More evidence for a structured distribution of electronic states in a-As$_2$Se$_3$

LETTER TO THE EDITOR

More evidence for a structured distribution of electronic states in a-As$_2$Se$_3$

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Abstract. We have examined specimens of vitreous a-As$_2$Se$_3$ using transient photocurrent techniques. These techniques allowed us to probe the electronic states contained within the mobility gap of this material. Analysis of the unique transient photocurrent data reveals a structured density of states rather than a broad featureless distribution which is sometimes said to exist in this material.

Chalcogenide semiconductors have attracted a considerable amount of attention because of the interest in using them for the purposes of detecting radiation. Amorphous selenium/arsenic alloys are currently being considered for this purpose and information on the electronic structure of these materials which controls the transport is much sought after (Aiyah, Kasap, Polischuk and Baille (1993)).

An experimental technique often used to probe the electronic density of states is that of transient photoconductivity for which it is now generally agreed that the form of the decay of the photocurrent after flash illumination is reflective of carrier interaction with localized states having a range of trapping and release times (see Marshall 1983 for a review). This is certainly the case if the trapping centres are distributed over a range of energies. Previous work has demonstrated that information on the nature and energy distribution can be deduced from the transient photocurrent. Attention has mainly been directed at the transient photoconductive response following flash excitation of holes, both in the 'time of flight' (TOF) and in the related 'transient photodecay' (TP) experiments.

For arsenic triselenide, transient decays approaching (to a first approximation) a power law form have been reported by Orenstein and Kastner (1981), Monroe and Kastner (1986) and Wolverson and Phillips (1988) who have suggested that this constitutes evidence for a featureless exponential distribution of traps (Kastner (1985)). However, such an interpretation is not universally accepted and Marshall has demonstrated that a combination of non-exponential arrays of localized states are also capable of generating current decays of the power law form (see Marshall 1983).

Arsenic triselenide represents a particular case where both exponential and structured distributions have been inferred. Evidence for the existence of a more structured distribution of trapping centres has been presented by a variety of authors including Sharp, Marshall and Fortuna (1981), Hammam, Adriaenssens and Grevendonk (1985), Marshall and Barclay (1985). These authors provide evidence for the existence of fairly well defined defect levels situated at energy positions $E_1 \sim 0.65$ eV and $E_2 \sim 0.42$ eV above the valence band edge. Additional evidence for structure has come from noise and photoconductivity measurements (Main and Owen (1973) and Adriaenssens (1986)).

In this paper, we present TOF and TP data for specimens of amorphous arsenic triselenide. The data will be analysed in terms of previously proposed density of states $N(E)$ models for arsenic triselenide.

For the TOF and TP experiments, thin platelets of vitreous material, of thickness 30–100 microns, prepared by the compression of bulk glass between quartz plates at a temperature close to the glass transition temperature were used. Details of the two experimental techniques are described elsewhere (Spear (1969) and Marshall (1983) and references cited within). For the former, the top and bottom electrodes were gold layers sufficiently thin to allow the ultra violet excitation radiation to penetrate. In the case of the TP experiment, the above mentioned specimens were fitted with gold electrodes in the coplanar configuration. The interelectrode gap was approximately 60 microns, and drift fields were typically of order 10^4 V cm. Variation of the illumination intensity caused no discernible change in the shape of the photocurrent decay, suggesting that intensity dependent bimolecular recombination effects could be ignored over the time scale of the experiment (Orenstein, Kastner and Vaninov (1982)). Additionally, monomolecular recombination can also be neglected because of the very long trap limited recombination lifetime found in a-As$_2$Se$_3$ (> 1 s at room temperature; Mort, Chen, Morgan and Grammatica (1981)).

From the TOF data we found that the hole carrier mobility exhibited a field dependence of the form

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

where $\mu_d(F)$, $\mu_d(0)$ are respectively the mobility at field F and zero field, and $a(T)$ is a temperature dependent parameter having the dimensions of length. This is in agreement with the findings of Marshall and Miller (1973). Extrapolation to zero field yields a mobility activation energy of 0.61 eV. When the mobility data is combined with the DC conductivity data (Sharp *et al*) we find, assuming that trap limited band transport is dominated by states close to an energy E_t, a trap density of 1×10^{16} cm^{-3} for states located at approximately 0.61 eV above the valence band. Furthermore, the change in shape of the transit pulses with temperature suggest the presence of a mobility controlling feature. Thus the results provide evidence for carrier interaction with a structured $N(E)$ rather than an exponential tail.

Further evidence for a structured distribution comes from our TP data which were taken over a range of temperatures from 106 K to 390 K (see figure 1). Here the decays are not of the featureless power law form and that this is especially true for the 383 K and 336 K data where one has difficulty in fitting a power law over more than two decades. However, one may use the 'intuitive' thermalization concept to perform a spectroscopic analysis (see below).

