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LOW-TEMPERATURE STEADY-STATE PHOTOCONDUCTIVITY IN AMORPHOUS SELENIUM FILMS

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Steady-state photocurrents are measured in amorphous selenium (a-Se) films as function of illumination intensity for temperatures between 210 K and 297 K. The Lux-Ampère characteristic, $I_{ph} \propto G^{\gamma}$, shows a maximum exponent of 1.08 ± 0.06 around 250 K while lower values are measured at room temperature and 210 K. The photocurrent overshoots its steady-state value upon initial turn-on of a high light intensity by an amount that has a minimum in the 250 K region. Both phenomena indicate the presence of a deep electron trap near the a-Se equilibrium Fermi level.

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1. Introduction

Although amorphous selenium (a-Se) has now for three decades been used as the primary model system in the discussion of the negative-U model of charged coordination defects in the chalcogenide glasses [1], relatively little work was undertaken in that period to characterize the a-Se electronic density of states (DOS) experimentally. However, the recent interest in the application of a-Se for X-ray medical diagnostic imaging [2] has now led to renewed attention for the electronic properties of the material, with trapping of charge carriers into defect states in the bandgap being a primary concern. To locate the energy positions of those defects in the gap, different aspects of time-of-flight (TOF) transient photocurrent measurements have been used in the past by Abkowitz [3] and by Song et al. [4], but the results did not agree with each other. Therefore, several series of steady-state and transient photoconductivity measurements were carried out on a-Se films [5-8] to resolve the issue. The results give evidence for an acceptor-like center some 0.4 eV above the valence band edge, and for a donor-like one about 0.5 eV below the conduction band edge, E_c. More recently, Koughia et al. [9] analyzed TOF electron transients and deduced three distinct defect levels: a prominent one at 0.3 eV below E_c, a weaker one around 0.5 eV, and a further deep density beyond 0.65 eV, the energy limit of their analysis. While the 0.5 eV energy evidently matches the corresponding level out of our earlier analysis, the 0.3 eV and deep levels are also supported by further experimental observations. Whereas attention in our previous TOF experiments focused mainly on the post-transit region, careful study of the pre-transit electron currents has now revealed unmistakable evidence for a distinct trap at ~ E_c – 0.28 eV [10].

The presence of deep traps in a-Se has traditionally been deduced from xerographic experiments [3,11,12], but a recently observed anomalous behavior of the dark dc conductivity in a-Se [13] was also attributed to deep traps near the Fermi level. The normal change-over with decreasing temperature from thermally activated transport to a weaker temperature dependence was followed by an actual increase of the conductivity in the region around 250 K. The phenomenon was interpreted in terms of a shift of the Fermi level in a defect band near the middle of the band gap that makes more states available for a hopping process. We now report a set of a-Se steady-state photoconductivity measurements over the temperature range that showed the anomalous dark current. The results do offer further confirmation of the presence of a defect band in a-Se right near the equilibrium Fermi level.

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2. Experimental conditions

Amorphous selenium films of a few micrometers thick were thermally evaporated from pure 99.995% Se onto Corning 7059 glass substrates. For electrical measurements, gap-cell configurations were used with evaporated gold electrodes on top of the a-Se film. The gap cells had an active area of 0.5 mm × 10 mm. DC conductivity measurements were carried out in a 5×10^{-3} Pa atmosphere by means of a Keithley 427 current amplifier, with 50 V applied across the gap. A 250 W tungsten-halogen lamp plus monochromator (10 nm bandpass) was used for gap cell illumination with 2.64 eV light (470 nm), corresponding to the maximum photosensitivity of our samples. The more uniformly absorbed light of a He-Ne laser (1.96 eV) was used to ascertain that the 2.64 eV results were not just surface-related. Calibrated neutral density filters served to modify the light intensity. Photocurrents were monitored by connecting the Keithley current amplifier to a digital multimeter or, for studying the (slow) time evolution of the currents, to a strip chart recorder.

