The energy distribution of localized states in amorphous arsenic triselenide from transient photoconductivity measurements

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Abstract. DC conductivity, time of flight (TOF) and transient photoconductivity (TP) measurements were performed in order to characterize samples of amorphous arsenic triselenide prepared by thermal evaporation. Analysis of the hole carrier drift mobility data provides strong evidence for carrier interaction with a structured distribution of defect centres rather than the broad featureless distribution that has in the past been proposed for arsenic triselenide. Deviations from power law behaviour in the TP data also provide evidence for the existence of structure. We applied the 'intuitive' thermalization spectroscopic technique to the data and discovered defect centres situated at an energy position $E_2 \sim 0.42$ eV within the mobility gap. At high temperature the thermalization depth of holes is limited by a set of recombination centres situated at $E_1 \sim 0.65$ eV above the valence band edge.

1. Introduction

Chalcogenide semiconductors are currently of interest as x-ray imagers in the field of medical diagnosis. In particular, alloys of Se:As are used in xerographic and xeroradiographic systems (Aiyah *et al* 1993). Consequently information on the electronic properties and electronic structure of the alloys is desired. An experimental technique that can be used to probe the transport properties and the electronic structure is that of transient photoconductivity.

For this experiment it is now generally accepted that dispersion within a transient photocurrent decay, often observed in amorphous semiconductors, can be explained in terms of the interaction of carriers with localized states having a broad range of time constants (see Marshall 1983 for a review). This situation arises for carrier interaction with trapping centres distributed over a range of energies. Schmidlin (1977), Marshall (1977) and Scher (1977) (amongst others) demonstrated that it is possible to identify features within the energy distribution of localized states from transient photocurrent data. A number of studies have concentrated on the examination of the decay of the photocurrent following flash excitation of excess free carriers, both in time of flight configuration (TOF) and in the related 'transient photodecay' (TP) arrangement, the experimental details of which are well documented (Spear 1969, Marshall 1983).

Researchers have now turned to examining the spectroscopic worth of the above mentioned experiments, i.e., can reliable information about the density of states profile $g(E)$ be obtained from the transient photocurrent data? These studies involve the analysis of the shape of the current decay. For example transient photodecays approaching the power

law form have been reported for a variety of materials (Tiedje and Rose 1981 and Kastner 1985). This is said to constitute evidence for a featureless exponential distribution of traps within the mobility gap but such an interpretation is not generally accepted. It has been shown (see Marshall 1983) that a variety of non-exponential arrays of localized states are also capable of generating current decays of similar form. Thus a power law decay does not unambiguously constitute evidence for an exponential $g(E)$ and one must take appropriate account of even mild deviations from the power law form.

Amorphous arsenic triselenide represents a particular class of semiconductor for which both exponential and other more structured distributions have been suggested. For example, several researchers have inferred that an exponential distribution extends over an energy range 0.3–0.85 eV above the valence band edge (Orenstein and Kastner 1981, Khan *et al* 1983, Monroe and Kastner 1986, Wolverson and Philips 1988). On the other hand, Fisher and co-workers (1976), Sharp and co-workers (1981), Michiel and co-workers (1983) and Marshall and Barclay (1985) present evidence for a more structured distribution from their transport and TP measurements. Figure 1 displays the schematic density of states $g(E)$ proposed by Barclay and co-workers (1985), which contains two sets of trapping centres situated at energies $E_2 \sim 0.42$ eV and $E_1 \sim 0.65$ eV above the valence band edge. Further evidence for a structured distribution comes from electronic transport, noise and steady state photoconductivity measurements (Fisher *et al* 1976, Main and Owen 1973, Adriaenssens 1986).
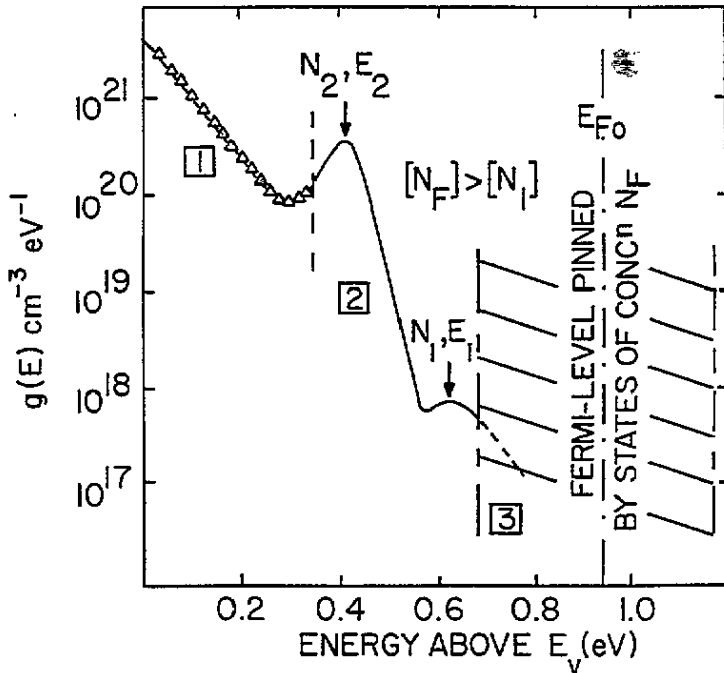

