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GAP-STATE SPECTROSCOPY IN AMORPHOUS SELENIUM

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Through a combination of steady-state and transient photocurrent spectroscopy it has been possible to locate several of the energy levels of the charged coordination defects (D^+ and D^-) that constitute the chalcogenide negative-U model in the amorphous selenium bandgap. However it has also been observed that the energy position of those levels is influenced by external influences such as light soaking or annealing of the samples. The post-transit time-of-flight photocurrents that reveal those energy positions have, therefore, been systematically studied in samples with different pre-histories. The optical absorption in the samples was further examined through the constant-photocurrent method (CPM), and by photothermal deflection spectroscopy (PDS). Although the TOF results provide information on the D^+ and D^- levels separately, while the CPM and PDS data reflect the integral optical absorption between both centres and the bands, the results do agree. The photo-induced changes that are observed are stable at room temperature.

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1. Introduction

Recent studies of the density of localized states (DOS) in the amorphous selenium (a-Se) bandgap by steady state photoconductivity (SSPC) measurements and the analysis of time-of-flight (TOF) post-transit currents [1-3] have resolved two discrete defect levels in the DOS. One level is located ~0.42 eV above the valence band edge, and the second one lies some 0.53 eV below the conduction band edge. Being linked to carrier recombination in the SSPC data and to emission of trapped charge in the TOF results, these two levels have been identified as the ones that govern thermal transitions involving the charged coordination defects of the standard negative-U model for a-Se [4]. An optical transition to one of those defects was identified in the spectral photoconductivity response [2]. On the other hand, the actual presence of negative-U centres in the chalcogenide glasses was recently questioned on the basis of the non-observation of any defect-related features in the optical absorption spectra of a-As_2S_3 [5]. It was argued that the sub-bandgap absorption there was just due to the disruption of the normal As-S bonding network by the occurrence of ~1 % homopolar As-As bonds in the material.

In a-Se, there are only the Se-Se bonds available to form the network and define the bandgap, with the coordination defects C_3^+ and C_1^- [4] of the negative-U model as primary candidates for causing sub-gap absorption. Studies of this sub-gap absorption were therefore undertaken by means of photothermal deflection spectroscopy (PDS) and the constant-photocurrent method (CPM) to see whether any resolved structure would match the energy diagram we deduced in our earlier work for the negative-U centres.

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A further point of interest will be observation at room temperature of light-induced changes in the position and intensity of the DOS feature that is resolved from the post-transit TOF analysis. Photo-induced changes in a variety of chalcogenide properties have of course been studied widely in the past [6], but very rarely have these studies included a-Se amongst the study objects. The best-known of these effects is the photodarkening of the material, i.e. the narrowing of the optical gap of the chalcogenides under the effect of illumination. The darkened sample can be bleached again by illumination with sub-gap light, or by annealing at a temperature close to the glass transition temperature. In a-Se room temperature is sufficiently high to anneal this photodarkening, since its glass transition temperature is just above room temperature. In other words, photodarkening is only stable in a-Se well below room temperature [7].

Of special interest for the defect structure of a-Se are the light-induced electron spin resonance (LESR) experiments that showed that a considerable defect density could be photo-induced in chalcogenide glasses at low temperatures, but that the defects annealed out completely at room temperature. While a-Se is only mentioned in passing in the original study of Biegelsen and Street [8], a detailed investigation of the LESR in a-Se has since been carried out by Kolobov et al. [9]. It was reported that no measurable ESR signal could be obtained at 20 K in the dark. Only by illuminating the a-Se sample with across-gap light could a signal be detected and measured. The intensity of this signal was seen to increase with illumination duration, fast at first and more slowly after some minutes, but no saturation of the photo-induced ESR signal was observed within 2 hours of continuous illumination. The ESR signal persists at low temperatures after the light is turned off, but annealing at 150K makes the signal disappear. It is assumed that the ESR signal is due to a combination of activated native defects and newly photo-induced ones, neither of which are stable near room temperature.

