JOURNAL OF MATERIALS SCIENCE 23 (1988) 3286–3289

Effect of chlorine on xerographic properties of a–Se:Te alloys

S. M. VAEZI-NEJAD*
Microelectronics Laboratory, Faculty of Technology,
School of Electronic Systems Engineering, Kingston Polytechnic, Kingston upon Thames, Surrey KT1 2EE, UK

C. JUHASZ
Solid State Research Group, Department of Electrical Engineering, Imperial College of Science and Technology, London SW7 2BT, UK

Amorphous selenium (a-Se) has an optical bandgap of ~ 2.1 eV and a photogeneration efficiency close to unity at ~ 2.7 eV which makes it sensitive to the blue region of the visible spectrum. Alloying with tellurium reduces the bandgap and hence increases the photosensitivity towards longer wavelengths. Experimental results have already been reported to show that charge acceptance, residual voltage, dark decay rate and drift mobility are all sensitive to tellurium. Charge acceptance and carrier drift mobilities decrease with tellurium whereas dark decay rate increases. All these effects are undesirable in xerography. Transient photoconductivity and residual voltage measurements were carried out to investigate the effect of a small chlorine addition on the xerographic properties of a–Se:Te alloys. Results will be presented to show that chlorine improves the residual voltage and charge acceptance. Transient photoconductivity data on hole transport shows that the xerographically important parameter of carrier range is also improved. Hole drift mobility shows a weak field dependence of the form $\mu_h \simeq E^n$ where the index n is sensitive to chlorine. No electron transport could be detected in any of the samples. These results are interpreted in the framework of shallow-trap controlled transport.

---

1. Introduction

One of the outstanding commercial applications of amorphous semiconductors is in xerography. A typical xerographic process consists of the following steps.

(a) Sensitization of the photoreceptor by electrostatic charging from a Corona discharge. Electric field required for sensitization is ~ $10^5\,\mathrm{V\,cm^{-1}}$. This means a photoreceptor which is typically 50 μm thickness should be capable of sustaining at least 500 V. Most photoreceptors generally have a higher charge acceptance resulting in electric fields well in excess of the required value.

(b) Exposure of the sensitized photoreceptor to light for image formation.

(c) Development of the image using a developer consisting of a mixture of black (or coloured) toner particles and carrier beads.

(d) Transfer of image from the photoreceptor to the paper.

(e) Print fixing.

(f) Removal of the toners left on the photoreceptor.

(g) Exposure of the toners left on the photoreceptor to intense light to reduce the surface potential to some uniformly low values typically ~ 100 V corresponding to fields of ~ $10^4\,\mathrm{V\,cm^{-1}}$.

There are, therefore, a number of desirable electrical characteristics that a useful photoreceptor should exhibit. The most important of these are:

1. High charge acceptance.
2. Slow dark decay of photoreceptor surface potential. The photoreceptor must retain electrical charge on its surface long enough for completion of the xerographic image transfer process. For conventional photocopy machines, normally the dark decay to half-potential should be around 0.5 min.
3. Rapid discharge when exposed to light. During the image exposure, the charge held at the top surface of the photoreceptor must be dissipated in illuminated areas more rapidly than in unilluminated regions in order to produce an electrostatic image. The electrostatic image is simply the change in potential pattern of the photoreceptor surface which corresponds to the ilumination pattern to which the photoreceptor has been exposed. Difference in potential is referred to as electrostatic contrast. The phenomenon of trapping prevents complete discharge of the photoreceptor, even when exposed far in excess of that required to produce adequate electrostatic contrast. Thus there is a minimum to which the potential of a photoreceptor can be reduced by exposure and it is called "residual potential".

There are other desirable characteristics such as

**Present address:* Electronics Laboratory, Faculty of Technology, Thames Polytechnic, Wellington Street, Woolwich, London SE18 6PF, UK.

TABLE I Charge acceptance of various a-Se : Te and chlorine-doped a-Se : Te single layer photoreceptors

Content (wt %)	Thickness (μm)	Charge acceptance (V)
Se + 3.5% Te	68	1010
Se + 5% Te	64	890
Se + 7% Te	62	810
Se + 10% Te	63	760
Se + 15% Te	61	700
Se + 2.3% Te + 20 p.p.m. Cl	60	1100
Se + 3.5% Te + 16 p.p.m. Cl	58	930
Se + 4.6% Te + 26 p.p.m. Cl	60	980
Se + 5% Te + 16 p.p.m. Cl	62	950
Se + 12.5% Te + 20 p.p.m. Cl	66	900

photosensitivity to a particular wavelength, crystallization resistance, temperature and humidity resistance, thickness uniformity and mechanically hard surface. Finally, a practical photoreceptor should perform these functions under repetitive cycles otherwise the photoreceptor is said to have become fatigued. Most fatigue effects generally disappear after a rest period.

