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Hole transport in selenium-based amorphous xerographic photoreceptors

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Xerographic time of flight (XTOF) and conventional time of flight (TOF) experiments were used to determine the response of various selenium-based amorphous monolayer photoreceptors to short light pulses. From the observed flight time, the hole drift mobility, μ_h, of charge carriers was deduced.

For pure and lightly doped a-selenium, transient photocurrent signals at low field in both experiments exhibit a decay during the time prior to transit time. This has been attributed to the loss of charge carriers from the propagation photoinjected charge packet and the time constant of the decay, τ_h, has been taken as the hole lifetime. Detailed analysis was carried out on transient signals obtained from both experiments to examine this interpretation. For a given composition, sample thickness, light intensity, substrate material and top contacts (in TOF only) were varied to ensure that the observed decay time constant τ_h is a meaningful bulk parameter. Hole transport measurements support the assignment of τ_h as hole lifetime.

μ_h and τ_h were measured as a function of composition and applied field. Experimental data suggest that the hole transport mechanism is shallow trap controlled. Light doping of selenium with arsenic creates shallow traps and hence causes hole transport to deteriorate. Addition of chlorine promotes hole transport by increasing the lifetime but the hole drift mobility is reduced. Addition of tellurium in the range 0–7 wt% progressively decreases hole drift mobility, due to an increase in the density of the shallow traps. When chlorine is added to Se–Te alloys, it improves the hole transport by increasing τ_h but the hole mobility falls. Hole drift mobility in all systems except for hole response in pure selenium is field dependent of the form $\mu_h^- \sim E^n$ where E is the applied field and n is a constant less than unity.

1. Introduction

Charge transport in low conductivity amorphous semiconductors has been the subject of considerable interest in recent years [1–5]. The conventional time of flight method (TOF) has up to now been one of the few fruitful tools for evaluation of drift mobility, μ, and carrier lifetime, τ, in these materials [6–9]. A relatively less familiar technique known as xerographic time of flight (XTOF) has been found very useful in recent years as an alternative and non-destructive technique [10–12].

The principle of operation of both techniques involves photoinjection of a thin charge sheet into the sample and observing its transport through the bulk under the action of an externally applied voltage. In TOF configuration, the sample is sandwiched between two electrodes across which the external field is applied. In XTOF, the surface of the sample resting on earthed electrode is floating and the applied voltage is in the form of an electrostatic charge, a configuration similar to that applied in the xerographic process. The purpose of this paper is to report the results on room temperature μ_h and τ_h in a selenium-based photoreceptors using both TOF and XTOF techniques.

Samples were fabricated by vacuum evaporation ($\sim 10^{-6}$ torr) of vitreous pellets from long stainless steel boats onto metal substrates. Various compositions of amorphous selenium alloyed were obtained by mixing the correct amounts by weight of pure selenium with portions of pre-alloyed master batches. The pure selenium pellets used were of different xerographic grades (99.999–99.9999 %). Scanning electron microprobe (SEM) analysis on the composition variation across the thickness of the samples was also carried out. In a few samples, due to fractionation effects, the top surface ($< 2\,\mu$m) was slightly richer in impurity than the bulk. For example, surface tellurium content of a Se–12 wt % Te is measured to be 13 wt %. Fractionation in samples containing arsenic was found to be quite apparent, in that concentration at the surface was sometimes as much as 50 % over the bulk value. The impurity contents mentioned in this

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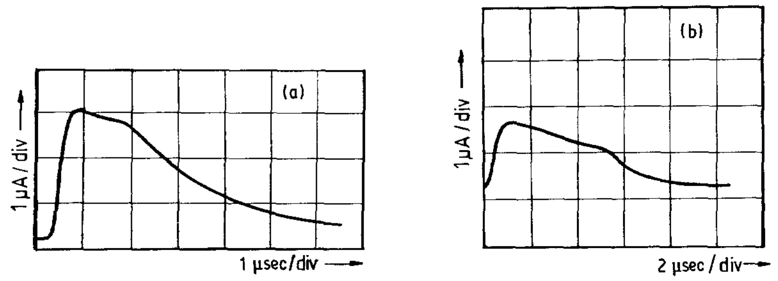

Figure 1 Typical low field (a) XTOF ($V_a = 115\,\text{V}$, $T_t = 1.75\,\mu\text{sec}$) and (b) TOF ($V_a = 40\,\text{V}$, $T_t = 4.9\,\mu\text{sec}$) transient current waveforms for a $58\,\mu\text{m}$ thick a-selenium sample.

paper refer to the bulk value. The compositional profile of the chlorine is not known due to the difficulties of the analysis. The chlorine content quoted as wt p.p.m. was obtained from the suppliers.

