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EXPERIMENTAL STUDY OF THE DENSITY OF STATES IN THE BAND GAP OF a-Se

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The energy levels of the thermally accessible states of the negative-U defects in a-Se have been determined from the activation energy of the steady-state photocurrents in the mono- and bimolecular recombination regimes, and independently from the hole and electron emission currents of the post-transit time-of-flight (TOF) signals. Indications for the distribution of tail states are obtained from standard transient photocurrent measurements in a gap cell geometry, as well as from an analysis of the drift mobility characteristics as measured through TOF with sandwich cells. Rather steep tail state distributions are found, with characteristic energies below 30 meV.

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1. Introduction

Amorphous selenium (a-Se) has served in many ways as a prototype for the group of chalcogenide semiconductors and the charged coordination defects with negative effective correlation energies (negative-U) that constitute one of their prime characteristics [1]. The image shown as Fig. 1a (after Elliott [1]), is indeed very familiar to anyone who has taken any interest in study of the chalcogenides. It illustrates the presumed charge transfer and bonding configurations that lead to the threefold coordinated, positively charged C_3^+ centre that connects Se chains, and the singly coordinated, negatively charged C_1^- dangling bond centre. Charged centres (also labelled D^+ and D^-) are required in the chalcogenides to account for the lack of unpaired-spin defects, *i.e.* the lack of equilibrium electron spin resonance signals [2]. The centres of Fig. 1a are thought to represent the combination of defects with the lowest energy in a-Se [3]. Due to the flexibility of the Se (or any other chalcogenide) lattice, polaronic lattice deformation changes the required transition energies for carriers to occupy or leave the centres. This phenomenon leads to the proposed multi-level a-Se energy diagram of Fig. 1b. However, while energy diagrams of the Fig.1b type have been experimentally verified for many of the chalcogenide compounds [1,4-6], no equivalent results have been published for elemental a-Se.

For a-Se, the material of choice during the early years of xerography, a 'standard' density of states model has been used. This consists of deep electron and hole traps near mid-gap, and shallow traps for electrons and holes near the band edges [7,8]. Evidence for the deep traps has mainly been obtained from the slow decay of surface potentials in xerographic experiments [9,10], but also from experiments such as the recent recombination study by Kasap *et al*. [11] whereby holes can be drifted repeatedly through a sample that has been prepared by filling its deep electron traps and where this negative charge does not dissipate between the measurements. It may be noted that a distribution of traps near the middle of the band gap was also invoked to model an anomalous dc

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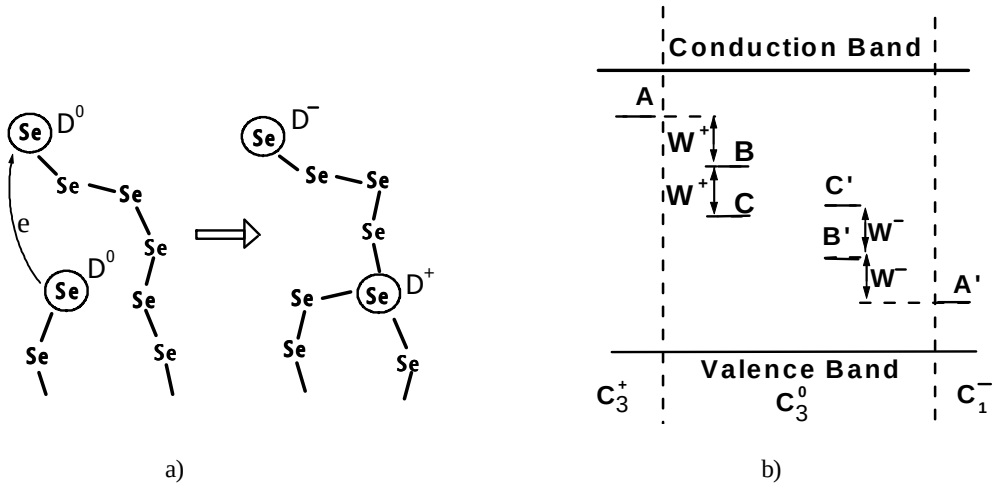
conductivity in a-Se [12]. The shallow traps are thought to lie roughly 0.3 eV from the band edges, primarily on the basis of measured drift mobility activation energies with such values [7,8,13,14]. Below, we will examine what role these 'standard' a-Se traps can play in the energy level scheme associated with the coordination defects of the negative-U model, and how these energy levels can be determined.