Photoreceptors in large numbers of photocopiers are based on amorphous selenium (a-Se) [1-4]. Single layer and double layer a-Se : Te alloys have already been discussed [5]. The purpose of this paper is to report the effect of chlorine in the range 16 to 26 p.p.m., on xerographic properties of these photoreceptors. Samples were prepared by thermal evaporation which has already been widely described and discussed [5-7]. Charge acceptance, dark decay and residual voltage were measured as described before [5]. Charge transport parameters, namely the drift mobility, μ, and carrier lifetime, τ, were found using electroded time of flight (ETOF) and xerographic time of flight (XTOF). The principle of operation of ETOF has been extensively reviewed by many authors [3, 4, 8-10]. XTOF is a less familiar technique and a practical apparatus has been recently described in detail by one of the authors [11].

3. Results and discussions

3.1. Sensitization, dark decay and residual voltage

The maximum voltage to which the free surface of a photoreceptor can be charged is referred to as the charge acceptance and it should give the required xerographic field of $10^5\,\mathrm{V\,cm^{-1}}$. As shown in Table I, all samples can be charged well in excess of the required field. To obtain these results it was found necessary to use a corona charging device similar to that which is used to form the electrostatic image in the xerographic process [11]. In a-Se : Te alloys, tellurium addition progressively reduces the charge acceptance. Tellurium concentration greater than 25 wt % was found to further improve the read sensitivity but at the expense of intolerable decrease in the charge acceptance and increase in the dark decay rate [12, 13]. Chlorine-doped Se : Te samples exhibited higher charge acceptance. For example, the charge acceptance of a 62 μm thick a-Se + 5% Te + 16 p.p.m. Cl sample was about 60 V higher than a 64 μm thick a-Se + 5% Te sample. In all samples, charge acceptance after several hundred cycles is reduced. This fatigue effect was found to disappear after a rest period of a few hours. In chlorine-doped Se : Te samples, addition of chlorine increased the dark decay rate. For example, the differences between the dark decay properties of alloys of 3.5% Te with 16 and 26 p.p.m. Cl are shown in Table II. Note that in 26 p.p.m. chlorine-doped samples, the fraction of potential remaining after 1 or 5 sec is considerably less than in 16 p.p.m. Cl-doped sample. The effect of chlorine addition is even worse in fatigued samples. The first cycle residual voltage measurement showed that chlorine addition reduces the residual voltage to acceptable levels corresponding to fields less than $10^4\,\mathrm{V\,cm^{-1}}$. For example, the first cycle residual voltages in a-Se + 3.7% Te + 16 p.p.m. Cl and a-Se + 4.6% Te + 26 p.p.m. Cl were +8 and +9 V, respectively.

TABLE II Effect of chlorine on the dark decay characteristics of a-Se + 3.5% Te + p.p.m. Cl

Sample condition	Fraction of potential remaining t sec after charging		
	Time, t (sec)	16 p.p.m. Cl	26 p.p.m. Cl
Well rested	1	0.96	0.93
	5	0.82	0.67
Fatigued (several hundred cycles)	1	0.94	0.90
	5	0.61	0.32

3.2. Carrier range

In a-Se based photoreceptors, it is more useful to measure time-resolved transits in the current mode of operation because of the dispersion and relatively long transit at low fields. Fig. 1 shows a typical XTOF transient hole current waveform for a 20 p.p.m. Cl-doped a-Se + 5.3% Te sample. From the break in the waveform, the transit time, T_t, is measured and the mobility, μ, is then calculated using

$$\mu = \frac{L^2}{T_t V_0} \tag{1}$$

where V_0 is the applied voltage and L is the sample thickness.