Figure 1. The schematic density of states for arsenic triselenide containing features at 0.42 eV and 0.65 eV (from Barclay *et al* 1985).

In this paper, we present TOF and TP data for samples of amorphous As_2Se_3, prepared by thermal evaporation. The measurements are examined using analytical procedures that allow $g(E)$ to be probed.

2. Experimental details and analysis

The general features for the TOF experiment were the same as those set out by Spear (1969). As in previous studies, signals due to electron transport were not detectable, and therefore our data refer to hole transport.

Details of the TP experiment technique, which involves samples fitted with electrodes in the coplanar configuration, have been published previously (Marshall 1983, Barclay 1994). Here, local charge neutrality is maintained so that any distortion effects caused by space charge accumulation as in the TOF experiments are eliminated.

For TOF data it has been reported by Marshall and Miller (1973) that the drift mobility estimated from the photoresponse curves exhibits the following field dependence:

$$\mu_d(F) = \mu_d(0)\exp(ea(T)E_\mu/kT) \tag{1}$$

where $\mu_d(F)$ and $\mu_d(0)$ are the mobility at field F and zero field respectively and $a(T)$ is a temperature dependence parameter having the dimensions of length. This equation was fitted to our data and $\mu_d(0)$ obtained by extrapolation (see below). We are of the opinion that such an extrapolation can give a reasonable estimate of $\mu_d(0)$ because contact effects are virtually non-existent in arsenic triselenide due to the small screening length of the holes.

In addition it is also possible to obtain information on the trap, density N_t, by combining mobility data with DC conductivity data. We must assume that the simple case of trap limited band transport dominates for carriers interacting with states close to a particular trap energy E_t. This assumption appears justified for our samples of arsenic triselenide because of the small variation of in mobility activation energy, E_μ, with applied field. N_t can thus be calculated from the following relation:

$$N_t = (\sigma/e\mu_d)\exp[(E_\sigma - E_t)/kT] \tag{2}$$

where σ and E_σ are the DC conductivity and DC conductivity activation energy respectively (Sharp *et al* 1981). Obviously, equation (2) is not valid for a broad featureless $g(E)$.

