

GAP STATES IN CHALCOGENIDE GLASSES

G. J. Adriaenssens, A. Stesmans

Laboratorium voor Halfgeleiderfysica, University of Leuven, Celestijnenlaan 200D,
B-3001 Leuven, Belgium

Charged co-ordination defects that contribute discrete electronic energy levels to the distribution of localized states in the band gap have been widely accepted as part of the negative-U model for chalcogenide glasses. However, since the density of these defects is lower than the density of localized tail states they fail to be resolved in direct optical spectroscopy. It is argued that, contrary to a recent suggestion and with the overwhelming evidence in their favour, this fact is not sufficient grounds for doubting the presence of the charged defects.

(Received August 12, 2002; accepted October 31, 2002)

Keywords: Chalcogenide glasses, Negative-U model, Co-ordination defects

1. Introduction

Early on in the systematic study of chalcogenide glasses it was discovered that they were very changeable materials whose structure and characteristic properties could readily be modified by changing external parameters such as applied field, illumination or temperature. This was the case with the early ovonic switches [1], over the multitude of reported photo-structural changes [2], to the current phase-change optical memory devices [3]. In all instances it was assumed that disorder- and defect-induced gap states were involved in some way, but pinning down the precise mechanisms proved to be non-trivial. In fact, even the nature of those gap states proved to be less than obvious in the chalcogenide glasses.

The early understanding of the structure of amorphous insulators and semiconductors accepted that the disorder would lead to the presence of a number of bonding defects involving unpaired electrons. Electron spin resonance (ESR) did indeed readily detect the, by now, well-known E' centre in SiO₂ [4] and the dangling bonds in a-Si [5]. These centres were understood to form part of the overlapping tails of the valence and conduction band states in what became known as the CFO model [6]. However, chalcogenides such as a-Se or a-As₂S₃ did not fit into that picture: They did not show the expected ESR signals in equilibrium. While spin resonances can be detected after optical excitation, they die out when the light is turned off. (It has since been discovered that germanium sulphides do form an exception to that rule; they do exhibit equilibrium ESR.) The absence of the equilibrium ESR signals in the chalcogenide glasses led Anderson [7] and Street and Mott [8] to formulate their negative effective correlation energy (negative-U) models, respectively in terms of the general lattice site and in terms of charged defects. The model is based on the logical deduction that the ESR results signify that a singly occupied electronic state creates an energetically less favourable situation than the occurrence of unoccupied or doubly occupied states. The large flexibility of the chalcogenide lattices, caused by the abundance of merely two-fold co-ordinated chalcogen atoms, and the ensuing ease of polaronic deformation upon double occupancy are behind this phenomenon.

The general negative-U model outlined by Anderson was later amplified by the work of Karpov and Klinger [9] on the self-localization of electron (and hole) pairs (SLEP), which started from the notion of soft-potential sites in the disordered lattice. Mid-gap pinning of the Fermi level, and excitation energies involving multiples of roughly one fourth the gap energy could be derived [10]. However, just like the Anderson model, the SLEP envisions a fully co-ordinated random

network. The actual occurrence of such fully co-ordinated network would – other than in computer simulations – not really be expected from an amorphous compound. Indeed, it is more realistic to expect the amorphous lattice to contain a certain number of mal-co-ordinated sites, including some dangling bonds. Of course, in view of the ESR evidence, those defects must then be devoid of unpaired electrons. The sum of these considerations led Street and Mott to propose a model which allowed for the presence of dangling bonds, but with the combination of positively and negatively charged dangling bonds, D^+ and D^- having respectively no and two spin-paired electrons, being energetically favoured over the neutral dangling bond D^0 with one unpaired electron. The latter only appears as an excited state. This defect-based version of the negative-U model was subsequently worked out in some detail by Kastner, Adler and Fritzsche [11] for the case of a-Se, with a singly co-ordinated, negatively charged, selenium (C_1^-) and a threefold co-ordinated, positively charged site (C_3^+) emerging as the most likely equilibrium defect configurations.