Transport parameters were evaluated by the conventional time of flight (TOF) and the xerographic time of flight (XTOF) techniques. The details of both measurements have already been discussed [6–13].

2. Results and discussions

2.1. Pure selenium

Fig. 1 shows hole transient current waveforms obtained from XTOF and TOF experiments. From the break in the waveform, the transit time T_t is measured. The mobility is then calculated from

$$\mu_h = \frac{L^2}{T_t V_a} \qquad (1)$$

where L is the sample thickness and V_a is the applied voltage. The trapping time, τ, is estimated from the analysis of the waveform. The signals should be recorded at low fields so that the effect of trapping can be observed. At high fields the transit time is smaller than the trapping time and the signal becomes nearly an ideal square pulse.

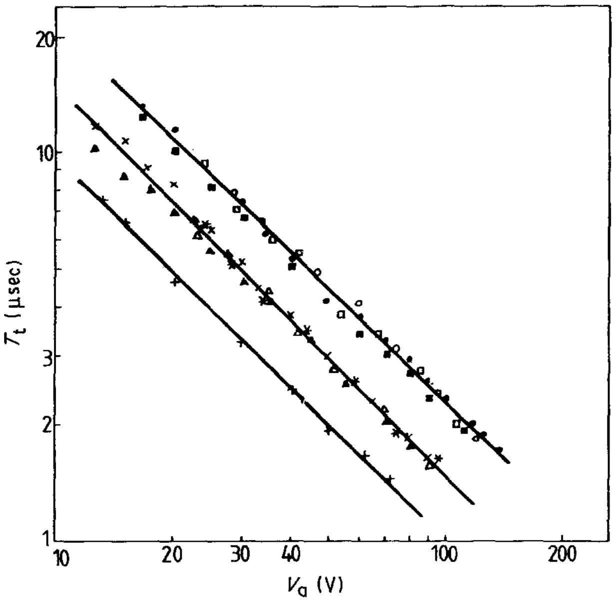

Figure 2 Log–log plot of transit time T_t against applied voltage V_a for a-selenium samples of various thickness and different substrates (results obtained from both XTOF and TOF experiments). (○XTOF, $L = 59\,\mu\text{m}$ Au-Se-Au; ● TOF, $L = 59\,\mu\text{m}$, Au-Se-Au; □ XTOF, $L = 59\,\mu\text{m}$, Al-Se-Au; ■ TOF, $L = 59\,\mu\text{m}$, Al-Se-Au; △ XTOF, $L = 49\,\mu\text{m}$, Au-Se-Au, TOF, $L = 49\,\mu\text{m}$, Au-Se-Au; *XTOF, $L = 49\,\mu\text{m}$, Al-Se-Au; ×TOF, $L = 49\,\mu\text{m}$, Al-Se-Au; +TOF, $L = 40\,\mu\text{m}$, Al-Se-Au). The full lines are for $\mu_h = 0.16\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$.

For pure or lightly doped a-selenium, it has been reported that the decay in the TOF current waveforms at low field is of the form [14–16]

$$I(t) \propto e^{-t/\tau} \qquad (2)$$

Log–log plots of transit time as a function of applied voltage for a-selenium samples of different thicknesses are shown in Fig. 2. From the slope of these lines, the hole drift mobility μ_h was calculated to be $0.16\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ and field independent. Note that XTOF and TOF experimental data fall on the same line. The decay of the transient signals in the time domain $0 < t < T_t$ in both experiments was found to satisfy Equation 2. For example, Fig. 3 shows the relationship between $\log_e I(t)$ and t obtained from the waveforms in Fig. 1. Note that the decay can be described by a single exponential function and although the applied fields are different by nearly a factor of three, the decay time constants τ_h are very close and independent of the type of experiment.