Photo-induced changes in the DOS defect structure have been measured before in chalcogenide compounds such as As_2Se_3 by, for instance, transient photoconductivity [10] or modulated photoconductivity [11]. Those changes consist of an increase of the defect density that is stable at room temperature and can be annealed out at higher temperatures, but no shift in the energy position of the defect level is reported. As far as we can ascertain, no photo-induced changes have been reported for chalcogenides that involve a change in the energy position of the defect level as we observe it for a-Se.

2. Experimental conditions

2.1 Sample preparation and measurement techniques

Films of a-Se were deposited by thermal evaporation in a vacuum background of 2×10^{-3} Pa on either bare or aluminium-coated Corning glass substrates. Sandwich cells are made with the latter by evaporating top semi-transparent aluminium contacts through a mask with circular openings of 2 or 3.5 mm diameter. Rectangular Al contacts defined a 0.5 mm × 4.0 mm gap cell on deposited layers without underlying Al film. The substrate temperature was not regulated during the evaporations. Films deposited under identical conditions have been checked by X-ray diffraction, and they were fully amorphous.

Transient photocurrent measurements are carried out with a standard TOF set-up. The 337 nm light pulse of a LSI nitrogen laser triggers a dye cell with Coumarin 440 to produce a 6 ns long, 440 nm pulse. Measurements are performed using single light pulses, i.e. without signal averaging. The signal displayed on an IWATSU 8132 digitizing storage oscilloscope, is transferred into a computer. An HP 214B pulse generator is used for the bias voltage for times up to 10 ms. During the measurements the sample is placed on a metal support in a vacuum chamber. The sample temperature is controlled to better than 0.5 K by a combination of liquid nitrogen cooling and regulated heating of the sample support.

For CPM, where the light intensity is measured that is required to keep the photocurrent at a fixed value while different wavelengths in the spectrum are scanned [12], a 250 W tungsten-halogen lamp plus monochromator were used with lock-in current detection. The required intensity is inversely proportional to the number of photogenerated charge carriers, i.e. to the product $\alpha\eta$ of optical absorption coefficient and generation quantum efficiency. Gap cells are used for these measurements. For PDS, which is an optical technique, electrodeless layers are co-deposited with the TOF samples. PDS is based on the measurement of the thermal energy released by light absorption. The sample is submerged in a transparent deflection medium (CCl_4) whose index of refraction is temperature dependent. As the sample is irradiated by monochromatic light, the medium will be heated. This causes the deflection of a laser beam parallel to the surface. The deflection is proportional to the absorption coefficient of the material. As we do not need to know absolute values for the optical absorption in this study, no calibration of the CPM and PDS data is required.

2.2 Post-transit photocurrent analysis

In the time-of-flight experiment, free carriers are photo-excited just below the top contact of a sandwich cell and generate a transient current while drifting to the other electrode. Although multiple trapping of the carriers in shallow localized states results in anomalous dispersion of the charge packet, at transit time, t_T, of the average carrier can be deduced from the current trace. At times larger than t_T, photocurrent is increasingly generated by the re-emission of carriers from deep traps. For $t >> t_T$, the depth of the emitting trap can be approximated as $E_t = kT\,ln(\nu t)$ where ν is the attempt-to-escape frequency, k is Boltzmann constant, and T is the temperature. The post-transit photocurrent I(t) will then be proportional to the number of released carriers at time t from the density of states $g(E_t)$ at the corresponding energy level. Assuming equal capture probability into all states and no re-trapping in deep states, the post transit current I(t) is directly related to the density of gap states g(E) through the relation (1)

$$I(t)t = \frac{Q_0 t_0 \nu}{2g(0)} g(E), \qquad E = kT\ln(\nu t) \tag{1}$$

where Q_0 is the total charge participating in the transient photocurrent, t_0 is the free-carrier time, and g(0) is the DOS at mobility edge.