The energy level schemes for electronic transitions involving the negative-U defects, as worked out in the original publications [8,11], have since found support in the interpretations of a wide range of experimental observations (see e.g. [12-14]). Nevertheless, on the basis of optical absorption measurements on highly purified As_2S_3 samples, the presence of these charged defects in the chalcogenide glasses has recently been questioned [15]. In the next sections, therefore, the notions and consequences of the charged defects version of the negative-U model will be reiterated, and it will be argued that, even when the direct observation of the defects often fails for lack of sensitivity, there is plenty of indirect evidence for their presence in the chalcogenide glasses.

2. The charged defects model

The very nature of the polaronic deformation origin of the negative effective electron correlation energy implies that the defects will be characterized by different transition energies to the bands depending on their electron occupancy, as well as by different energies for thermal *vs.* optical transitions to the defects since phonons can and photons cannot supply the necessary momentum to accommodate the accompanying lattice deformation. These considerations lead to an energy level scheme of the type illustrated in Fig. 1(a). Levels A^+ and A^- correspond to the defects in the equilibrium configuration q_0 and will play a role in optical absorption (transitions 1 and 1'), while the T and O levels mark the energy distances from the excited defect to the bands for, respectively, thermal and optical processes. The latter transitions occur at the non-equilibrium configuration q_n and include photoluminescence (2) and photoinduced absorption (3). Recombination of electrons and holes involves the most relevant thermal processes. An energy-configuration diagram showing the various possible transitions is shown for the positively charged defect in Fig. 1(b).

The energy levels depicted in the above diagrams have generally been found to agree very well with experimentally determined values for As_2Se_3 , As_2Te_3 and related materials [12, 14]. In fact, the position of distinct recombination levels (T) in the band gap was deduced from steady-state photoconductivity measurements well before the introduction of the negative-U centres [16-18], and turned out to be fully compatible with the latter. Indeed, as may also be seen in the examples in Fig. 2, the temperature dependence of steady-state photocurrents in the chalcogenides generally reveals a positively activated region at the high-temperature end and one with a negative slope at lower temperatures, with the activation energies being linked to the position in the band gap of donor-like and acceptor-like recombination centres.

The occupied D^+ and D^- sites and the corresponding thermal transition levels provide those centres in the negative-U model. That the observed photoluminescence with photon energies of roughly half the excitation energy [19] agrees with the proposed level scheme (transitions 2 in Fig. 1) need not surprise since it formed part of the original argumentation in favour of the defect-based negative-U model. Other transitions of the Fig. 1 diagrams were confirmed through various optical techniques, such as optical modulation spectroscopy for photoinduced absorption or bleaching transitions [20-21], or the study of luminescence excitation spectra [22]. A detailed discussion for the case of As_2Se_3 may be found in [14, 23].

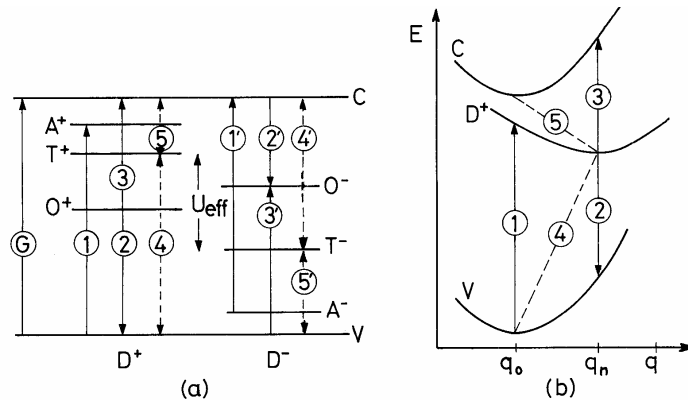


Fig. 1. (a) Energy level diagram for the positively and negatively charged defects D^+ and D^- , with A representing the ground state of the defect and T, O the excited levels for either thermal or optical transitions to the valence (V) or conduction (C) bands. G represents band-to-band optical excitation and the numbers 1 to 5 possible transitions. (b) The energy-configuration diagram for the D^+ defect, with q_0 the equilibrium, and q_n the non-equilibrium configuration.

