Steady-state photoconductivity in amorphous selenium glasses

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Abstract

Steady-state photoconductivity measurements are carried out for bulk and thin-film amorphous selenium (a-Se) samples in the temperature range between 190 and 340 K. The temperature and light-intensity dependences of the photoconductivity reveal the presence of both mono- and bimolecular recombination regimes. The current activation energies measured in the two regions point to energy levels in the gap for the recombination centres at 0.36 ± 0.06 and 1.35 ± 0.10 eV above the valence band mobility edge. These values put a-Se in line with the other chalcogenide semiconducting glasses that exhibit negative-U behaviour.

1. Introduction

Although amorphous selenium (a-Se) is one of the primary and most widely used amorphous semiconductors [1], as well as the standard model system in the discussion of charged defects with negative effective correlation energy in chalcogenide glasses (the *negative-U* centres) [2–6], some of its characteristics have not been fully explored to date. Its low glass transition temperature, T_g, of just over 313 K has undoubtedly played a role in creating this situation. However, a renewed interest in the material has recently been generated by the use of a-Se for x-ray medical diagnostic imaging applications [7]. The material being used there is actually the so-called 'stabilized a-Se', where the glass transition temperature is raised to ∼60 °C through the admixture of up to 0.5% As and ∼20 ppm Cl. Efforts to estimate the influence of these additives on the density of states (DOS) distribution of intrinsic a-Se are hampered by the lack of a clear image of that DOS.

Indeed, while the DOS diagram for an amorphous semiconductor is the key to understanding most of its electronic properties, a number of uncertainties and controversies persist in the case of a-Se. In 1988, by combining observations from earlier time-of-flight

(TOF) drift mobility measurements with new xerographic cycled-up residual voltage decay and xerographic dark discharge measurements, Abkowitz [8] proposed a DOS model with defect bands near mid-gap as well as at 0.26 and 0.35 eV respectively from the valence and conduction bands. Later, Song *et al* [9] argued on the basis of TOF post-transit photocurrent measurements and analysis that this 0.26/0.35 eV set of defect bands should actually be positioned deeper in the gap, about 0.45 and 0.60 eV from the respective bands. More recently, Khoughia *et al* [10] compared experimental and simulated TOF electron transients and concluded that the DOS shows a peak at ∼0.30 eV and a shoulder at 0.45–0.50 eV below the conduction band edge.

The conceptual models that deal with the negative-U centres in chalcogenides also provide estimates for the corresponding energy positions in the gap. For the levels involved in the thermal release of carriers, i.e. the levels responsible for the TOF signals, these models predict positions roughly halfway between the band edge and the Fermi level [2–5, 11]. Since the optical gap of a-Se is 2.1 eV [1], and the Fermi level lies in the middle of this gap [12], the theoretical estimates place the defect levels some 0.5 eV away from the bands, in rough agreement with the values deduced from the post-transit analysis. Nevertheless, further experimental confirmation remains desirable. Given that it was possible, for several of the chalcogenide compounds, to obtain the energy positions of appropriate negative-U levels from the temperature dependence of the steady-state photoconductivity [13–15], we have undertaken to perform the same analysis for a-Se. Recombination of photo-excited carriers will preferentially occur by way of the charged defect levels in the gap, whereby the type of recombination (monomolecular or bimolecular) can be linked to a defect level either above or below the Fermi level, and the corresponding thermal activation energy involved to its position in the gap [16–18].

However, conductivity measurements of a-Se films (with or without illumination) require special care due to the high dark resistivity of the material. For instance, a set of steady-state photocurrent measurements that resolved a linear dependence of the photocurrent on the light intensity for all temperatures and wavelengths [19] should not be trusted because the data were obtained with 60 nm thin films deposited on glass. (Although the substrate is not mentioned in [19], contemporary papers by the same group [20] indicate the use of glass substrates, and the resulting dark current activation energy of 0.7 eV clearly refers to Na ionic conductivity in the substrate [21] rather than the a-Se film on top.) This high dark resistivity, coupled to the high photosensitivity of a-Se, also makes it non-trivial to obtain photocurrents with good signal-to-noise ratio in the monomolecular recombination regime. Measuring the light intensity dependence of the photocurrents in that region—normally a way to confirm the internal consistency of the recombination model—is difficult for the same reason.