Fig. 4 shows the dependence of τ_h on the applied voltage for pure selenium samples of the same thickness. It is evident that the two experiments give similar

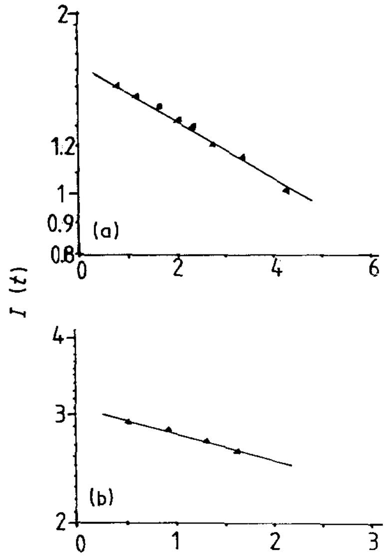

Figure 3 Semilogarithmic plot of hole current waveforms of Fig. 1. (a) TOF (hole) $V_a = 40\,\text{V}$, $\tau_h = 9.4\,\mu\text{sec}$, $H = 2\,\mu\text{sec}$, $V = 1\,\mu\text{A}$. (b) XTOF (hole) $V_a = 115\,\text{V}$, $\tau = 9.3\,\mu\text{sec}$, $H = 1\,\mu\text{sec}$, $V = 1\,\mu\text{A}$.

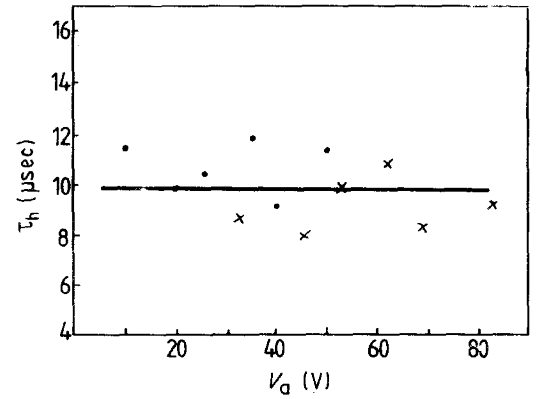

Figure 4 Dependence of hole lifetime τ_b on applied voltage V_a for a-Se (results obtained from both TOF (●) and XTOF (x) experiments). $L = 58\,\mu m$.

results. In order to examine the contact effects on both μ_h and τ_h, TOF experiment was carried out on similar samples with different top and bottom contacts. Typical transient current waveforms for gold, aluminium and copper as top electrodes are shown in Fig. 5. Semilogarithmic representation of these waveforms in Figs 6 and 7 shows clearly that both μ_h and τ_h are independent of the top contact and the applied field. From the results in Fig. 8, it can also be concluded that τ_h is independent of bottom contact. τ_h and μ_h were also found to be independent of the excitation intensity as long as the intensity is not too high to result in waveforms with a progressive rise in the current and a sharp break at a time $T_t' < L^2/\mu V_a$, due the space change of the injected carriers [17, 18]. These observations indicate clearly that μ_h and τ_h are transport properties of the samples.

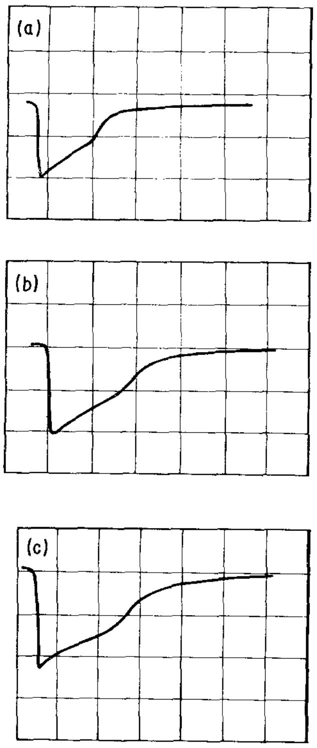

Figure 5 Effect of top contact on TOF hole current waveform in a-Se samples: (a) gold top contact, $V_a = 30$ V (b) aluminium top contact, $V_a = 20$ V (c) copper top contact, $V_a = 10$ V. $5\,\mu$sec div^{-1}.