We found that for the annealed evaporated sample the shape of the transit pulse shape was prone to space charge distortion. Consequently, an analysis of the pulse shape proved difficult. Nevertheless, a 'cusp' in the transit pulse associated with space charge distortion forms a useful feature for the determination of transit time, t_t, since it occurs at about $0.8t_t$ provided the number of photogenerated carriers is kept constant (Spear 1969). It should also be noted that no discernable change in the position of the cusp as a function of intensity was observed, thus a reliable estimate of t_t is obtained for the temperature range investigated. This is in contrast to the work of Juska and co-workers (1994), who found an intensity dependent cusp. However it should be stressed that their work was performed on thin amorphous silicon p–i–n diodes. Returning to our data figure 2 shows that the zero-field mobility computed using equation (1) possesses three different distinct regimes. Since the behaviour above 350 K is influenced by residual annealing effects (Pfister and Morgan 1980), it cannot be analysed in terms of transport mechanisms. However for temperatures between 350 K and 305 K an activation energy of 0.62±0.02 eV is obtained using a curve fitting procedure, which decreases to 0.43±0.02 eV for temperatures below 305 K. It should be noted that a larger value of E_μ is estimated between 350 K and 305 K for a broad distribution of $g(E)$. We can combine mobility data with conductivity data and use equation (2) to estimate the trap density at E_1 (see figure 1). We find a defect density
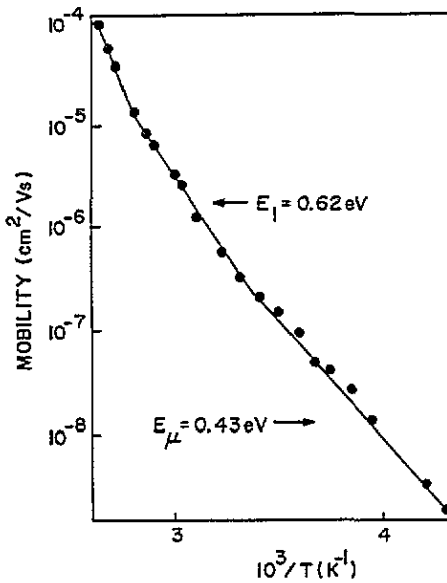
Figure 2. The temperature dependence in the drift mobility for annealed evaporated samples displaying different activated behaviour.

of 1.3×10^{16} cm^{-3}, which compares well with that found for vitreous material (Barclay 1994; see table 1).

Below 305 K one finds a lowering of the activation energy of both the DC conductivity and the drift mobility in accordance with a change in conduction mechanism from transport in extended states to hopping. Following Sharp *et al* (1981) we would like to propose that the hopping occurs within the E_2 energy feature. This process will dominate when the average time for thermal release to the band becomes greater than the expected hopping time between sites, i.e.

$$\nu^{-1} \exp(E_2/kT) > \nu^{-1} \exp(2R/R_0) \exp(w/kT)$$

where R is the hop length, $1/R_0$ is the localization parameter of the centres, and w is an appropriate hopping activation energy. We find a trap density of $\sim 10^{18}$ cm^{-3} taking $w = 0.02$ eV and R_0 to be 1.1 nm (Sharp *et al* 1981). Hopping in the E_1 level can be neglected as this is expected to occur at much lower temperatures (~ 115 K). Here we must note that a low-temperature hopping mechanism was also proposed by Monroe (1985) to account for his experimental data.

As mentioned previously, the form of the decay of the transient photocurrent can give considerable information concerning the nature of the energy dependence of the trapping centres with which the holes interact. We found the photodecays not to be of the power law form and this constitutes evidence for structure in the density of states. This is especially noticeable in the 368 K and 345 K data curves shown in figure 3, where one has difficulty in fitting a power law over more than two decades.

3. Discussion and analysis

The above experimental evidence clearly points to the presence of a structured distribution of localized states within the mobility gap as opposed to a featureless exponential distribution.
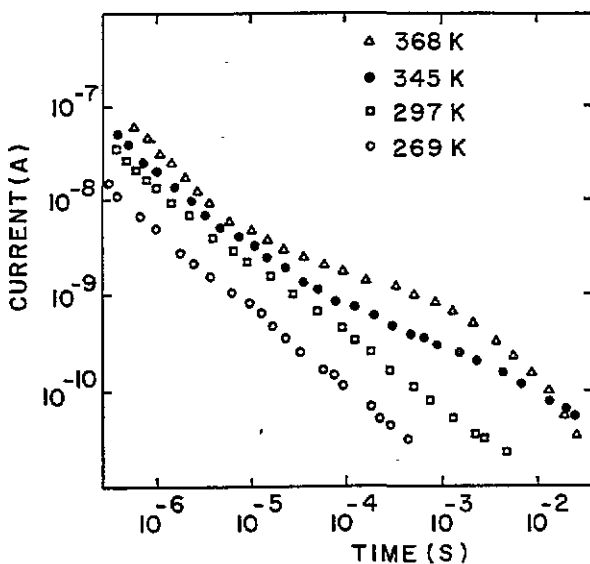
Figure 3. Structured TP data for the evaporated sample.