We shall now analyse the data using the 'intuitive' thermalization concept which allows us to obtain $N(E)$. In the following discussion we must assume that the capture cross sections for all localized states are equal: note that if this were not this case, $N(E)$ would be replaced by the product of trap density and capture cross section. Here we use the concept of a thermalization energy and following Marshall and Main (1983) obtain

$$N\bigl(E_d\bigr) \sim \frac{N_0 e \mu_d E A}{v\sigma k T i(t) t} \tag{2}$$

where N_0 is the total density of excess electrons, μ is the free hole mobility, $v\sigma$ is the capture coefficient of the states (v is the attempt-to-escape-frequency and σ the capture cross section), E the applied field and A, the conduction path cross sectional area.
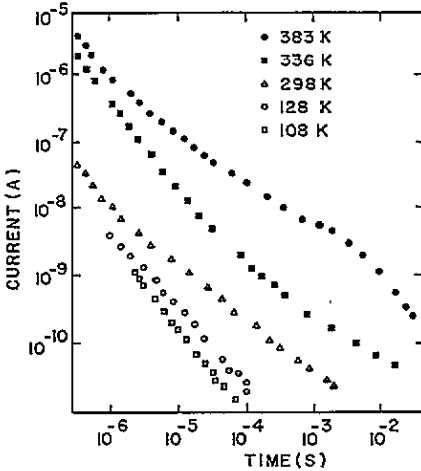
Figure 1. TP data from vitreous materials showing deviations from power law behaviour.
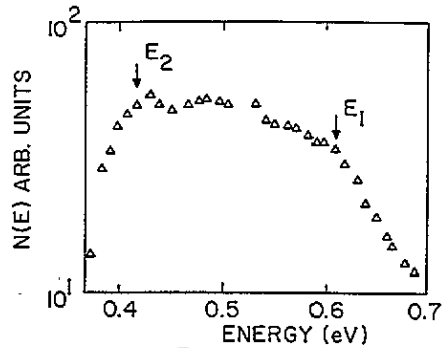
Figure 2. The density of states profile obtained from the TP data by applying the 'intuitive' thermalization concept.

This allows us to estimate $N(E)$ directly from the decay data taking $E = kT \ln \nu t$. Although this simple analysis has been subject to various objections (see Main, Bruggemann, Webb and Reynold (1992)), Marshall and Barclay (1985) have demonstrated that the general features of the $N(E)$ profiles are smaller to those obtained from the more complex and more accurate 'volterra' technique. Figure 2 shows the result of applying the procedure to the 336 K data trace for $\nu = 1 \times 10^{12}$ Hz. The data is unique because of the dramatic changes in $N(E)$. Examining figure 2 we see that $N(E)$ rises to a plateau at an energy of 0.41 eV after which there is a slow progressive decrease in the density with energy until there is a sudden drop at 0.61 eV. Thus the energy position of the structure is in agreement with that estimated from the mobility–DC conductivity measurements, suggesting that there is a feature centred about 0.6 eV above the valence. One should also add that strong evidence for the presence of another feature at about 0.4 eV above the valence band exists for specimens of As_2Se_3 prepared by thermal evaporation and RF sputtering (Marshall and Barclay (1985) and Barclay (to be published)) which agrees with our findings. The intermediate region between the features could approximate to a power law. The fact that no minimum in the density occurs in this region can be attributed to a combination of the following factors. Firstly, in this region we have a convolution of the two features. Secondly, the approximations introduced in the 'intuitive' thermalization concept result in a blurring of the features by a few kT. Thus one can easily predict how a featureless photodecay can occur even for carrier interaction with a structured $N(E)$ particularly at low temperatures. Clearly, therefore, our results do add support for the presence of a structured $N(E)$ rather than a continuous featureless broad distribution.

An interesting proposition is that the states causing the structure are metastable. Indeed the early work of the author and his colleagues confirms the existence of such states in As_2Se_3 (Barclay, Sarr and Brebner 1987). Adriaenssens has also suggested this and put forward the soft-configuration model of Klinger and Karpov (1982) in order to explain his TP data which contained some evidence for metastability. He made this suggestion after he and colleagues discovered that the structure cannot be due to oxygen contamination (Hammam, Adriaenssens, Dauwen, Seynhaeve, and Grevendonk (1990)). Adriaenssens

also stressed that other models such as the charge defect model (Silver, Pautmeier and Baessler 1989) may lead to the generation of a continuous $N(E)$ but this is less compatible than the soft-configuration model. However, we are of the opinion that the origin of the structure and the nature of the defects involved need to be examined further via TP, steady state photoconductivity and optical absorption measurements if we are to conclude that the change in the shape of the photodecay after lightsoaking is caused by the conversion of metastable states contained within a broad distribution of soft sites to the energy levels situated around 0.4 eV and 0.6 eV.

We have performed TOF and TP experiments in order to characterize a-As_2Se_3 in terms of its electronic structure. The behaviour of both the drift mobility and DC conductivity is analysed using a trap-limited transport mechanism and explained by hole interaction with a feature located 0.61 eV above the valence band edge which dominates the transport. The $N(E)$ determined from the TP data contains features sited at energies similar to that obtained from the drift mobility data. The nature of·the defects causing the features requires further investigation.

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