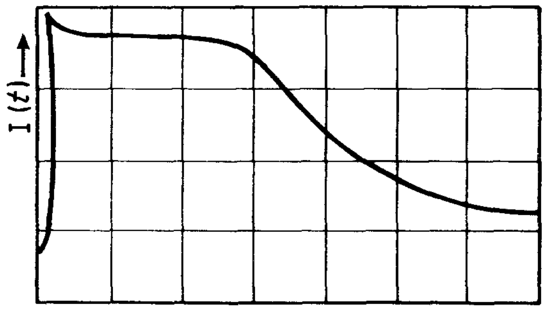

Figure 1 Oscilloscope trace of typical XTOF hole transient current waveform in 20 p.p.m. Cl-doped a-Se + 5.3% Te sample of thickness 58 μm. V_0 = 200 V, T_t = 28.5 μsec. Horizontal scale: 10 μsec per division. Vertical scale: 5 mV per division.

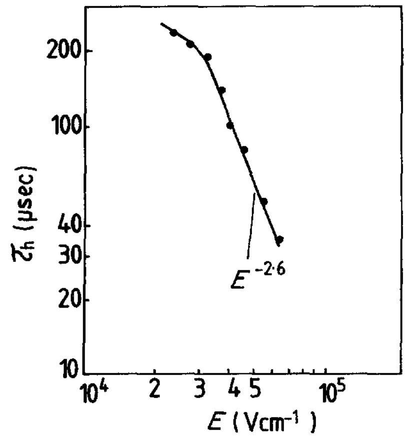

Figure 2 Field dependence of τ_h in a–Se + 3.7% Te + 10 p.p.m. Cl photoreceptor from XTOF experiment.

Hole carrier life time is estimated from the exponential decay of the signal at low fields in the time domain of $0 < t \leqslant T_t$. As can be seen from Fig. 1, the signal contains an initial rapid decay in the form of a spike. For calculation of the exponential decay time constant, τ_h, this deviation was neglected. μ_h in the samples was found to be field dependent.

From the logarithmic plot of τ_h against E, the value of τ_h at zero field was obtained by extrapolation and taken as the hole life time. For example, Fig. 2 shows the results for a–Se + 3.7% Te + 10 p.p.m. Cl. Note that over a wide range of field, τ_h can be expressed as

$$\tau_h \propto E^{-K} \tag{2}$$

where E is the applied field and K is a constant.

In all samples, electron response showed a rapid decay with no apparent break. Similar results were obtained using ETOF experiments.

It is interesting that electron response in chlorine-doped a–Se has also been found to be undetectable [1, 13–15]. There are basically two plausible explanations. First it is possible that the signal is limited by the presence of many traps in the sample. Secondly, it might be argued that combinational doping may have increased the conductivity of the samples so that XTOF or ETOF experiments are no longer applicable. To explore this latter possibility a series of electron dark decay experiments were carried out. Results showed that although the dark decay is rapid, the resistivity calculated from the initial stage of the dark decay is $\sim 10^{13}\,\Omega$cm which is sufficiently high for XTOF or ETOF experiments.

Fig. 3 shows the negative dark decay curves for two different batches of a–Se + 3.7% Te + 16 p.p.m. Cl photoreceptors. If a charged sample at the initial stage of the dark decay is treated as a capacitor with the photoconductive insulating layer as the dielectric medium, then from a simple RC equivalent circuit for the charged sample the rate of decay of the charged sample can be written as [2, 16]

$$-\mathrm{d}Q/\mathrm{d}t = Q/RC \tag{3}$$

using $Q = CV$ and $1/RC = \delta/\varepsilon_0\varepsilon_r$, Equation 3 becomes

$$\delta = -\varepsilon_0\varepsilon_r \mathrm{d}/\mathrm{d}t\,(\ln V)$$

$$\varrho = \frac{1}{\varepsilon_0\varepsilon_r}(\mathrm{d}/\mathrm{d}t \ln V)^{-1} \tag{4}$$