2. Experimental conditions

Amorphous selenium films of varying thickness in the micrometre range were evaporated from either 99.995% pure Se or from stabilized Se (a-Se + 0.5% As + ∼20 ppm Cl) onto high-resistivity Corning 7059 glass substrates. For electrical measurements, gap-cell configurations were mostly used with evaporated gold electrodes on top of the films or on some bulk samples of the stabilized Se. The gap cells had active areas of 0.5 mm × 10 mm on the films and 0.5 mm × 3 mm on the bulk samples. Additional samples were prepared in sandwich configuration between aluminium electrodes, the top one being semi-transparent. DC conductivity measurements were carried out in a 5×10^{-3} Pa atmosphere by means of a Keithley 427 current amplifier, with typically 100 V applied across the gap for film and bulk samples. A 15 mW He–Ne laser or a 250 W tungsten–halogen lamp plus grating monochromator (10 nm bandpass) were used for gap cell illumination in the photoconductivity
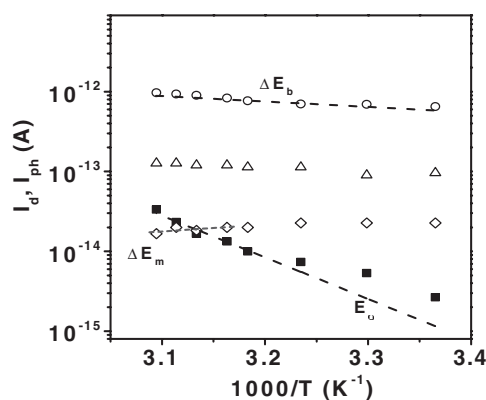
Figure 1. The temperature dependence of dark current I_d (full symbols) and steady-state photocurrents at 2.64 eV illumination for an a-Se film with three different light intensities: $I_0 = 2 \times 10^{13}$ photons cm^{-2} s^{-1} (■), $5 \times 10^{-2} I_0$ (△) and $3.8 \times 10^{-3} I_0$ (◇). 50 V was applied across a 0.5 mm gap.

measurements. For sandwich cells voltages up to 5 V were used with illumination from near-infrared light-emitting diodes.

3. Experimental results

Steady-state dark and photoconductivity measurements performed on a large number of both intrinsic and stabilized a-Se film and bulk samples did not show any noticeable differences in relation to the absence or presence of the stabilising agents. Figure 1 shows a representative set of dark and photocurrent data, measured at different light intensities as a function of temperature between 297 and 323 K, and with an applied field of 10^3 V cm^{-1}. For pure a-Se films, data points above 313 K were taken during brief excursions above T_g; no subsequent evidence for crystallization was seen. The full symbols in figure 1 show the temperature dependence of the steady-state dark current. For temperatures above 315 K ($10^3/T < 3.17$), the dark conductivity is thermally activated with activation energy $E_\sigma = 1.05 \pm 0.08$ eV, indicating band conduction at the top of the valence band. TOF drift mobility measurements have shown that this transport is trap-controlled [22]. The above E_σ value agrees with earlier measurements on a comparable set of samples [12]. Below room temperature the dark current levels off and starts to be dominated by hopping in the localized states near the Fermi level [12].

The open symbols in figure 1 show the temperature dependence of the photocurrent in an a-Se film in a log I_{ph} versus $10^3/T$ diagram for three different light intensities: I_0, $5 \times 10^{-2} I_0$ and $3.8 \times 10^{-3} I_0$, where $I_0 = 2 \times 10^{13}$ photons cm^{-2} s^{-1} represents the full light intensity at 470 nm (2.64 eV) illumination. The observed a-Se photocurrent behaviour is quite similar to the one that is generally seen with amorphous arsenic chalcogenide semiconductors [16, 17, 23]. At low temperatures and high light intensities, i.e. when the photocurrent is larger than the dark current, a bimolecular recombination regime leads to an exponentially decreasing I_{ph} with $1/T$. Activation energy values, ΔE_b, in the range 0.12–0.18 eV are found in a-Se films. In the high-temperature region and at low light intensity, where the photoconductivity becomes smaller than the dark conductivity, monomolecular recombination takes over and an exponentially increasing photocurrent is seen versus $1/T$. Here the measured values for the activation energy ΔE_m varied from 0.14 to 0.28 eV. As mentioned in the introduction, it is not easy to access this monomolecular region, which leads to considerable uncertainty in the value of ΔE_m.
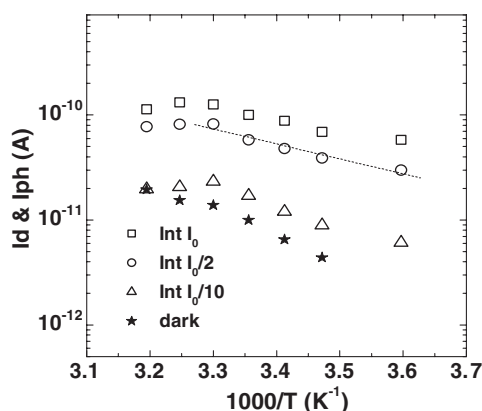
Figure 2. Dark current and photocurrents from an a-Se bulk sample illuminated at 1.96 eV with $I_0 = 5 \times 10^{17}$ photons cm^{-2} s^{-1} and with 100 V applied across a 0.5 mm gap.