3. Experimental results

Steady-state dark and photoconductivity measurements were performed on a-Se films available from earlier studies [5-7], as well as on newly prepared samples. All confirmed the reported typical behaviour near and above room temperature, with an thermally activated dark current above 300 K and a transition from the monomolecular to the bimolecular recombination regime in the photocurrent [5,7]. Below room temperature, where the observation of an anomalous maximum in the dark conductivity was reported earlier [13], a similar effect is now observed in the photocurrent. The open symbols in Fig. 1(a) 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, 5×10^{-2} I_0, and 3.8×10^{-3} I_0, where $I_0 = 2 \times 10^{13}$ photons cm^{-2} s^{-1} represents the full light intensity. We see that below 278 K ($10^3/T > 3.6$) the increase in the dark current (full symbols) is mirrored in the behaviour of the photocurrents. The maximum in the photocurrent intensity occurs at somewhat higher temperatures than the one that maximizes the dark current, and the offset between those maxima increases with increasing illumination intensity.

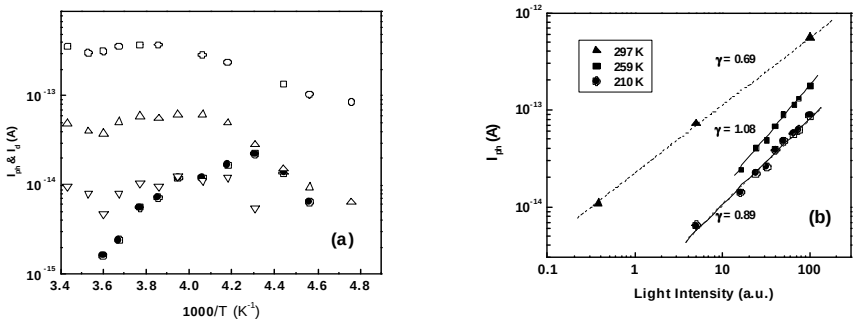

Fig. 1. (a) Temperature dependence of the steady-state photocurrent for an a-Se film under 470 nm illumination for three intensities: $I_0 = 2 \times 10^{13}$ photons cm^{-2} s^{-1} (○), 5×10^{-2} I_0 (Δ), and 3.8×10^{-3} I_0 (∇). 50 V was applied across a 7 μm thick co-planar cell. The full symbols indicate the level of the dark current; (b) Dependence of the photocurrent on the light intensity at indicated the temperatures; the slopes γ correspond to the exponents of the $I_{ph} \propto (Intensity)^{\gamma}$ relationship.

Fig. 1(b) shows Lux-Ampère characteristics for the photocurrents induced by 2.64 eV (470 nm) illumination at three temperatures. The chosen temperatures, room temperature (297 K, $10^3/T = 3.4$), 259 K ($10^3/T = 3.9$), and 210 K ($10^3/T = 4.8$), are characteristic for the regions above, near, and below the low-temperature photocurrent maximum. At all temperatures the photocurrent, I_{ph}, grows with light intensity, and therefore photocarrier generation rate G, according to $I_{ph} \propto G^{\gamma}$. Fitting these data for 297, 259, and 210 K, the values of γ are 0.69 ± 0.02, 1.08 ± 0.06, and 0.88 ± 0.04 respectively. In other words, the photocurrent light-intensity dependence changes from sub-linear to super-linear and back to sub-linear as the photocurrent passes through its low-temperature maximum.

The above results were obtained with the 2.64 eV illumination that resulted in the largest photocurrents. However, since the a-Se absorption depth is shallow for such photons, a follow-up set of measurements was carried out with the more uniformly absorbed 1.96 eV light of a He-Ne laser to ascertain that the observed behavior is not just due to surface states. The shift in dominant recombination regime from bimolecular to monomolecular and back to bimolecular was again observed with decreasing temperature.