3. Results

3.1 Spectral response curves

Fig. 1 shows typical PDS and CPM spectra, measured at room temperature, from evaporated a-Se layers. The PDS signal is directly proportional to the a-Se optical absorption coefficient and shows the expected behaviour in agreement with a Tauc gap of 1.95 eV, an exponential Urbach tail (E_0 = 62 meV), and low-energy absorption from gap states. The local maximum in the absorption around 1.5eV corresponds to the optical transition from the valence band edge to the D^+ (C_3^+) level of the negative-U energy diagram, as proposed earlier on the basis of spectral photocurrent data [2]. The same sub-gap absorption generates the CPM signal in the 1.5 eV neighbourhood, but is then followed by a marked minimum around the bandgap energy of 1.95 eV. This minimum is due to the pronounced geminate recombination of photogenerated electron-hole pairs at the bandgap energy. A higher light intensity is then needed to keep the measured photocurrent constant, resulting in the lower CPM signal. This phenomenon was already recognised by Tanaka et al. [13]. Since the energy level of the negative-U D^- (C_1^-) centre is expected to lie just above the valence band, it will contribute to the absorption in 1.7 to 1.8 eV range. Both PDS and CPM curves show significant signal strength in that region.

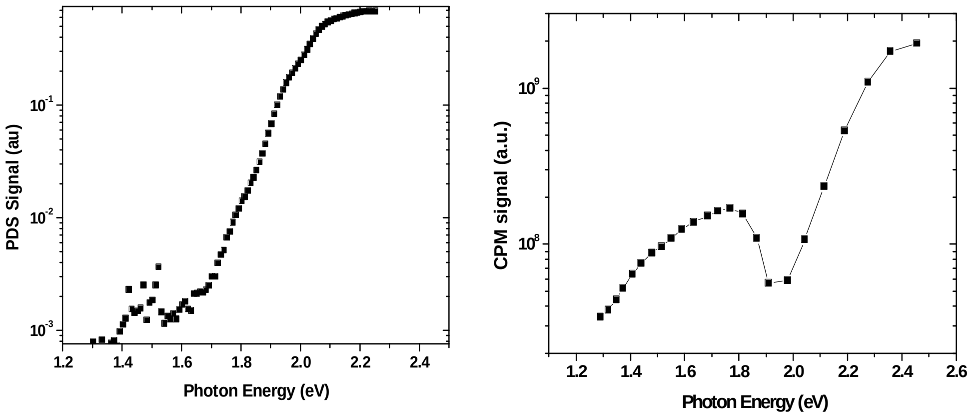

Fig. 1. Spectral dependence of the optical absorption in a 5 μm thick a-Se film as measured by PDS (left panel), and of the product of optical absorption and photocarrier generation quantum efficiency as measured by CPM with a gold-electroded gap cell on a 16 μm thick a-Se layer (right panel).

3.2 Post-transit photocurrents

The top frame of Fig. 2 shows hole TOF transient photocurrents from a 5μm thick a-Se layer with Al circular top contacts of 3.5 mm diameter. Curves 1 and 2 of Fig. 2 were measured with two different applied fields when the sample was fresh. Curve 3 was obtained after many measurements using the same top contact of the sample, and curve 4 shows the result of a subsequent measurement through a neighbouring top contact that had been co-illuminated with its neighbour but without an electric field being applied. All measurements were made at room temperature. The TOF transit time, corresponding to the change of slope at ~3 × 10^{-7} s, is clearly not being influenced by the repeated measurements. Application of a lower field, as for curve 2, does result in the anticipated lengthening of the transit time.

