time-of-flight (ITOF for short).

Carriers trapped in deep states during an interruption period Δt will not be recovered when restoring the field. This should lead to a decrease in the transient current from the pre-interruption value I_1 to

$$I_2(\Delta t) = I_1 \exp(-\Delta t/\tau) \tag{1}$$

where τ is the lifetime of free carriers, and therefore the change in the current on re-establishing the same electric field is proportional to the loss of charge. Notably, the ITOF technique has a unique capacity to (i) monitor the trapping over a very long time scale until detection of the recovered photocurrent is no longer possible; (ii) investigate trapping at zero electric field; and (iii) to study sample inhomogeneities by interrupting the progress of the carrier packet at different locations.

3. Experimental arrangement

In spite of such obvious advantages, the interrupted-field technique has not gained widespread use. This is explained by the experimental difficulty in eliminating the large displacement current, caused by the voltage switching, from the small transit signal to be detected. In most circuit arrangements, the switching surge is designed to cancel out using a bridge-type network (Kasap *et al* 1990). Technically, this either requires a battery operated floating point amplifier, a floating power supply, or the precision to switch opposite voltages at the same time and at the same rate. Although these solutions have been successfully applied before (Helfrich and Mark 1962, Kasap *et al* 1988, Polischuk and

Kasap 1991), in this work a novel detector switch was designed to overcome the floating voltage requirements. This is a simplified development of circuits earlier used by Hirsch *et al* (1984) and Methley (1986).

In this arrangement, a CMOS gate circuit is inserted between the sample and the detector, as shown in figure 3. The gate grounds the sample through the shunt switch during the time of the transient surges produced by the bias transitions. Once the transient is over, the detector is connected through the serial switch to the sample. This arrangement is readily added to a conventional TOF system, but demands complex control over the driving signals (figure 4). Five independent time settings were required: first bias 'on' period, interruption time, second bias 'on' period, electron beam delay and detector dead-time. These objectives were realized by developing a versatile software-programmable timer board which was installed in the IBM PC control computer.

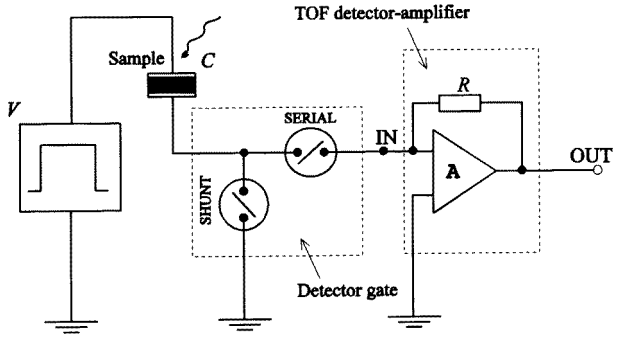


Figure 3. Interrupted TOF arrangement utilizing a grounded CMOS switch and current detector.

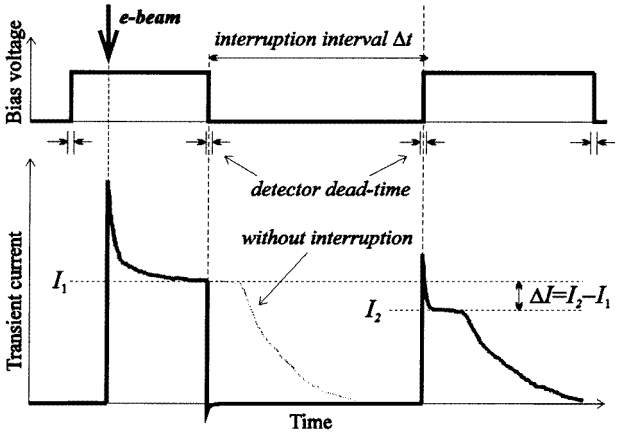


Figure 4. Schematic trace of interrupted TOF signal. The field switching and the time of beam excitation are marked.