The experimental support for the charged defects model in the arsenic chalcogenides is not matched by a generally accepted model for the identity of the defects. The possibly combined occurrence of hetero- and homopolar bonding with a number of different bonding co-ordinations makes it difficult to offer a convincing choice. For the elemental a-Se, this situation is reversed: There exist a widely employed 'standard' model for the defects [10, 13], but there is not much experimental evidence in support of the specific energy levels it implies. The fact that a-Se has a low glass transition temperature (~ 310 K) undoubtedly has contributed to that situation. Also the fact that an attempt to calculate the presumed negative effective correlation energy by incorporating the postulated defects in a crystalline matrix [24] failed, and came up with a *positive* U instead, contributed to some questioning of the existence of the negative- U centres in a-Se. Only a more recent series of extended X-ray-absorption fine structure (EXAFS) and electron spin resonance (ESR) measurements by Kolobov et al. [25] offered convincing proof for the correctness of the standard a-Se model. The energy positions in the gap of the thermally accessible $T^{+/-}$ levels of a-Se have recently been identified through post-transit analysis of Time-of-Flight photocurrents [26]. Their positions do agree with the notions of the negative- U model.

3. Tail states

Apart from the localized gap states due to the charged defects, the chalcogenide glasses will obviously also exhibit the tail-state distributions inherently present in all amorphous semiconductors. For the valence band tail, the width of that distribution can – to first approximation – be estimated from the Urbach slope of the optical absorption curve. Since holes are the more mobile carriers in the chalcogenides, it is also possible to probe that tail by appropriate electrical transport measurements. Accordingly, Monroe and Kastner [27] used a transient photocurrent (TPC) experiment to conclude that in As_2Se_3 , and from 0.3 eV to 0.86 eV into the gap, the localized states are exponentially distributed with an exponential width E_0 of nearly 50 meV. Other investigators did arrive at comparable results [14]. In view of the energy range covered by these transient experiments, it was anticipated that evidence for the D^- centres of As_2Se_3 would be seen, but that has not been the case.

More recently, Tanaka reported on optical absorption spectra from As_2S_3 samples with very low impurity content [15], and also reported that no evidence for the charged defects could be seen in the distribution of tail states. Tanaka estimated that the tail states involved up to 1 at.% of all bonds, and pointed out that this exceeds the number of charged defects deduced from the negative- U models. These numbers agree with the earlier estimates (for a- As_2Se_3) of an equilibrium defect density of $\sim 4 \times 10^{17} \text{ cm}^{-3}$ [28] and an exponential tail state distribution $g(E) = g_0 \exp(E/E_0)$ which for the

customary $g_0 \approx 5 \times 10^{21} \text{ cm}^{-3}$ would reach that value only some 0.5 eV, i.e. roughly $E_g/4$, into the gap. In the negative-U model, such energy position would correspond to the occupied defect state. In other words, if all D^- centres in a sample would be occupied, the density of discernible T^- levels would just be of the order of the tail state density at that energy, which illustrates the difficulty faced by any attempt at direct spectroscopic observation of the charged defects. Moreover, as outlined in [29], the lack of TPC data from the chalcogenides for times shorter than 1 μs could result in the non-resolution of even a fairly prominent defect peak. It is not advisable, therefore, to use the failure of direct spectroscopic observation of the charged defects as an argument for their absence from the sample.