The transport behaviour can readily be understood in terms of carrier interaction with energy features situated at 0.42 ± 0.02 eV (E_2) and 0.62 ± 0.02 eV (E_1) above the valence band. Thus our results clearly contradict those found earlier by Kastner (1985) and Khan *et al* (1983). Before embarking on a spectroscopic analysis of the results, however, we should like to make the following points in response to Khan *et al* (1983), who suggest that deviation from power law behaviour in TOF transients may be caused by contact induced effects. They also suggest that power law behaviour observed from about 10 μs to 10 ms when blocking contacts are used constitutes evidence for multiple trapping within an exponential distribution of states. However our results clearly show that deviations in the current decay do occur over this time range for coplanar specimens and since contact effects are negligible in the TP experiment this constitutes genuine evidence for a structured $g(E)$.

We shall now present an analysis of the data using the 'intuitive' thermalization concept to investigate $g(E)$. In the following discussion we assume that the capture cross-sections for all localized states are equal. One should note that if this were not the case $g(E)$ should be replaced by the product of trap density and capture cross section. In the 'intuitive' thermalization approach, Marshall and Main (1983) devised a simple procedure for obtaining the trap distribution. Assuming that the majority of charge is trapped rather than free and that trapped charge located close to E_t is in quasithermal equilibrium with the valence band, the following expression is obtained:

$$g(E_d) \sim 1/i(t)t. \tag{3}$$

Therefore it is possible to obtain information about $g(E)$ directly from the decay data. They also demonstrated that the introduction of the simplifying assumptions results in a blurring of the localized states over the energy range $\sim kT$. Marshall and Barclay (1985) made a comparison with the more accurate Volterra approach and found good agreement in the energy positions of the main features. Thus the approach is a valid one when applied to a current decays containing a low degree of structure. Main and co-workers (1992) have also

investigated the accuracy of the approach and found reasonable agreement to within a few kT in the energy positions of the main features. Remarkably, taking the attempt to escape frequency to be $\nu = 10^{12}$ s^{-1}, the value estimated from TP curves for sputtered material (Barclay 1985), we find the energy position of the feature at short times to be 0.46 ± 0.02 eV in rough agreement with the energy feature located at E_2. Furthermore, examinations of the 368 K data reveals a knee point at times comparable to the trap limited monomolecular lifetime τ^*_{mr} found by Orenstein and co-workers (1982). This time represents the maximum depth to which carriers can thermalized before recombination occurs. Using the following relationship:

$$E_t = kT \ln \nu\tau^*_{\mathrm{mr}}$$

we find E_t to be 0.67 ± 0.02 eV, placing the hole recombination centres at about E_1. The 297 K and 269 K curves are virtually featureless. This is because the statistical spread of the carriers that interact with the traps increases as the temperature is lower. Such behaviour should not be taken as evidence for an exponential distribution of states.

The above findings are consistent with those for annealed vitreous and RF sputtered specimens. A comparison of trap depths and densities is shown in table 1 (Barclay 1994). One can observe from the table that there is overwhelming evidence, irrespective of how the samples are prepared, for the structured $g(E)$ proposed by Barclay et al (1985). Note $g(E) = N(E)/kT$.

Table 1.

	σ_0 (Ω^{-1} cm^{-1})	E_σ (eV)	E_μ (eV)	N_t [a] (cm^{-3})	$\mu_0 N_v$ [a] (cm^{-3})
Above 305 K					
vitreous	750	0.92	0.61	1×10^{16}	1.4×10^{19}
evaporated	550	0.90	0.62	1.3×10^{16}	2×10^{19}
sputtered	50–100	0.93	0.44	8×10^{18}–2×10^{19}	8×10^{19}–2×10^{20}
Below 305 K					
evaporated	—	0.46	0.43	$\sim 10^{18}$ [b]	

[a] Corrected by an appropriate factor taking account of the temperature dilation of the mobility gap.
[b] Calculated assuming a hopping transport mechanism at the E_2 level as discussed in the text.