The samples were wire-bar coated from viscous solutions in dichloromethane onto sheets of aluminized polyester. The dried layers were uniformly 16 μm thick. After evaporating a thin Al electrode onto the free surface, the sample was mounted on a simple holder placed in the electron beam apparatus (Németh-Buhin 1996). Excitation was by a single beam pulse

through the top Al coating. Typically, the beam cross-sectional area was 0.1 cm^2, the pulse width 10 μs, the charge per pulse 5 pC, and the beam energy 5 keV giving a penetration depth of 1–2 μm. The experiments described were all carried out at room temperature.

Typical ITOF signals in DBH are shown in figure 5. First the output signal was recorded without electron beam excitation (S2) i.e. in the absence of any transit current. The measurement was then repeated with excitation yielding a superimposed signal (S1) of the transient current (S3) and the detector noise (S2). Since the amplifier was operating in the linear regime, the transit component S3 was simply obtained by subtracting S2 from S1. For short Δt (a few ms), the transient signal may be recomposed and compared to an uninterrupted waveform. The similarity between S3 = S1–S2 in figure 5 and the uninterrupted signal in figure 2 is remarkable. This proves the validity of the subtraction to recover the true transit component from the noise-laden primary signal.

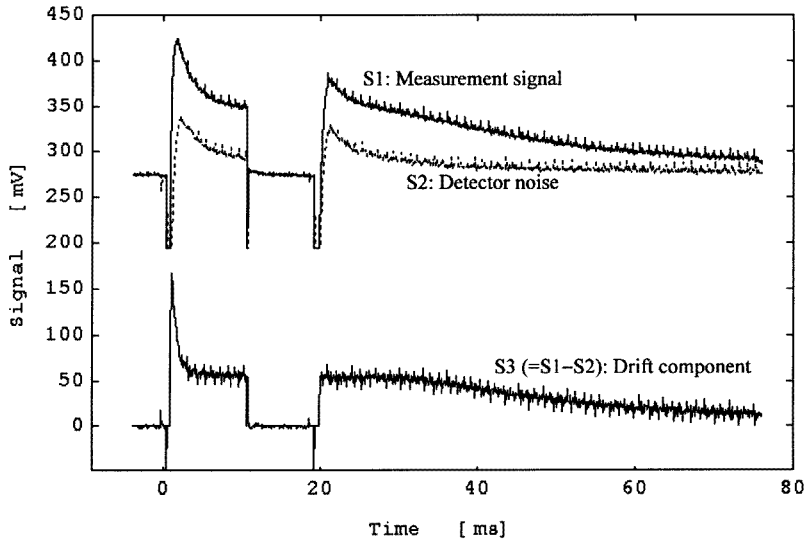


Figure 5. Transient signals with 10 ms interruption in 30% DBH-doped polycarbonate at room temperature and $F = 250$ kV cm^{-1}.

It was found that the detector noise (S2) increased with the bias voltage and could not be reduced by simply increasing the detector dead-time. This led to the conclusion that the major part of the noise appearing as an exponential decay is related to the discharge of the shunt switch after being hugely overloaded by the displacement current. Although an additional tunable switch to compensate for the switching transient was incorporated in the gate design, it could only reduce but not completely cancel the transient.

4. Results and discussions

Using the above arrangement, interrupted hole transit measurements were carried out in DEH-, BD- and DBH-doped polycarbonate layers (figure 1). At moderate electric fields, (say 250 kV cm^{-1}) the flight was interrupted at half the transit time to stop the carriers near the middle of the transport layer of thickness L. The total amount of transiting charge Q was kept small so that the dispersion of the carrier packet under its self-field did not result

in carrier loss to the electrodes during Δt. This requirement is equivalent to the following condition

$$\Delta t/t_{tr} < (CV/2Q)\exp(\beta F_0^{1/2}) \tag{2}$$

where C is the capacitance of the bombarded area, V is the bias voltage, $F_0 = V/L$ is the electric field before interruption, β is the Poole–Frenkel coefficient and t_{tr} is the transit time of carriers in an uninterrupted experiment. Equation (2) was derived by calculating the time required for a carrier to travel from the centre to either surface of the sample with a mobility $\mu = \mu_0 \exp(\beta F^{1/2})$ in the self-field of the carrier packet approximated by $F = F_0 Q/CV$. Inserting typical values of $CV \simeq 10$ nC, $\exp(\beta F_0^{1/2}) \simeq 8$ (for DEH at $F_0 = 250$ kV cm^{-1}) and $Q \approx 40$ pC, one gets $\Delta t < 1000 t_{tr}$.