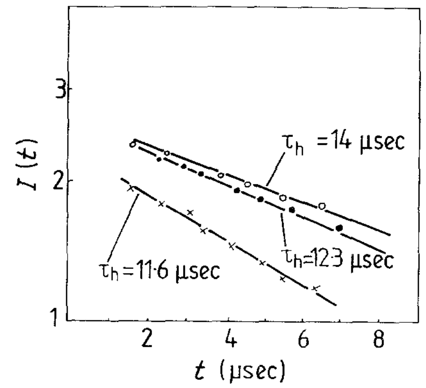

Figure 6 Semilogarithmic representation of hole current waveforms of Fig. 5. (× gold, ● aluminium, ○ copper).

2.2. Effect of impurity

In a-Se + 0.3 wt % As, the transient signal exhibited a single exponential decay as in pure selenium and τ_h was independent of applied field. In a-Se–Cl, a-Se–Te, a-Se–Te–Cl and a-Se–Te–Cl–As, small addition of impurities caused a slight deviation from the single exponential decay. The signals contained an initial rapid decay in the form of a spike followed by a relatively slower decay. For example, Fig. 9 shows the semilogarithmic plots of $I(t)$ against t for a-Se + 3.7% Te + 10 p.p.m Cl at electric fields of $4 \times 10^4\,\mathrm{V\,cm^{-1}}$ and $4.7 \times 10^4\,\mathrm{V\,cm^{-1}}$. Note that the transit time is well defined. The decay time constant of the initial spike (τ_s) and the remaining portion of the signal prior to transit time (τ_h) are field dependent. The field dependency of τ_s and τ_h is illustrated in log–log plots in Fig. 10.

Over most regions of the applied field both τ_s and τ_h can be expressed as τ_s or $\tau_h \; \alpha \; E^{-k}$ where k is a constant. As the method of excitation involves the creation of a charge sheet beneath the top surface of the sample, it has been argued that the initial spike is due to the movement of electrons towards the top surface [18, 19]. If this is the case, then due to the large difference in electron and hole mobility in our samples, a large spike due to the holes in electron response

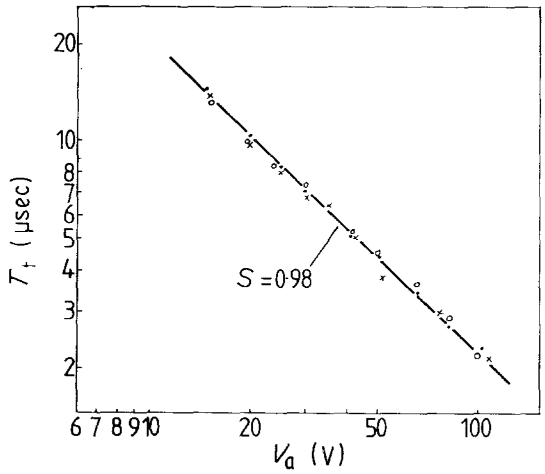

Figure 7 Log–log plot of hole transit time T_t against applied voltage V_a for a-Se sample with different top electrodes. (× gold, ● aluminium, ○ copper) $L = 58\,\mu m$, $\mu = 0.16\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$.

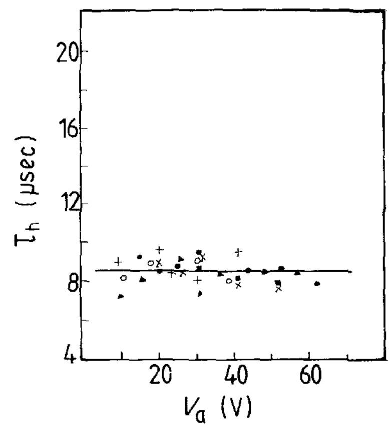

Figure 8 Dependence of hole lifetime on applied voltage V_a for a-Se using both XTOF and TOF experiments. (● Au–Se–Au, ■ Al–Se–Au, ▲ Au–Se–Au, × Al–Se–Au, + Al–Se–Au, ○ Au–Se–Au).