Our earlier studies of steady-state photoconductivity in a-Se [5,7] showed that the bimolecular recombination process is the dominant one at room temperature. It is known that, under these conditions, the photocurrent will overshoot its eventual steady-state value upon turn-on [14]. Fig. 2(a) shows such typical behaviour of the kinetics of the photocurrent turn-on at room temperature for the higher illumination intensities. At the lowest light intensity (down a factor 3.8×10^{-3} from the highest one), the photocurrent does no longer show any overshoot but just increases monotonically to its steady-state level. Such behaviour signals the dominance of the monomolecular recombination process. A remarkable feature of the observed overshoot in the photocurrent transients is its dependence on the temperature. Fig. 2(b) demonstrates this for the intermediate illumination intensity. While the overshoot is obvious at room temperature (297 K), it decreases with decreasing the temperature and has, in fact, disappeared at 259 K where dark and photocurrents are near their lo-temperature peak value. At still lower temperatures where dark and photocurrent have passed their respective maxima, as for the 210 K shown in Fig. 2(b), the overshoot of the photocurrent reappears, signalling the return of bimolecular recombination dominance.

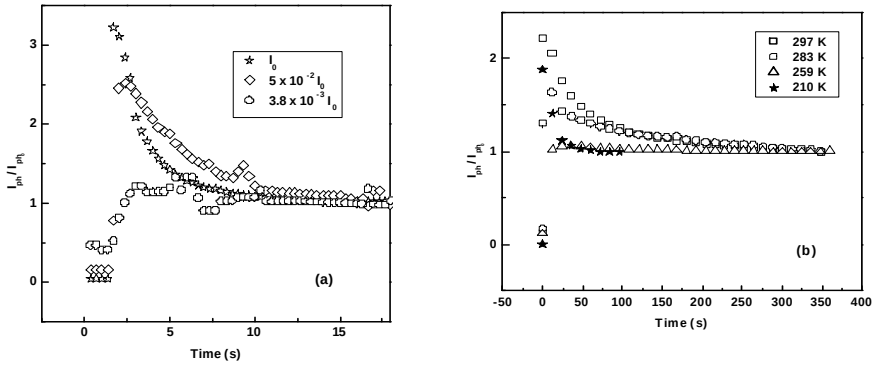

Fig. 2. (a) Room temperature photocurrent rise in an a-Se film gap cell at the indicated intensities of 470 nm illumination with $I_0 = 2 \times 10^{13}$ photons cm^{-2} s^{-1}. The photocurrents are normalized to their steady-state level I_{ph0}; (b) Photocurrent turn-on when illuminated with the intermediate intensity of 5×10^{-2} I_0 at the indicated temperatures.

4. Discussion

Both the changes in the light-intensity dependence of the photocurrent with decreasing temperature, i.e. the changing slopes of the Lux-Ampère characteristic, and the accompanying changes in the turn-on kinetics point to the same phenomenon: The recombination mechanism first moves away from the bimolecular behaviour that is traditionally seen for chalcogenides at low temperatures, and then moves back to it once the temperature region around 250 K where the dark and photocurrents go through a maximum has been past. The observed super-linearity of the photocurrent's light intensity dependence near 250 K points to the presence of a sensitising centre near the a-Se equilibrium Fermi level as source of those changes in the recombination mechanism [15].

Indeed, steady-state illumination will establish quasi-Fermi levels for electrons and holes away from the equilibrium Fermi level, with rising illumination levels moving them further apart and rising temperatures moving them closer together. The observed sensitisation of the photocurrent occurs when the quasi-Fermi level for electrons is moved through an above-mid-gap defect level with specifically low capture probability for holes [16]. The shift in the temperature at which the maximum in the photocurrent is seen with changing light intensity in Fig. 1(a) agrees with this notion since a higher light intensity will be needed to move the quasi-Fermi level past the defect when a higher sample temperature favours the opposite motion.