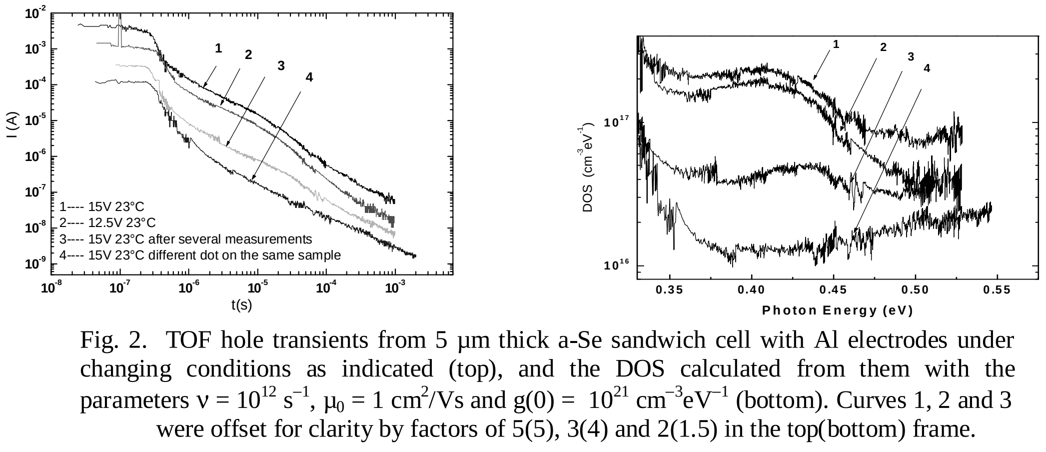

Fig. 2. TOF hole transients from 5 μm thick a-Se sandwich cell with Al electrodes under changing conditions as indicated (top), and the DOS calculated from them with the parameters $\nu = 10^{12}$ s^{-1}, $\mu_0 = 1$ cm^2/Vs and $g(0) = 10^{21}$ $cm^{-3}eV^{-1}$ (bottom). Curves 1, 2 and 3 were offset for clarity by factors of 5(5), 3(4) and 2(1.5) in the top(bottom) frame.

For post-transit currents on the other hand, it is the repeated illumination of the sample that makes a difference while the change of applied field has no influence. While a highly similar convex curvature is seen around t = 10^{-5} s in the post-transit current of traces 1 and 2, no such curvature is observed on curves 3 and 4 that were taken after repeated illumination of the sample. A clearer image of the changes in the post-transit current, which is due to carrier emission from deep traps, can be obtained by extracting the underlying DOS by means of Eq. (1). The lower part of Fig. 2 shows the DOS distributions that correspond to the 4 curves shown in the upper part. The DOS maximum seen on curves 1 and 2 around 0.42 eV is in full agreement with our previously reported results [1,2]. However, in curves 3 and 4 this DOS structure has moved deeper in the gap. Since the shift is more pronounced with curve 4, i.e. when measured at the companion spot that was co-illuminated but not field-stressed, we assume that we are seeing a photo-induced change in the DOS of a-Se. That change is stable at room temperature.

A twin sample to the one that led to the results described in the previous paragraphs was kept under ambient room lighting and temperature conditions for two weeks before being used for TOF measurements. The two samples were co-deposited and turned into TOF samples at the same time. The hole TOF transients obtained with this second sample are shown for 2 measurement temperatures in Fig. 3. The general behaviour of the transient photocurrent is again the one typically seen with a-Se samples, but with the emission from the deep states occurring at later times than what is normally seen with freshly prepared samples (see above and Refs. [1,2]). Fig. 3 also shows the DOS structure above the valence band edge that is resolved from the current traces through Eq. (1). A clear maximum around the energy of 0.55 eV is seen, very reminiscent of the shift in the DOS seen with the companion sample after many TOF measurements. There is one further aspect in the change in the DOS that deserves some attention. The density of states in the shifted localized level is noticeably more pronounced against its background than is the case for the peak density in the freshly prepared samples. The DOS rise by more than a factor of five in Fig. 3 may be compared to the increase by just a factor of two for curves 1 and 2 of Fig. 2.

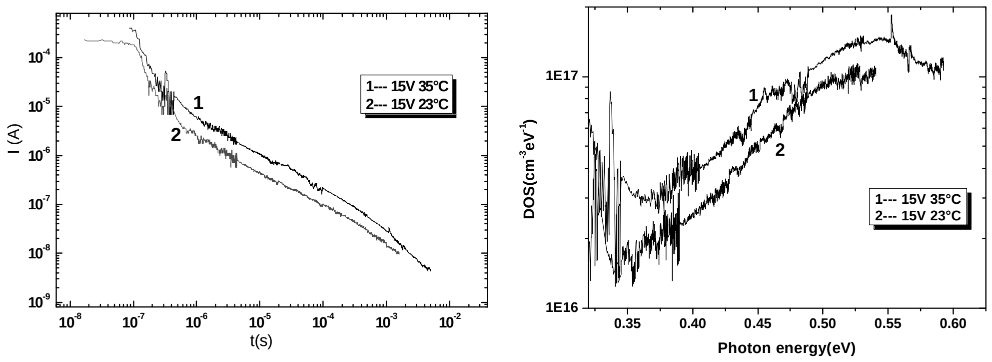

Fig. 3. TOF current transients and the DOS resolved from the post-transit emission currents from an a-Se sandwich cell exposed to natural light and room temperature ambient conditions, and measured at 23 °C and 35 °C. The curves are offset slightly for clarity, and the parameters listed with Fig. 2 were used for the DOS conversion.