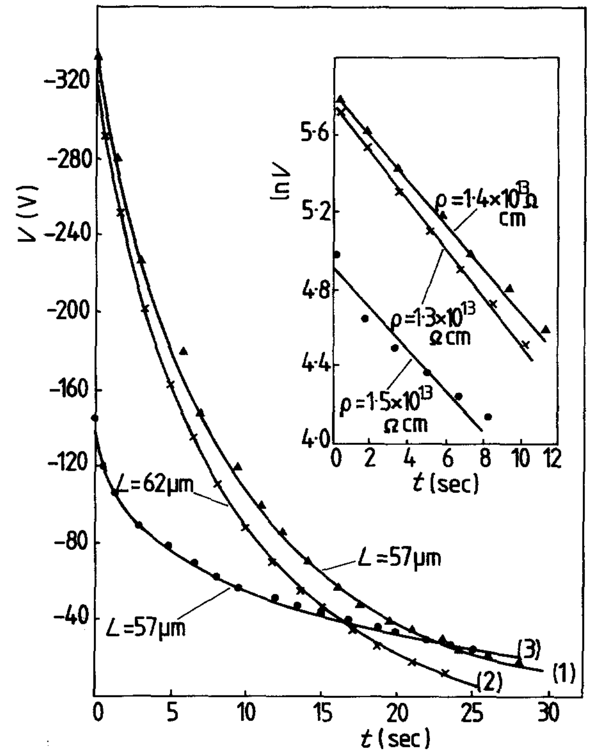

Figure 3 Electron dark decay curve for two batches of a–Se + 3.7% Te + 10 p.p.m. Cl photoreceptors. The inset shows plots of ln V against time. ϱ is the effective resistivity and L is the sample thickness. (x), (▲) The same batch; (●), (▲) different batch.

Thus the resistivity can be calculated from the knowledge of dielectric constant and slope of the dark decay curve. The inset in Fig. 3 shows plots of ln V against time and the corresponding values of ϱ.

As in a–Se : Te alloys [5], the hole drift mobility data show a weak algebraic field dependency of the form

$$\mu \propto E^n \tag{5}$$

when n is a constant less than unity. Figs 4 and 5 show typical results. Results for a–Se + 3.5% Te + y p.p.m. Cl in Fig. 4 show that the index n increases with chlorine addition. By comparing Figs 4 and 5 it can be seen that n also increases with tellurium content. Note that the field dependence shows no low field cut-off (constant drift mobility) region. Charge transport data in various samples are summarized in Table III. The product of carrier range and electric field is known as Schubweg S and it is another xerographically

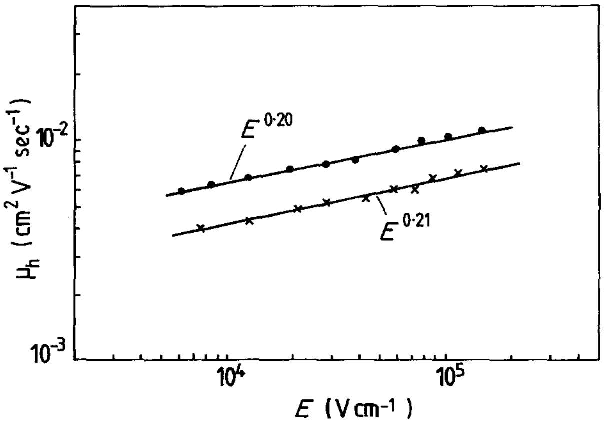

Figure 4 Log–log plots of hole drift mobility plotted against electric field for a–Se + 3.5% Te + y p.p.m. Cl photoreceptors. (●) Se + 3.5% Te + 10 p.p.m. Cl; (x) Se + 3.5% Te + 16 p.p.m. Cl.

TABLE III Charge transport parameters of various selenium-based samples

Content	Thickness (μm)	τ_{ho} (μsec)	μ_h at $E = 10^5\,\mathrm{V\,cm^{-1}}$ ($10^{-3}\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$)	Carrier range ($10^{-7}\,\mathrm{cm^2\,V^{-1}}$)	Schubweg S (μm)
a–Se	58	10	170	17	29L
a–Se + 3.5% Te	68	83	12	9.96	15L
a–Se + 5% Te	64	120	9	10.8	17L
a–Se + 3.5% Te + 10 p.p.m. Cl	61	190	10	19	31L
a–Se + 3.7% Te + 10 p.p.m. Cl	58	220	9.8	21.56	37L
a–Se + 4.6% Te + 16 p.p.m. Cl	60	312	9.6	29.95	50L
a–Se + 4.6% Te + 26 p.p.m. Cl	59	360	8.7	31.32	53L
a–Se + 5% Te + 26 p.p.m. Cl	62	410	6.8	27.88	45L

important parameter which is also included in this table. S is the distance a charge carrier travels before being trapped. As is recorded in Table III, S is several times greater than the sample thickness L. If S is comparable or less than L, then a considerable number of the photo-injected carriers will be trapped and the sample will exhibit an unacceptably high residual voltage and becomes unsuitable for xerographic process. Note that S is expressed as the multiple of L for comparison purposes. These results clearly show that chlorine addition improves the hole Schubweg. A widely proposed physical interpretation of these data is shallow trapping [3, 4]. In ETOF or XTOF experiments one determines the total time a carrier is free and immobilized in shallow traps in the course of its transit through the sample. The drift mobility, μ, is related to the microscopic mobility, μ_0, by