An interesting proposition made earlier by the present author and his colleagues (Barclay et al 1987) is that the defect states within arsenic triselenide are metastable, and Adriaenssens (1990) has made a preliminary investigation of this possibility by examining the transient photocurrent decays as a function of light soaking. Adriaenssens found some evidence for metastability and suggested that a soft-configuration model may be used as a valid approach accounting for the changes in $g(E)$ caused by light soaking. His suggestion that the model of Klinger and Karpov (1982) involving critically soft configurations, which could if necessary include set defect configurations, situated at well defined energies, into the continuous random network, is an interesting one. However we feel that further justification is required with regard to the following aspects. First of all, one has to confirm that there is genuinely a conversion from a broad distribution of general sites to the well defined defect levels, i.e., does the existence of power law behaviour in TP data prove that a

broad exponential distribution exists? Clearly our study provides strong evidence for a structured $g(E)$, the change to power law behaviour at low temperatures only being caused by a statistical smearing effect. Furthermore, the value of ν obtained from the present author's earlier study (Barclay 1985) indicates that the defects are neutral and not charges as suggested by Adriaenssens (1990). Since we also believe that the states involved may be metastable we feel that further work is required in order to gain more information on the nature of the states before a compatible model can be suggested.

4. Conclusions

We have performed TOF and TP experiments to gain more information about the transport properties and the form of the defect distribution that affects these within arsenic triselenide. The behaviour of both the drift mobility and the DC conductivity for $T > 305$ K are interpreted in terms of multiple trapping within trapping centres situated at E_1 and E_2 above the valence band edge. Deviation from power law behaviour in the TP data obtained from measurements perform supports a structured $g(E)$.

Application of the 'intuitive' thermalization technique to the data obtained at different temperatures provides additional evidence for the existence of the features at E_1 and E_2.

Acknowledgment

References

Adriaenssens G J 1986 *Defects in Glasses (Mater. Res. Soc. Symp. Proc., Boston)* Symp. P, vol 61, ed F L Galeener, D L Griscom and M J Weber (Pittsburgh, PA: Materials Research Society) p 111
—— 1990 *Phil. Mag.* B **62** 79
Aiyah V, Kasap S O, Polischuk B and Baille A 1993 *J. Non-Cryst. Solids* **164–166** 777
Barclay R P 1985 *PhD Dissertation* Abertay Dundee University
—— 1994 *J. Phys.: Condens. Matter* **6** L431
Barclay R P, Marshall J M and Main C 1985 *J. Non-Cryst. Solids* **77–78** 1269
Barclay R P, Sarr M and Brebner J L 1987 *J. Non-Cryst. Solids* **97–98** 687
Fisher F D, Marshall J M and Owen A E 1976 *Phil. Mag.* **33** 261
Kastner M A 1985 *J. Non-Cryst. Solids* **77–78** 690
Khan B A, Kastner M A and Adler D 1983 *Solid State Commun.* **45** 187
Klinger M I and Karpov V G 1982 *Sov. Phys.–JETP* **55** 976
Juska G, Viliunas M, Klima O, Sipek E and Kocka J 1994 *Phil. Mag.* B 277
Main C, Bruggemann R, Webb D P and Reynolds 1992 *Solid State Commun.* **83** 401
Main C and Owen A E 1973 *Proc. 13th Session Scottish Univ. Summer School in Physics (Aberdeen)* 1972 ed P G Le Comber and J Mort (London: Academic) p 527
Marshall J M 1977 *Phil. Mag.* **36** 959
—— 1983 *Rep. Prog. Phys.* **46** 1235
Marshall J M and Barclay R P 1985 *Physics of Disordered Materials* ed D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 567
Marshall J M and Main C 1983 *Phil. Mag.* B **47** 471
Marshall J M and Miller G R 1973 *Phil. Mag.* **27** 1151
Michiel H, Adriaenssens G J and Marshall J M 1983 *J. Phys. C: Solid State Phys.* **16** L1005
Monroe D 1985 *Phys. Rev. Lett.* **54** 146
Monroe D and Kastner M A 1986 *Phys. Rev.* B **33** 8881 and references therein
Orenstein J and Kastner M 1981 *Phys. Rev. Lett.* **46** 1421

Orenstein J, Kastner M and Vaninov V 1982 *Phil. Mag.* B **46** 23
Pfister G and Morgan M 1980 *Phil. Mag.* B **41** 191
Scher H 1977 *Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors (Edinburgh)* ed W E Spear p 209
Schmidlin F W 1977 *Phys. Rev.* B **16** 2362
Sharp A C, Marshall J M and Fortuna H S 1981 *J. Physique Coll.* **42** 159
Spear W E 1969 *J. Non-Cryst. Solids* **1** 197
Tiedje T and Rose A 1981 *Solid State Commun.* **37** 49
Wolverson D and Philips R T 1988 *Phil. Mag.* B **57** 635