Photo-induced structural changes in chalcogenides do – as a rule – anneal out close to or at the glass transition temperature. Therefore, the light-exposed sample that was discussed in the previous paragraph was annealed at 43 °C for 24 hours. Subsequently measured hole TOF photocurrents are displayed, together with the resolved DOS curves in Fig. 4. Comparison of the DOS after annealing with its counterpart before annealing (Fig. 3) reveals that, apart from a small shift by some 0.05 eV towards the valence band edge, annealing did not return the DOS to the initial conditions found in a freshly prepared a-Se sample. Fig. 4 further shows that the applied electric field influences the position of the defect peak. A field-induced shift, due to the Poole-Frenkel effect, was observed in earlier measurements on fresh samples [1], but the magnitude of the effect is larger here.

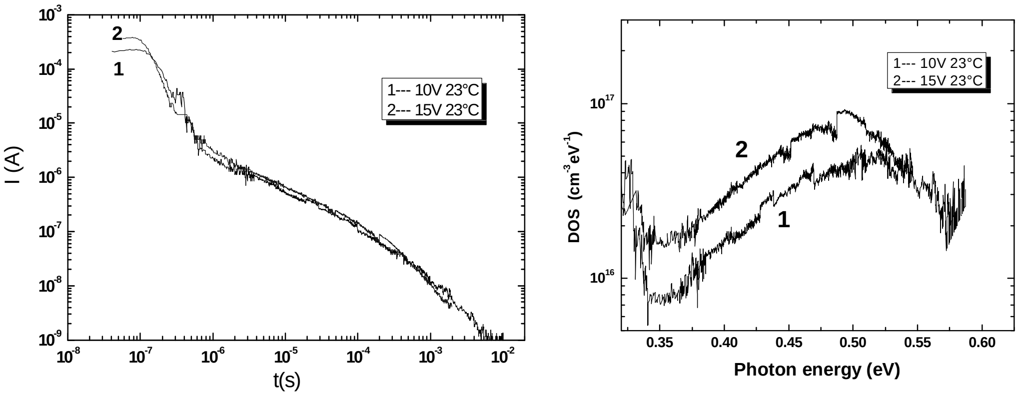

Fig. 4. TOF current transients and the DOS resolved from the post-transit emission currents from the a-Se sandwich cell used for the data of Fig. 3, after annealing at the glass transition temperature for 24 hours.

The experimental results that are described above have been confirmed with other sample series, prepared and measured under comparable conditions. Data were also collected from samples that were kept in the dark after preparation for times equal to the ambient exposure times of a companion sample. Such 'dark' samples could not be distinguished from fresh samples, indicating that aging is not the cause of our observations. Further studies with varying illumination conditions of the samples are still in progress.

4. Discussion

The identification in our earlier papers [1-3] of the discrete energy levels in the a-Se gap, one at ~0.42 eV above the valence band edge and one at ~0.53 eV below the conduction band edge, as part of the energy level scheme that follows from the chalcogenide negative-U model, finds further support in the PDS and CPM measurements reported in this study. In the negative-U system, the 0.42 eV thermally activated transition in the hole current should result from the polaronic deformation of the D^- lattice defect (C_1^- in the a-Se model of Kastner et al. [4]), with the equilibrium D^- level lying close to the valence band. Both PDS and CPM spectra do indicate an absorption shoulder in the 1.7 to 1.8 eV energy range that would account for optical excitation of electrons from the D^- level to the conduction band. Similarly, the ~1.5 eV transition that was ascribed to the valence band to D^+ transition in [2], is again prominently present in both PDS and CPM spectra. The fact that absorption in the 1.5-1.8 eV region does contribute to photoconduction, rather than being quenched by geminate recombination like the band-to-band absorption, does show that the absorption there is through defect rather than bandtail states. A similar indication is found when the phase of the PDS signal is monitored (not shown in Fig. 1). Above 1.75 eV the phase remains constant while it fluctuates strongly below that energy, indicating absorption through different types of localized states. Preliminary evidence from a further PDS and CPM study in which freshly-prepared and light-soaked a-Se samples are being compared, additionally indicates that increased absorption in the 1.7-1.8 eV region goes together with the enhancement of the defect peak reported in section 3.2 above. The combined observation of those two phenomena suggests that new negative-U-type defect centres are being created by the illumination.