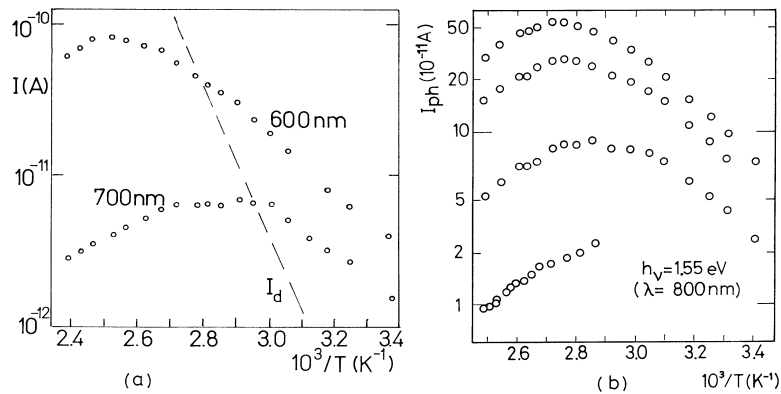


Fig. 2. Temperature dependence of steady-state photocurrents: bulk a-(Ge₂Se₇)₈₈Sb₁₂ sample (with reduced illumination intensity at 700 nm); a-As₄₇Se₅₃ bulk sample at light intensities from 0.46 to $16.0 \times 10^{13} \text{ photons.s}^{-1}.\text{cm}^{-2}$.

4. Modified materials

With the equilibrium density of the charged defects being so low that direct observation of their presence often fails, looking at non-equilibrium situations or otherwise modified materials has helped to clarify matters. Optical excitation of chalcogenide samples at low temperatures does produce sufficiently long-lived paramagnetic centres for their ESR observation, in agreement with the negative-U model. However, since in As₂S₃ the attainable density of such centres exceeds by far the accepted density of native charged defects [30], it had to be concluded that defect creation must be involved along with the anticipated excitation of the intrinsic defects. These optically induced defects also show negative-U characteristics and tie in with other photoinduced changes in the chalcogenide, but they do complicate the analysis in terms of the basic charged defects model. Non-equilibrium defect concentrations have also been observed through photoconductivity measurements of either unannealed as-quenched or light-soaked As₂Se₃ samples [14, 31]. In these cases, the spectral features observed in the photocurrent traces do fit in the energy level schemes of Fig. 1.

Perhaps some of the clearest spectroscopic evidence for the charged-defect-induced energy levels in the gap is related to the presence (or introduction) of non-intrinsic charged states in the chalcogenide samples. Such impurity centres and the requirement of over-all charge neutrality of the sample will result in the enhancement of the concentration of one of the intrinsic charged defects and thus offer a good opportunity for detecting its presence and characteristics. Indeed, as discussed in [32], additives such as oxygen or halides that tend to form negative ions in the chalcogenide matrix will induce an increased concentration of D^+ centres and, by the law of mass action, at the same time cause a reduction of the D^- concentration. That such effects can in fact be observed is illustrated by the data in Fig. 3 where results are compared from pure As₂Se₃ bulk samples and samples that have been intentionally doped with oxygen. The steady-state photocurrents in Fig. 3(a) do show a change of slope for both curves at 1.6 eV, which is indicative of optical transitions from the A^- level of Fig. 1(a) to the conduction band, as well as a pronounced shoulder at 1.4 eV for the curve from the oxygen containing sample. This feature corresponds to transitions from the valence band to the A^+ level, and

shows that the density of D^+ centres has been raised by the addition of oxygen. It of course also allows a determination of the position of that A^+ level. The photoinduced transmission changes shown in Fig. 3(b) confirm that interpretation: The sample containing oxygen shows a marked reversal from photoinduced absorption to photoinduced bleaching as the photon energy crosses 1.4 eV because the normal absorption into the 1.4 eV level is now being blocked by the configuration change of the D^+ site upon capture of an electron that was excited by the pump beam. Only when the density of D^+ sites is artificially raised, is this process observed against the background of photoinduced absorption into the distribution of tail states.