a) b)

Fig. 1. a) Conceptual image of the C_3^+ and C_1^- charged coordination defect centres in a-Se (after [1]); b) The energy level scheme expected for those defects (after [3]).

2. Negative-U defect levels in a-Se

The xerographic potential decay measurements that reveal the presence of mid-gap states involve thermal transitions of the trapped carriers. These transitions can therefore not be identified as the energy levels C and C' of Fig. 1b, since the latter mark optical transitions in the polaronically-deformed lattice rather than thermal transitions. In other words, the deep traps in a-Se cannot be seen as a manifestation of the negative-U centres; they must have a different origin. The shallow traps, on the other hand, might be considered as manifestations of the thermally accessible B and B' levels of Fig. 1b, although that they are located closer to the band edges than expected in the negative-U model. The shallow energy levels indicated in [7] and [8], and put at ~0.25 eV above the valence band and ~0.33 eV below the conduction band, are derived from time-of-flight (TOF) transient photoconductivity measurements. After initial optical excitation, the TOF experiment involves only thermal transitions such that reference to the B/B' levels becomes plausible. However, the specific energies postulated for those shallow levels in [7,8] are based on an unwarranted interpretation of the TOF results. As analysed in detail by Marshall [15], and as already pointed out in [16], an electric field dependence of the drift mobility values of the type reported for holes by Kasap and Juhasz [14] indicates a continuous distribution of gap states in the energy range under examination, rather than a discrete defect level.

Nevertheless, transient photocurrent measurements showing a kink in the current decay were interpreted as further support for the level at 0.25 eV above E_V [17]. This interpretation was based on simulations that showed how a discrete feature on top of an exponential DOS would produce such kink, with its position in the time domain indicating the energetic location E_t of the discrete trap according to $E_t = kT\ln(\nu t)$, where k is the Boltzmann constant, T the temperature and ν the attempt-to-escape frequency [18]. The experiments were carried out with a microstrip transmission line with an a-Se dielectric, to allow room-temperature measurements in the nanosecond domain [17]. We have attempted to confirm those results by examining standard transient photocurrents in a-Se gap cells at lower temperatures, but have failed to find the change of slope that would indicate the presence of a defect level at ~ 0.25 eV. However, as will be shown in the next section, our experiments offered evidence for a discrete level some 0.4 eV above E_V.

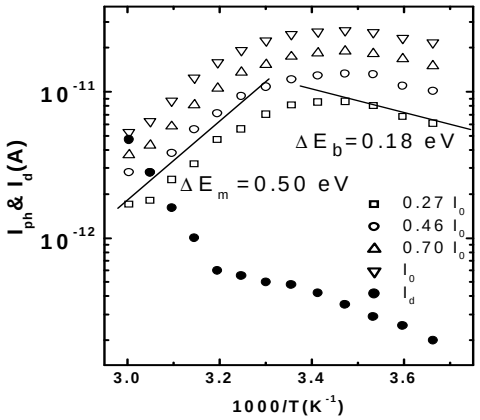


Fig. 2. Steady-state dark (I_d) and photocurrents under 890 nm illumination, with $I_0 = 4 \times 10^{16}$ photons/cm/s, of a 265 μm thick a-Se sandwich cell with 100 V applied. Photocurrent activation energies in the monomolecular and bimolecular recombination regimes are shown.