TABLE I Effect of impurity on carrier lifetime in a-Se based photoreceptors

Impurity (wt %)	τ_{ho} (μsec)	
	XTOF	TOF
Se + 0.3 % As	19	21
Se + 0.3 % As + 30 p.p.m. Cl	13	12
Se + 30 p.p.m. Cl	–	50
Se + 40 p.p.m. Cl	–	70
Se + 60 p.p.m. Cl	–	95
Se + 3.5% Te	75	80
Se + 3.7% Te + 10 p.p.m. Cl	240	260
Se + 2.3 % Te + 0.3 % As + 20 p.p.m. Cl	120	130

should be observed. Furthermore, the duration of the spike should be inversely proportional to the appropriate mobility. However, detailed analysis of transient signals in systems discussed here does not support the above explanation for the spike. If this initial spike is neglected, then from the semilogarithmic plot of τ_h against applied field, the value of τ_h at zero field can be obtained by extrapolation and regarded as the hole lifetime. The summary of results is shown in Table I where τ_{ho} refers to the value of τ_h at zero field. Note that in a-Se–Cl system, the XTOF experiment was not possible due to the rapid dark decay of the applied surface voltage. As shown in the table of results, addition of arsenic slightly increases the hole lifetime, whereas combinational doping of arsenic and chlorine restores the lifetime to that of pure selenium. Gradual addition of chlorine progressively increases τ_{ho}. This behaviour has been reported by other investigators [18]. The addition of tellurium also increases τ_{ho} but by a smaller factor. This is expected because otherwise the transient signal becomes trap limited. As found earlier, τ_h in a-Se is 10–14 μs, which is comparable with transit time in Se–Te systems. The presence of a break in the transient signal implies that τ_{ho} in Se–Te alloys has increased. The addition of arsenic and As + Cl to Se–Te further increases τ_{ho}. The maximum value of τ_{ho} is 260 μs for a-Se + 3.7 %Te + 10 p.p.m. Cl sample.

Fig. 11 shows the plot of log μ_h against log E in these systems. Note that except in pure selenium, field dependence of drift mobility can be expressed algebraically as

$$\mu_h \sim E^n \tag{3}$$

where n is a constant less than unity. The values of n in this equation and μ_h at $E = 10^4\,\mathrm{V\,cm^{-1}}$ are given in Table II. From the data shown in this table and that given in Fig. 11, the following results emerge.

(i) The field dependence of μ_h in all systems can be expressed by Equation 3 with n having a minimum value of 0.02 for a-Se + 0.3 % As + 30 p.p.m. Cl and a maximum value of 0.28 for a-Se + 60 p.p.m. Cl.

(ii) Addition of 0.3% As to pure selenium slightly reduces μ_h (Table II). Arsenic modified the tail states of the conduction band by gradually shifting the mobility edge to high energies and this reduces the trapping factor Θ in

$$\mu = \Theta\mu_0 \tag{4}$$

where μ is the drift mobility and μ_0 is the microscopic mobility.

(iii) Introducing 30 p.p.m.Cl to a-Se + 0.3 % As further reduces μ_h and its field dependency.

(iv) Addition of chlorine alone reduces the magnitude of μ_h and increases its field dependency. For example, the value of n is 0.13 for Se + 30 p.p.m. Cl and 0.28 for Se + 60 p.p.m. Cl.

(v) Tellurium addition in the range of 0–5 wt % progressively decreases μ_h. For 12 wt % Te concentration or greater, μ_h gradually increases. Note that the field dependence of μ_h, on the other hand, progressively increases. It is commonly believed that the transport mechanism in Se–Te alloys is shallow-trap controlled. The reduction in μ_h is due to the extra hole traps introduced by tellurium [21–23].