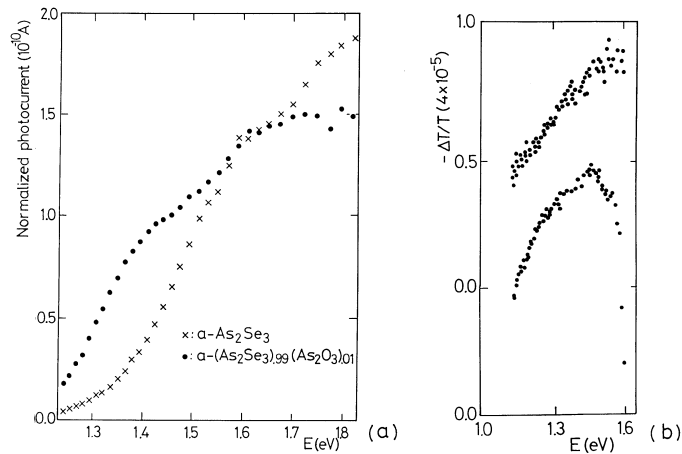


Fig. 3. Spectral characteristics of pure and oxygen containing bulk As_2Se_3 samples [21]: (a) Steady-state photocurrents at constant number of incident photons for pure As_2Se_3 (375 K), and for a sample containing 1% of As_2O_3 (385 K); (b) Photoinduced change in optical transmission for oxygen – free sample (upper curve) and for a sample containing 0.2% of As_2O_3 (lower curve); data taken at 295 K.

A similar effect may be anticipated when chlorine is incorporated in a-Se, as is the case for the ‘stabilized’ Se used for xerography or digital X-ray imaging. The post-transit photocurrent experiments described in [26] were therefore duplicated with such stabilized a-Se and duly failed to resolve the T^- feature on the hole transient [33], in agreement with the notion that the D^- density will be depressed by the Cl. A reduced signal-to-noise ratio with the stabilized films prevented the observation of the deeper-lying T^+ signature on the electron transient.

5. Conclusions

The number of experimental observations that can be explained by the charged defects version of the negative-U model is very large and varied, from the absence of dark ESR and the possibility of light-induced ESR, over the pinning of the Fermi level, the large polaronic effect on the luminescence, the discrete recombination levels in the gap, the onset energies of photoinduced absorption or bleaching, to the alteration of the D^+/D^- balance upon introduction of an ionic impurity species, to cite just the most obvious ones. Based on these observations, a density of defect centres emerges which is decidedly lower than the number of localized states in the band tails.

There is no reason, therefore, why in simple optical spectroscopy or time-resolved photocurrent transients the lower density of charged defects would not be obscured by the higher density of tail states. It would not be justified to use such observations as a basis for questioning the existence of charged centres in the material. Instead, techniques that rely on specific properties that can discriminate between the localized tail states and the charged defects should be used to investigate this issue. Examples of such techniques are the dual-beam photoinduced absorption or bleaching measurements which show distinct absorption edges if discrete levels are involved, or the steady-state

photocurrent temperature dependencies where the charged states will show up as much more effective and well-defined recombination centres than the neutral tail states.

In summary: Contrary to a recent suggestion [15], there is no conflict at all between the presence in the chalcogenide glasses of charged defects with negative effective electron correlation energy and discrete energy levels in the band gap, and the non-observance of such levels by optical spectroscopy.