Similar temperature dependences of the photocurrent are found in bulk a-Se samples. However, the transition between the mono- and bimolecular recombination regimes is now more spread out in temperature since successively deeper-lying layers of the bulk sample will be subject to increasingly lower illumination intensities. The optically excited free carrier density will thus vary through the sample, while the thermally excited 'dark' density remains constant. Figure 2 shows an example of such a transition. An He–Ne laser (632.8 nm) was substituted for the 470 nm excitation used above in order to moderate the variation in optical excitation density. While the ΔE_b slope ($\cong 0.28$ eV) is readily available, and the transition to a different regime is seen, no clear monomolecular recombination regime is observed.

To get a better definition of the I_{ph} slope in the monomolecular regime, and hence a credible value for ΔE_m, near-infrared illumination at 890 nm (1.39 eV) and a sandwich cell were used. Such illumination produces a low but uniform optical excitation through the sample, which sharpens the bimolecular to monomolecular transition, while the sandwich structure ensured that the current levels remain measurable. The results are displayed in figure 3 and indicate values for ΔE_m that extend the range given above to ~ 0.35 eV. It is remarkable that the change in recombination regime takes place in spite of the fact that the measured dark current remains large with respect to the photocurrent throughout. This fact, as well as the very weak temperature dependence of the dark current, indicates that a hopping contribution in states near the Fermi level is dominant, but that the conduction in the valence band and the corresponding density of thermally generated carriers there is weighed against the photo-generated carrier density in determining the recombination mode. The dashed line in figure 3 indicates the estimated contribution of the band transport to the dark current.

The change in recombination mechanism also can be seen from the light intensity dependence of the photoconductivity in chalcogenides. This dependence has been determined at different temperatures for our a-Se gap cells. Figure 4 shows the photoconductivity induced by the 470 nm illumination as a function of photon flux over two orders of magnitude at two different temperatures. For both film and bulk samples the photocurrent, I_{ph}, grows with light intensity, and hence the photocarrier generation rate G, according to $I_{ph} \propto G^\gamma$ with $\gamma = 0.5$ at the lower temperature (297 K), while at the higher temperature $\gamma \approx 0.66$ is found. The value $\gamma = 0.5$ signifies bimolecular recombination behaviour [16]. Since $\gamma = 1$ would be required for a fully monomolecular regime, our value of 0.66 indicates that we are still in the transition region between the two recombination regimes. In fact, the data in figures 1 and 2 confirm
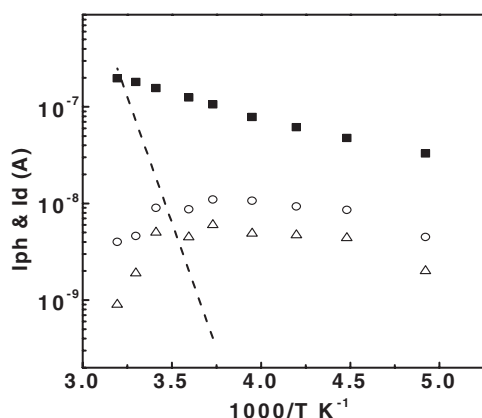
Figure 3. Temperature dependence of the dark and photocurrents (at two intensities, 6 and 2×10^{16} photons $cm^{-2}\,s^{-1}$, of the 1.39 eV illumination) through an a-Se sandwich cell. The dashed line represents the band contribution to the dark current (see the text).
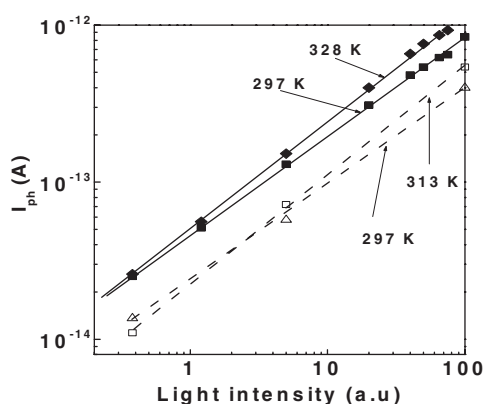

Figure 4. The dependence of the photocurrent on the light intensity, at two different temperatures, for a-Se film (open symbols) and bulk (full symbols) samples.

that the transition to monomolecular behaviour has only started. Nevertheless, the results in figure 4 provide further evidence that the change-over in the recombination process, that has become a hallmark of arsenic chalcogenide semiconductors and their negative-U centres, can also be resolved in a-Se samples.