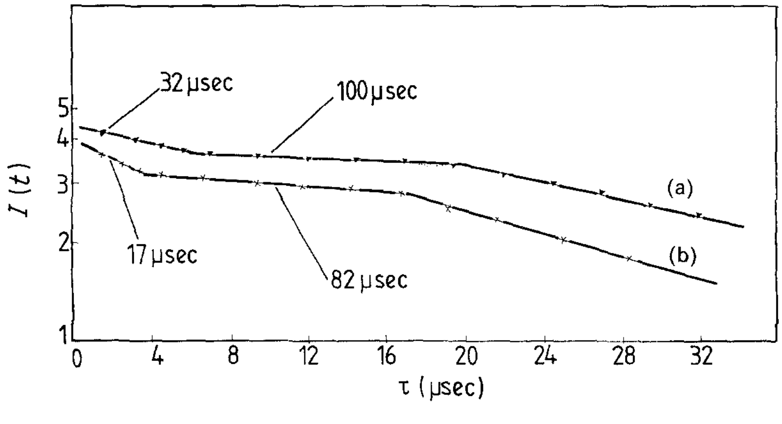

Figure 9 Semilogarithmic representation of XTOF transient hole currents in a-Se + 3.7 % Te + 10 p.p.m. Cl photoreceptor. (▲ $E = 4.0 \times 10^4\,\mathrm{V\,cm^{-1}}$, × $E = 4.7 \times 10^4\,\mathrm{V\,cm^{-1}}$).

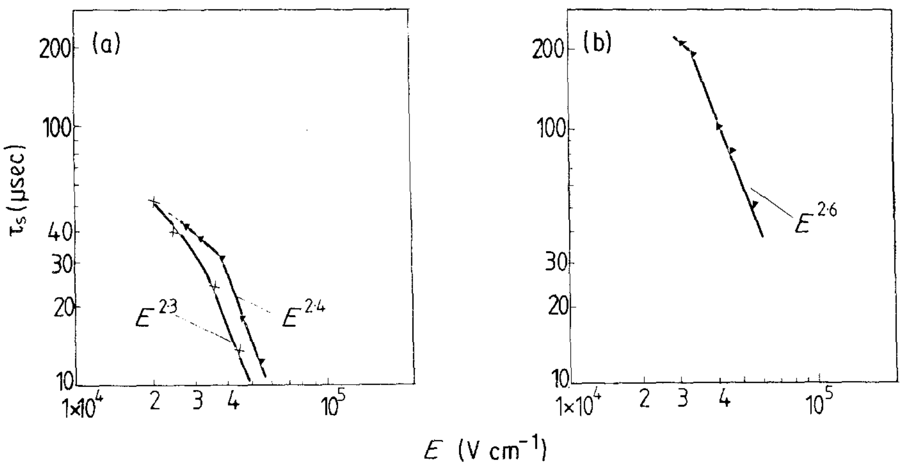

Figure 10 Field dependence of XTOF transient hole current in a-Se + 3.7% Te + 10p.p.m. Cl (▲) and a-Se + 5% + 10p.p.m. Cl (x) photoreceptors: (a) log–log plot of the spike time constant τ_s against applied electric field E; (b) log–log plot of the hole current time constant τ_h against applied electric field E.

(vi) When chlorine is added to a-Se–Te, μ_h is slightly reduced due to additional shallow traps introduced by chlorine. Further addition of arsenic to this system causes an increase in the magnitude of μ_h at a given field but the field dependence somewhat decreases. It may be argued that this behaviour is because of a trap compensation mechanism in which arsenic complements the effect of chlorine.

3. Conclusions

In order to ascertain that the hole drift mobility, μ_h and carrier lifetime, τ_h, are meaningful parameters characteristic of bulk transport, two different experimental techniques of XTOF and TOF were employed, and transient signals were closely compared and analysed in detail. It was shown that in all systems hole transit times are well defined and they scale correctly with the sample thickness.

In pure selenium, μ_h and τ_h are independent of the experimental techniques, electric field, sample thickness, light intensity and electrode materials. The data suggests that the hole transport is shallow trap controlled. In this case, the carriers move through extended states while rapidly being trapped and released by a set of shallow traps of release time much shorter than the transit time. Experimentally we have determined the sum of the times the carrier is free and immobilized in shallow traps in the course of its transit through the sample. As the carrier contributes to the current only during the free time, the drift and microscopic mobilities are related by

$$\mu = \mu_0 \frac{\tau_0}{\tau_0 + \tau_t} \qquad (5)$$

where τ_0 is the mean free time in the extended state and τ_t is the average dwell time in a shallow trap.