At low fields the long transit times allow long Δt. On the other hand, with decreasing field the TOF signal also becomes smaller unless the transiting charge Q is increased. Taking these factors into account and the fact that the detector noise was much reduced 1 ms after switching, the optimum transit time for the ITOF measurements lies in the 10 ms range. This condition for the best signal-to-noise ratio explains the choice of the measurement parameters.

In figures 6(a) and (b) the ratio of the transit currents I_2, measured after, and I_1, measured before the interruption, is shown for DEH and BD, respectively. Surprisingly, in both cases this ratio seems initially to follow a logarithmic dependence on Δt. Such behaviour cannot be associated with carrier trapping (equation 1), and therefore a capture time cannot be deduced from the observed decrease. Another interesting aspect of the results is that, after an interruption of longer than 1000 ms, the ratio became independent of Δt. This observation by itself provides strong evidence against the existence of deep trapping states in the materials under test, in agreement with the theoretical expectations for trap-free transport. The origin of the non-exponential signal decrease in the $\Delta t < 1000$ ms range remains to be considered.

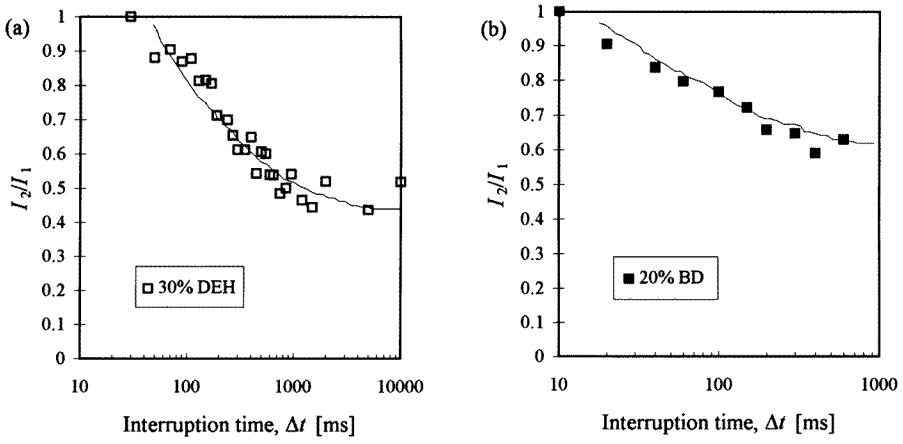


Figure 6. Relative decrease of the drift current following interruption in (a) 30% DEH- and (b) 20% BD-doped polycarbonate transport layers.

The only reference in the literature to ITOF experiments on a MDP is that by Kanemitsu and Imamura (1990). These authors claim to have observed deep trapping in DEH-doped polycarbonate with carrier life-times in the range 20–40 ms. In the present authors' opinion

such a small value is unacceptable. For example, in DEH transits were routinely recorded with flat plateaus exceeding 1000 ms. Unfortunately, Kanemitsu and Imamura show only a schematic diagram of an interrupted signal and do not disclose any experimental details of their measurements.

Looking for other references to ITOF measurements on comparable materials in the literature, we can find only a handful applying to selenium- and silicon-based photoreceptors. Unequivocally, the amplitude of the recovered photosignals in a-Se (Kasap *et al* 1988, Polischuk *et al* 1991), Cl doped a-Se (Methley 1986) and a-Si:H (Spear *et al* 1983) were reported to decrease exponentially with Δt. Moreover, the carrier life-times inferred from these measurements agreed with those determined from the initial decay of the transient signal (Methley 1986). Unfortunately, since MDPs are very different from Se and Si compounds, direct comparison between these materials is not possible.