$$\mu = \mu_0 \frac{\tau_C}{\tau_C + \tau_r} \qquad (6)$$

where τ_C is the capture time and τ_r is the release time, both τ_C and τ_r depend on the detail of the trap model. For example, in the case of a set of traps of density N_t at a discrete energy E_t below the extended state with mobility μ_0, Equation 6 becomes

$$\mu = \mu_0 \frac{N_c}{N_t} \exp\left(-E_t/KT\right) \qquad (7)$$

where N_c is the effective density of states at the band edge. A field dependence of the drift mobility in the presence of traps could arise from the field dependence of the drift mobility of each of the parameters in Equation 6.

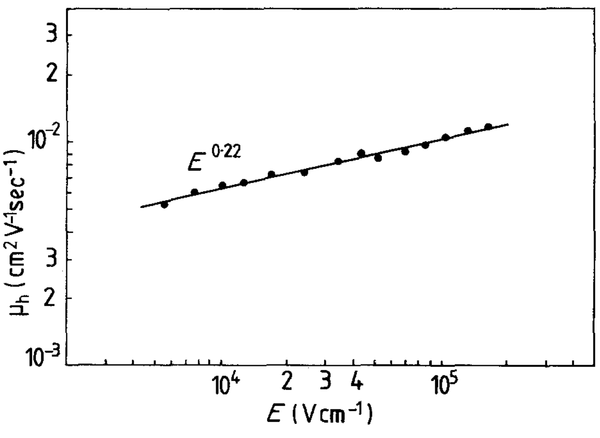

Figure 5 Log–log plot of hole drift mobility plotted against electric field for a–Se + 3.7% Te + 10 p.p.m. Cl.

4. Conclusion

Xerographic properties of various chlorine-doped a–Se:Te alloys, namely charge acceptance, dark decay, residual voltage and carrier range, were measured as a function of applied field and chlorine content. It was shown that addition of chlorine to Se:Te alloys improves the charge acceptance and the dark decay. Chlorine also causes further reduction in the residual voltages. All these effects are desirable in xerography. In spite of the fall in hole drift mobility, carrier range is improved due to substantial increase in the hole carrier life time. Transient electron response exhibited a rapid decay which was argued to be a property of the samples and not an experimental effect. Drift mobility and carrier life time were found to be field dependent as in a–Se:Te alloys.

References

1. S. M. VAEZI-NEJAD, PhD thesis, University of London, UK (1984).
2. R. M. SCHAFFERT, (ed.), "Electrophotography principles and optimisation" (Research Studies Press, Letchworth, Herts, 1984) Ch. 4.
3. N. F. MOTT and E. A. DAVIS (eds), "Electronic Processes in Non-Crystalline Materials", 2nd Edn (Clarendon Press, Oxford, 1979) p. 530.
4. J. MORT and D. M. PAI (eds) "Photoconductivity and Related Phenomena" (Scientific Publishing Co., Amsterdam, 1976).
5. C. JUHASZ, S. M. VAEZI-NEJAD and S. KASAP, *J. Mater. Sci.* **22** (1987) 2569.
6. J. C. SCHOTTMILLER, *J. Vac. Sci. Technol.* **12** (1975) 807.
7. M. D. TABAK and W. J. HILLEGAS, *ibid.* **9** (1972) 387.
8. W. D. SPEAR, *J. Non. Cryst. Solids* **1** (1969) 197.
9. R. WOLF, "Advances in Materials and Device Research", Vol. 3, Applied Solid State Science (Academic, New York, London, 1972).
10. K. KIYOTA, A. TESHIMA and M. TANAKA, *Photogr. Sci. Engng* **24** (1980) 289.
11. S. M. VAEZI-NEJAD, *Int. J. Electron.* **62(3)** (1987) 361.
12. S. M. VAEZI-NEJAD and C. JUHASZ, to be published.
13. *Idem, J. Semiconductor Sci. Technol.* **2**(1987) 809.
14. M. ABROWITZ and J. M. MARKOVICS, *Solid State Commun.* **44** (1982) 1431.
15. C. JUHASZ, S. M. VAEZI-NEJAD and S. O. KASAP, *J. Img. Sci.* **29(4)** (1985) 144.
16. P. H. KECK, *J. Opt. Soc. Amer.* **41** (1951) 53.

Received 18 September 1987
and accepted 11 January 1988