Light doping of selenium with arsenic causes hole trapping and hence deterioration in the hole transport. Addition of chlorine promotes hole transport by increasing τ_h; but the hole drift mobility is reduced. Combinational doping of selenium, arsenic and chlorine has an interesting effect on the transport parameters in that arsenic and chlorine tend to act in a compensating manner to each other. Addition of 30 p.p.m. chlorine to Se + 0.3 % As, for example, improves the hole transport. The addition of tellurium in the range 0–7 wt % progressively decreases μ_h due to the longer residence time of the carriers at the shallow traps. For tellurium concentrations greater than ~7 wt %, the hole mobility gradually increases. When chlorine is added to Se–Te alloys, it improves the hole transport by increasing τ_h. The hole mobility,

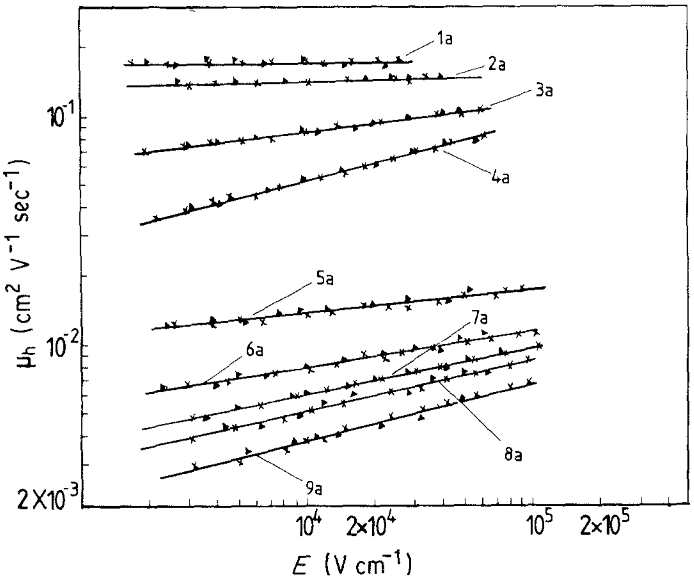

Figure 11 Electric field dependence of XTOF (▲) and TOF (×) hole drift mobility in various selenium based systems; 1(a) a-Se (L = 59 μm); 2(a) a-Se + 0.3 % As (L = 48 μm); 3(a) a-Se + 30 p.p.m. Cl (L = 46 μm); 4(a) a-Se + 17 % Te (L = 66 μm); 5(a) a-Se + 0/3 % As + 2.3 % Te + 20 p.p.m. Cl (L = 39 μm); 6(a) a-Se + 3.5% Te (L = 68 μm); 7(a) α-Se + 5 % Te (L = 60 μm); 8(a) a-Se + 5.3 % Te + 16 p.p.m. Cl (L = 62 μm); 9(a) a-Se + 12.5 % Te + 20 p.p.m. Cl (L = 62 μm).

TABLE II Effect of impurity on the hole drift mobility in a-Se based photoreceptors

Impurity content	μ_h at $E = 10^4\,\mathrm{V\,cm^{-1}}$	n in $\mu_h \sim E^n$
Se + 0.3 % As	0.14	0.03
Se + 0.3 % As + 30 p.p.m. Cl	0.12	0.02
Se + 30 p.p.m. Cl	8.7×10^{-2}	0.13
Se + 40 p.p.m. Cl	4.6×10^{-2}	0.23
Se + 60 p.p.m. Cl	1.8×10^{-2}	0.28
Se + 3.5% Te	8×10^{-3}	0.17
Se + 5 % Te	6.2×10^{-3}	0.19
Se + 12 % Te	8×10^{-3}	0.23
Se + 17% Te	5.3×10^{-2}	0.27
Se + 2.3 % Te + 20 p.p.m. Cl	7.3×10^{-3}	0.14
Se + 3.7 % Te + 10 p.p.m. Cl	5.8×10^{-3}	0.18
Se + 5 % Te + 16 p.p.m. Cl	5.4×10^{-3}	0.20
Se + 12.5 % Te + 20 p.p.m. Cl	4×10^{-3}	0.26
Se + 2.3 % Te + 0.3 % As + 20 p.p.m. Cl	13×10^{-3}	0.12

however falls with the chlorine content. Hole drift mobility in all systems except for a-Se was found to be field dependent of the form $\mu_h \sim E^n$. The consistency of μ_h–E plots among samples of different thickness and the fact that two different experiments provide similar results suggests that the observed field dependency is a bulk property of the samples. Such a dependency has also been reported by other investigators [15, 16] and it could arise from the field dependence of each of the parameters in Equation 5.

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