Further systematic experiments revealed new features. For demonstration, the recorded signals are plotted by moving the beginning of the time scale to the end of the interruption interval, as shown in figure 7. In this presentation, the increase in the effective transit time (the time a carrier spends in the sample under non-zero bias) with Δt is obvious. It suggests that, after interruption, the holes move more slowly with longer Δt. Also note that the signals develop a hump. Immediately after the sweeping field is switched on, the signals start to increase from the non-zero I_2. The growth is seemingly broken by the arrival of carriers at the collecting electrode. However, the total charge collected during and after transit hardly drops even for Δt as long as 10 s, reaffirming the virtual absence of traps.

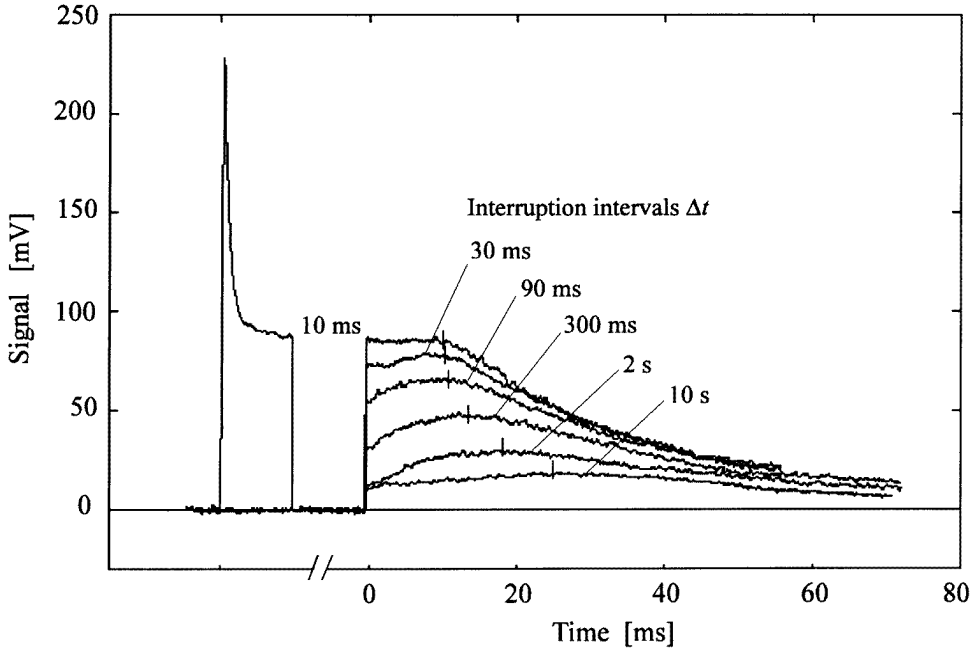


Figure 7. Transit signals for various interruption intervals in 30% DBH-doped polycarbonate at room temperature and $F = 250$ kV cm^{-1}. The transit signals are plotted here such that the beginning of the time-scale is moved to the end of the interruption interval. The arrival of the first carriers at the collecting electrode is marked by short vertical lines.

A straightforward explanation for the slow current growth after interruption is 'heating' of the carriers by the electric field. The observation of the TOF plateau indicates that by the time of the interruption, thermal equilibrium of carriers is well established. According to the disorder theory (Bässler 1993), in the presence of an electric field F, the mean energy of the equilibrium population of carriers is raised by $(F/F_0)^{1.5}$ (with $F_0 \simeq 1.8$ MV cm^{-1}) from its zero-field value σ^2/kT below the centre of the gaussian DOS. However, when the bias is switched off, the carrier packet must start to settle around a lower energy level appropriate to zero field. This process will be referred to as 'cooling'. Carriers settled at this lower energy also have lower mobility as they must hop further and overcome a higher energy barrier upon each transition. Carrier cooling and the concomitant mobility decrease account for the observed decrease in I_2. After re-establishing the field, the equilibrium distribution will slowly change and the carriers gradually move to higher energy levels. This process, here called 'field heating', accounts for the increase in the mobility and thus in the transit current. Assuming an infinitely thick sample and the absence of deep trapping, the transit current should eventually reach its pre-interruption value I_1. However, the time available is limited by the finite sample size as carriers start to reach the collecting electrode.