The most remarkable aspect of the photo-induced changes that we observed in the a-Se defect structure is that they are stable at room temperature, and are barely influenced by annealing at the glass transition temperature. The observation of photo-induced changes in a-Se that are stable at room temperature is not evident. Up to now, observed photo-induced changes have proven unstable at room temperature. The well-known LESR signals of Biegelsen and Street [8] or Kolobov et al. [9]

anneal out completely at 150 K, just as did the photodarkening observed by Nagels at low temperatures [7].

That the effect is photo-induced follows from the observations that prolonged exposure to the light, even in the absence of any field stressing of the sample as was the case for curve 4 in Fig. 2 or the sample used for Fig. 3, does lead to the observed shifting of the defect peak above the valence band edge. Along with the changes in the energy position of the peak, its intensity with respect to the background is also changing. However, it is difficult to ascertain whether this relative change is due to an increase of the defect density, to a recession of the background, or to a combination of both, given that some of the constants that are needed in Eq. (1) for the DOS calculation have to be estimated and may conceivably be subject themselves to change under prolonged illumination. More analysis is clearly needed to resolve these questions. It may be added at this point that the observation of photo-induced changes in the defect structure that is revealed by electron rather than hole transits is more difficult, just as the observation of the DOS structure on the conduction band side of the gap itself is more difficult. An apparent minor shift of the defects towards the conduction band is seen in some samples, but on this point as well, a more extended study is needed to clarify the results.

Possible alternative reasons for the observed effects may be examined. Since the samples are sandwich cells it is justified to exclude humidity or oxidation as possible causes. But as the contacts have to be semi-transparent for the TOF measurements, light soaking and aging remain as possible causes. We can exclude aging on the basis of our experience with various a-Se samples that were intermittently used for measurements, and stored in the dark otherwise over many months, without any significant changes in the results. Crystallization of the a-Se layer can also be excluded as cause on the basis of our attempts to anneal out the photo-induced changes: Annealing at the glass transition temperature would have increased the amplitude of the peak if crystallization were in play, rather than just shift it back a bit towards its original position as seen in Fig. 4. The parameters used in Eq. (1) might themselves play a role in the observed shift if they should be subject to light-induced variations. Indeed, the energy scale is determined by the relationship $E = kT\mathit{ln}(\nu t)$, where $\nu = 10^{12}\ s^{-1}$ has been used for all calculations. A photo-induced change of this parameter by two orders of magnitude would cause a room-temperature shift of some 0.1 eV in the position of the defect peak, but the likelihood of such change is decidely remote. As none of the above suggestions offers a good explanation for the observed changes in the a-Se DOS upon illumination, and as the feature that is most prominently changed has been tied to one of the charged coordination defects of the negative-U model, the most logical assumption seems to be that we are seeing a photo-induced change in the native negative-U defects, possibly even involving the generation of some additional centres. The set of such defects that is frozen in upon condensation of the amorphous film conceivably contains a number of them that can be further relaxed under optical excitation, thus shifting their average energy deeper into the gap as well as increasing the peak’s prominence over the background by reducing the width of the distribution of defects.

5. Conclusions

PDS and CPM studies of the optical absorption in a-Se films have revealed the presence of the optical transitions that are required in the chalcogenide negative-U model to accompany the thermal transitions that were identified by steady-state and transient photocurrent methods before [1-3]. Therefore, a-Se is, beyond any doubt, a negative-U system. By using the TOF technique to measure transient hole photocurrents in freshly prepared samples as well as extensively illuminated samples and samples that were exposed for weeks to ambient light and temperature, evidence of photo-induced changes in the a-Se defect structure was obtained. Those changes, consisting of a shift of the defects to deeper energies and a possible increase of their density, are stable at room temperature. These effects can only be partially reversed by annealing the sample at the glass transition temperature.

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