References

- [1] S. R. Ovshinsky, *Phys Rev. Lett.* **21**, 1450 (1968); S. R. Ovshinsky, in *Structure and Properties of Non-Crystalline Semiconductors (Proceedings of ICALS 6, Part B)*, ed. B. T. Kolomiets (Nauka, 1976), p. 426.
- [2] K. Shimakawa, A. Kolobov, S. R. Elliott, *Adv. Phys.* **44**, 475 (1995).
- [3] N. Yamada, *MRS Bulletin*, September 1996, p. 48; T. Ohta, *J. Optoelectron. Adv. Mater.* **3**, 609 (2001).
- [4] R. A. Weeks, *J. Appl. Phys.* **27**, 1376 (1956).
- [5] M. H. Brodsky, R. S. Title, *Phys. Rev. Lett.* **23**, 581 (1969).
- [6] M. H. Cohen, H. Fritzsche, S. R. Ovshinsky, *Phys. Rev. Lett.* **22**, 1065 (1969).
- [7] P. W. Anderson, *Phys. Rev. Lett.* **34**, 953 (1975).
- [8] R. A. Street, N. F. Mott, *Phys. Rev. Lett.* **35**, 1293 (1975).
- [9] M. I. Klinger, V. G. Karpov, *Sov. Phys. JETP* **55**, 976 (1982).
- [10] V. G. Karpov, *Sov. Phys. JETP* **58**, 592 (1983).
- [11] M. Kastner, D. Adler, H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
- [12] R. A. Street, in *Electronic Phenomena in Non-Crystalline Semiconductors (Proceedings of ICALS 6, Part A)*, ed.: B.T. Kolomiets (Nauka, 1976), p. 116.
- [13] S. R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman, 1990), chapter 6.
- [14] G. J. Adriaenssens, *Phil. Mag. B* **62**, 79 (1990).
- [15] K. Tanaka, *J. Optoelectron. Adv. Mater.* **3**, 189 (2001).
- [16] C. Main, A. E. Owen, in *Electronic and Structural Properties of Amorphous Semiconductors*, eds. P. G. Le Comber and J. Mort (Academic Press, 1973), p. 527.
- [17] J. G. Simmons, G. W. Taylor, *J. Phys. C: Solid State Phys.* **7**, 3051 (1974).
- [18] T. A. Arnoldussen, C. Menezes, Y. Nakagawa, R. H. Bube, *Phys. Rev. B* **9**, 3377 (1974).
- [19] R. A. Street, I. G. Austin, T. M. Searle, B. A. Smith, *J. Phys. C: Solid State Phys.* **7**, 4185 (1974).
- [20] Z. Vardeny, J. Tauc, *Phys. Rev. Lett.* **54**, 1844 (1985).
- [21] M. Hammam, G. J. Adriaenssens, J. Dauwen, G. Seynhaeve, W. Grevendonk, *J. Non-Cryst. Solids* **119**, 89 (1990).
- [22] S. P. Depinna, B. C. Cavenett, W. E. Lamb, *Phil. Mag. B* **47**, 99 (1983).
- [23] G. J. Adriaenssens, *Mat. Res. Soc. Symp. Proc.* **91**, 111 (1986).
- [24] D. Vanderbilt, J. D. Joannopoulos, *Phys. Rev. B* **27**, 6311 (1983).
- [25] A. V. Kolobov, M. Kondo, H. Oyanagi, R. Durny, A. Matsuda, K. Tanaka, *Phys. Rev. B* **56**, R485 (1997).
- [26] H. Z. Song, G. J. Adriaenssens, E. V. Emelianova, V. I. Arkhipov, *Phys. Rev. B* **59**, 10607 (1999).
- [27] D. Monroe, M. A. Kastner, *Phys. Rev. B* **33**, 8881 (1986).
- [28] T. Thio, D. Monroe, M. A. Kastner, *Phys. Rev. Lett.* **52**, 667 (1984).
- [29] D. P. Webb, C. Main, S. Reynolds, R. Brüggemann, in *Proceedings of the 12th EC PVSEC (Amsterdam, 1994)* p. 124.
- [30] D. K. Biegelsen, R. A. Street, *Phys. Rev. Lett.* **44**, 803 (1980).
- [31] R. P. Barclay, M. Sarr, J. L. Brebner, *J. Non-Cryst. Solids* **97**, 687 (1987).
- [32] H. Fritzsche, P. J. Gaczi, M. Kastner, *Phil. Mag. B* **37**, 593 (1978).
- [33] E. V. Emelianova, N. Qamhieh, M. Brinza, G. J. Adriaenssens, S. O. Kasap, R. E. Johanson and V. I. Arkhipov, in *Proceedings of the XIIIth International Symposium on Non-Oxide Glasses, Pardubice, September 2002*, to be published.