This is the first direct experimental observation of field heating and cooling which has considerable significance as such processes can occur only in a broadened distribution of energy states. As far as the authors can see, the conventional model for polaron transport (Emin 1973) cannot account for the relaxation pattern observed. In that model, the spread of carrier ground state energies due to spatial disorder is neglected, and carriers hop at a discrete energy level at half the polaron binding energy. Carrier settling cannot take place in such monoenergetic transport states.

It is important to note that the cooling time for carriers appears to be much longer than the heating time. According to figure 6, the transit current measured after the interruption becomes independent of the interruption time above 1000 ms. On the other hand, the signal recovery or increase after interruption takes place on the scale of the transit time i.e. in the order of 10 ms (figure 7). Comparing these values, we can conclude that field heating is two orders of magnitude faster than the cooling process, at least under these conditions. Such a difference between cooling and heating times can be understood in the framework of the disorder model. Since the number of deep states in the tail of the gaussian DOS is small, the carriers may wander (diffuse) for some time before finding one (cooling). In contrast to this, a carrier occupying a deep state is surrounded by sites with higher energy. Hence, heating can occur relatively fast once the activation energy is provided by the field for the deep-lying carrier to make a transition out of its state.

The explanations above can fully account for the observed change of the transit current before and after the interruption, while being consistent with negligible carrier trapping.

5. Conclusions

In summary, the technique of interrupted time-of-flight has been demonstrated here to be a powerful tool to study carrier kinetics in doped polymers. The results of these measurements lend strong evidence against any deep trapping of carriers in all the three MDPs studied. The behaviour of the current after interruption may be associated with cooling and field heating of carriers, strongly supporting the disorder theory of transport. However, the effects of temperature and electric field have not yet been systematically investigated. Since both these parameters strongly affect the equilibrium carrier distribution, it is expected they both play important roles in the carrier relaxation times observed during the interruption.

Such experiments promise to provide a new approach to the understanding of the transport phenomenon in doped polymers.

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References

Abkowitz M and Enk R C 1982 *Phys. Rev.* B **25** 2567
Bässler H 1993 *Phys. Status Solidi* b **175** 15
Borsenberger P M and Weiss D S 1994 *Organic Photoreceptors for Imaging Systems* (New York: Dekker) ch 7
Emin D 1973 *Electronic and Structural Properties of Amorphous Semiconductors* ed P G Lecomber and J Mort (New York: Academic) ch 7
Gibbons D J and Spear W E 1966 *J. Phys. Chem. Solids* **27** 1917
Helfrich W and Mark P 1962 *Z. Phys.* **166** 370
Hirsch J, Ko A Y and Irfan A Y 1984 *IEEE Trans. Electr. Insulat.* **EI-19** 190
Kanemitsu Y and Imamura S 1990 *J. Appl. Phys.* **67** 3728
Kanemitsu Y, Funada H and Imamura S 1990 *J. Appl. Phys.* **59** 697
Kasap S O, Polischuk B and Dodds D 1990 *Rev. Sci. Instrum.* **61** 2080
Kasap S O, Thakur R P S and Dodds D 1988 *J. Phys. E: Sci. Instrum.* **21** 1195
Methley S G 1986 *PhD Thesis* University of London
Movaghar B, Grünewald M, Ries B, Bässler H and Würtz D 1986 *Phys. Rev.* B **33** 5545
Németh-Buhin A 1996 *PhD Thesis* University of London
Okuda M, Motomura K, Naito H, Matsushita T and Nakau T 1982 *Japan. J. Appl. Phys.* **21** 1127
Pacansky J, Waltman R J, Grygier R and Cox R 1991 *Chem. Mater.* **3** 454
Polischuk B and Kasap S O 1991 *Meas. Sci. Technol.* **2** 75
Spear W E 1957 *Proc. Phys. Soc.* B **70** 1139
Spear W E, Steemers H L and Mannsperger H 1983 *Phil. Mag.* B **48** L49