4. Discussion

Electrical conduction in a-Se is mainly due to holes [24], which means that the dark current activation energy E_σ corresponds, to first approximation, to the energy distance between the Fermi level, E_F, and the valence band mobility edge, E_V. In the analysis of the photocurrent temperature dependence as worked out for chalcogenide materials by Main and Owen [16], Simmons and Taylor [17] or Okamoto *et al* [18], these E_F and E_V levels serve as references for the energy positions of the recombination centres that dominate in either the monomolecular or bimolecular recombination regime. At high temperatures and low illumination intensities, the photocurrent $I_{ph} \propto \exp(\Delta E_m / kT)$ defines the energy location in the gap of a discrete
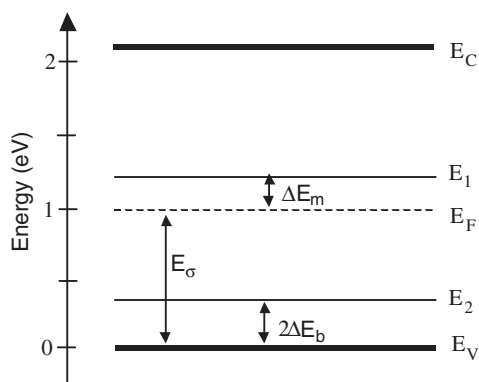
Figure 5. Energy level diagram for the recombination centres in a-Se.

donor-like recombination centre as $E_1 = E_V + E_F + \Delta E_m$. The low-temperature photocurrent $I_{ph} \propto \exp(-\Delta E_b/kT)$ in turn locates an acceptor-like recombination centre at the energy $E_2 = E_V + 2\Delta E_b$. In chalcogenides these centres have been identified as negative-U centres, i.e. charged defects with negative effective electron correlation energy [4, 18].

Applying the above relationships to our steady-state photoconductivity results for a-Se, we deduce energy values $E_2 - E_V = 0.36 \pm 0.06$ eV and $E_1 - E_V = 1.35 \pm 0.10$ eV for the thermal transitions involving negative-U defects. With respect to the conduction band, the E_1 level finds itself at $E_C - E_1 \cong 0.75 \pm 0.10$ eV if we use the accepted gap value of $E_g \cong 2.1$ eV. These energy relationships are illustrated in figure 5. The 0.36/0.75 eV set of levels we thus obtain with respect to the bands is closer to both the theoretical values of $\sim E_g/4 \cong 0.5$ eV and the 0.45/0.60 eV pair from post-transit TOF than to the earlier 0.26/0.35 eV set proposed in [8]. These earlier values are in fact based on a misinterpretation of the original TOF data sets of Kasap and Juhasz [22]. Indeed, in analogy to the pioneering work on TOF in chalcogenides by Marshall and Owen [25], it was assumed in [8] that the activation energy of the drift mobility corresponds to the energy position in the band gap of a prominent trapping centre. Marshall [26] has since shown that such an interpretation is unwarranted, and that a field dependence of the drift mobility as seen for a-Se does actually signal a broad featureless distribution of traps in the relevant energy range.

One common feature of all experimental data sets is the asymmetric position of the defect levels with respect to the band edges; in each instance they are shifted towards the valence band. An analogous asymmetric shift of the negative-U energy levels towards the valence band has been reported for a-As$_2$Se$_3$ [14, 27], a-As$_2$Te$_3$ [27], a-AsSe$_2$ [28], a-As$_{47}$Se$_{53}$ [28] and a-GeSe$_2$ [15]. The assumption that the two-fold co-ordinated chalcogen sites induce a common preferred defect configuration in all of these compounds would explain such group behaviour. While a specific model for the defect configurations is available for a-Se [3, 29] at present, it is not obvious how to extend it to the chalcogenide compounds.

5. Conclusions

Based on steady-state dark and photoconductivity measurements performed on amorphous selenium bulk and film samples as a function of temperature and light intensity, we confirm the presence in the band gap of defect levels with the signature of chalcogenide negative-U centres. The acceptor- and donor-like levels are located at $\sim$0.36 eV and $\sim$0.75 eV, respectively, from

the valence and conduction bands. These values are in fair agreement with our interpretation of earlier transient photocurrent measurements on comparable samples.

The fact that no experimental differences were observed in our measurements between the pure and the stabilized a-Se samples does not imply that the added As and Cl do not influence the DOS in the gap. The low dark conductivity of a-Se, and the need to have even lower photoconductivity in order to achieve a monomolecular recombination regime, strongly reduce the sensitivity of our steady-state methods, and may obscure possible changes in the DOS. The large uncertainties in some of the resolved energy values are manifestations of the same problem. Consequently, while the steady-state measurements were able to show that amorphous selenium does fit the general pattern established by the other chalcogenides, details of possible DOS changes upon the introduction of stabilizing elements will have to be obtained from other experiments.

Acknowledgments

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