Not finding the above attempts at locating the thermally accessible levels of the negative-U centres in a-Se convincing, we have used standard steady-state photoconductivity techniques to obtain this information [16,19]. Indeed in chalcogenide glasses, the activation energies of the steady-state photocurrent in the monomolecular and bimolecular recombination regimes do reveal the energy position of the discrete recombination centres; the latter actually being the negative-U centres [4]. The technique was used successfully for many chalcogenide compounds [6,20], but is hindered in a-Se by the high resistivity and photosensitivity of the material. Together with the low glass transition temperature, these characteristics make it difficult to measure photocurrents smaller than the dark current, and thus to observe the monomolecular recombination regime. Nevertheless, as shown in Fig. 2, by using thick sandwich structures and uniform infrared illumination, we have obtained good values for the photocurrent activation energies ΔE_m and ΔE_b, from which defect levels at $2\Delta E_b = 0.36$ eV and $E_F + \Delta E_m = 1.45$ eV above the valence band can be resolved using standard analysis techniques [4]. We were also able to confirm these energy positions via analysis of the post-transit currents from both hole and electron TOF signals, in full agreement with the pioneering study by Song *et al.* [21]. On the basis of our study of several series of samples by both the steady-state and post-transit photocurrent methods, we are confident in that the thermally accessible defect levels in a-Se are located at (0.40 ± 0.02) eV and (1.43 ± 0.02) eV above the valence band. These levels are probably the 'shallow' traps of the traditional model; with the room temperature band gap being ~ 1.95 eV. They are both within ~ 0.5 eV of the band edge, and thus are able to thermally emit a trapped carrier within 1 ms (using $\nu = 10^{12}$ s^{-1}).

3. Distribution of tail states

While the negative-U centres are related to actual coordination defects in the lattice, the general disorder of the amorphous lattice leads to the existence of tails of localised states at the band edges. These tails are thought to be broad and exponentially distributed, on the basis of the well-known case of As_2Se_3, but for a-Se little specific information seems to be available. We have, therefore, carried out two types of transient photocurrent measurement, and have extracted the DOS distribution of the valence band tail. If the tail-state distribution is exponential, the electric field dependence of the TOF drift mobility allows the determination of the characteristic width of the tail. Applying this method for our a-Se sandwich cells, we find that the valence band tail can be described fairly well by the distribution $g(E) = g(0) \exp(-E/E_0)$ with $E_0 \cong 23$ meV. No result could be obtained for the conduction band tail, since the electron drift mobility in a-Se turns out to be field-independent. Details of these results have been reported elsewhere [22].

Fig. 3 shows transient photocurrent data obtained with a gap cell of hot-pressed bulk a-Se. At the lower temperatures, the current transients start out along a power law $I(t) \propto t^{-(1-kT/Eo)}$ that allows the determination of an exponential width of $E_0 \cong 29$ meV. Also of interest in these transients

is the temperature-dependent depression seen at the higher temperatures. It is the signature [18] of a discrete feature in the DOS, located 0.40 eV above the valence band, in full agreement with the results given in section 2.

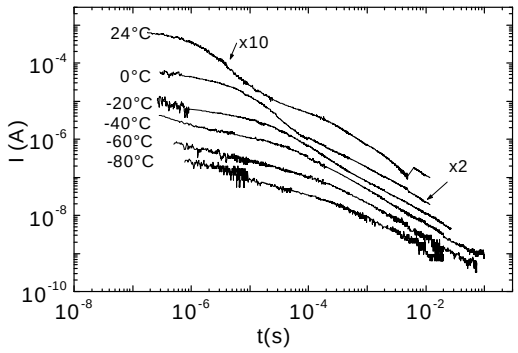


Fig. 3. Transient photocurrents from hot-pressed bulk a-Se gap cell after pulsed laser excitation.

4. Conclusions

Discrete energy levels belonging to the negative-U coordination defects can be identified in a-Se. They induce recombination levels at (0.40 ± 0.02) eV and (1.43 ± 0.02) eV above the valence band. A roughly exponential valence band tail, with a width E_0 < 30 meV, is resolved.

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