In order to try next to estimate the position of this electron trap in the band gap, a rather specific model density of states for the a-Se will be required, as may be learned from the calculations by Gu et al. [17] for hydrogenated amorphous silicon. Given the strong polaronic effects at the a-Se negative-U centres, this is beyond the reach of the present study. Nevertheless, the photocurrent results support the idea of a defect centre close to the equilibrium Fermi level that was used in [13] to explain the dark conductivity maximum by a statistical shift of the Fermi level. Such level would also correspond to the deep electron trap whose influence has been detected in numerous experiments [11,12,18]. From a study of the dark discharge of residual potentials in a-Se films, Kubilius et al. [19] calculated that those deep levels, about 0.85 eV away from the transport path, would be exponentially distributed with a characteristic energy of $E_0 = 50$ meV. On the same assumption of an exponential distribution of traps, the current decay from the top of the overshoot to the steady-state value follows a power law $I_{ph} \propto t^{-(1-\alpha)/2}$, with $\alpha = kT/E_0$ [14]. Applying this rule to the transients of Fig. 2(a), we find values for E_0 between 24 and 41 meV, indicating that the deep trap distribution will definitely not be purely exponential as well as that it will be steeper than indicated by the earlier 50 meV.

As a further test for our interpretation of the low-temperature dark and photocurrent results, we also studied transient photocurrents following pulsed optical excitation in the same low-temperature range that produces the photosensitisation. No special features were observed. Since the transient experiment probes mainly the tail states [8], it confirms the role played by the mid-gap states in the observed phenomena.

5. Conclusion

Steady-state photoconductivity measurements in a-Se reveal a current maximum below room temperature in the region where an anomaly in the dark conductivity was reported earlier. Both phenomena are linked to the present of a deep electron trap with low capture probability for the current carrying holes, leading to a sensitisation of the photocurrent at low temperature.

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References

[1] M. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).
[2] S. O. Kasap, J. A. Rowlands, J. Mater. Sci.: Mater. Electron. **11**, 179 (2000).
[3] M. Abkowitz, Philos. Mag. Lett. **58**, 53 (1988).
[4] H. -Z. Song, G. J. Adriaenssens, E. V. Emelianova, V. I. Arkhipov, Phys. Rev. B **59**, 10610 (1999).
[5] N. Qamhieh, M. L. Benkhedir, M. Brinza, J. Willekens, G. J. Adriaenssens, J. Phys.: Condens. Matter **16**, 3827 (2004)
[6] M. L. Benkhedir, M. S. Aida, G. J. Adriaenssens, J. Non-Cryst. Solids **344**, 193 (2004).
[7] M. L. Benkhedir, M. Brinza, G. J. Adriaenssens, J. Phys.: Condens. Matter **16**, S5253 (2004).
[8] M. L. Benkhedir, M. S. Aida, N. Qamhieh, A. Stesmans, G. J. Adriaenssens, J. Optoelectron. Adv. Mater. **7**, 329 (2005).
[9] K. Koughia, Z. Shakoor, S. O. Kasap, J. M. Marshall, J. Appl. Phys. **97**, 033706 (2005).
[10] M. L. Benkhedir, M. Brinza, G. J. Adriaenssens, to be published.
[11] M. Abkowitz, S. Mitra, J. Appl. Phys. **61**, 1038 (1987).
[12] S. O. Kasap, M. Baxendale, C. Juhasz, J. Appl. Phys. **62**, 171 (1987).
[13] N. Qamhieh, J. Willekens, M. Brinza, G. J. Adriaenssens, J. Phys.: Condens. Matter **15**, L631 (2003).
[14] M. S. Iovu, S. D. Shutov, V. I. Arkhipov, G. J. Adriaenssens, J. Non-Cryst. Solids **299**, 1008 (2002).
[15] A. Rose, Concepts in Photoconductivity and Allied Problems, Krieger, Huntington (1978).
[16] G.W. Taylor, J. G. Simmons, J. Phys. C: Solid State Phys. **9**, 1013 (1976).
[17] B. Gu, D. Han, C. Li, S. Zhao, Philos. Mag. B **53**, 321 (1986).
[18] S. Kasap, B. Fogal, M. Z. Kabir, R.E. Johanson, S. K. O'Leary, Appl. Phys. Lett. **84**, 1991 (2004).
[19] A. Kubilius, B. Petretis, V. I. Arkhipov, A. I. Rudenko, J. Non-Cryst. Solids **87**, 290 (1986).