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DEFECTS IN SEMICONDUCTING CHALCOGENIDE GLASSES

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The model of charged intrinsic defect states with a negative effective correlation energy has served as a useful conceptual basis for understanding numerous observations in chalcogenide glasses. Recent doping experiments raised doubts concerning the validity of the original defect model. We show that the doubts are unfounded. Light-induced diffusion of Ag and reversible property changes induced by light are shown to be associated with creation of defects. The microscopic structure of some defects is identified.

I. Introduction

The origin and nature of the dominant native defects in chalcogenide glasses have been the subject of intense scrutiny for several years. The vitality of this research no doubt owes much to the paradoxical quality of the properties of chalcogenide glasses; the best known example of such a paradox is that these glasses are diamagnetic [1] despite defect densities which can exceed $10^{17}cm^{-3}$. Several phenomenological models [2,4] have been proposed which account well for the properties of intrinsic glasses; these models also predict [5,6] how some of the properties would change if charged dopants were added. An important feature of these models is the key role played by the nonbonding (lone pair) valence electrons in p-orbitals of the Group VI elements [7] which makes the defect chemistry in these materials very different from that of tetrahedrally coordinated semiconductors.

In this paper we shall briefly review these models, and then compare their predictions with recent measurements on the effects of doping on electrical transport [8,9], photoluminescence, and on the photo-induced spin densities [10]. These doping experiments have (in my view unnecessarily) led some workers to question the simplest models for intrinsic defects. We shall also briefly outline the application of the models to photodarkening [11] and photodoping [12] experiments. Finally we shall present recent ESR results [13] which provide microscopic evidence for the identification of specific photo-induced paramagnetic centers in chalcogenide glasses.

II. Intrinsic Defects

In order to explain the diamagnetism of semiconducting glasses, Anderson [14] suggested that strong electron-phonon coupling acts as a net attraction between electrons in localized states thus favoring a paired electron ground state. Street and Mott [2] and Mott et al. [3] specialized this concept to chalcogenide glasses and suggested point defects, such as dangling bonds, which can be in either of three charge states D^-, D° and D^+. The negative effective correlation energy of Anderson is realized when the reaction

$$2D^\circ \rightarrow D^+ + D^- \tag{1}$$

is exothermic. This is plausible because of the strong local relaxation involving lone pair electrons of neighboring chalcogens. Kastner et al. [4,15] proposed the valence alternation model in which the positive defects D^+ are over-coordinated chalcogen or pnictide atoms (C_3^+ or P_4^+) and that negative defects D^- are undercoordinated (C_1^- or P_2^-). The subscript indicates the coordination number of chalcogen (C) and pnictide (P) atoms, whose normal coordination is 2 and 3, respectively.

A negative effective correlation energy is associated only with those charged defect centers which can interconvert by charge transfer into their oppositely charged counterpart:

$$e + D^+ \rightleftarrows D^\circ \rightleftarrows D^- + h \tag{2}$$

Bonding constraints may hinder this interconversion for some charged defects in IV-VI glasses [16]. We shall not discuss these here. The creation energy of a valence alternation pair, $E_{vap} \sim 0.5\text{-}0.7$ eV, should be approximately equal to the positive correlation energy of placing the second electron on the under-coordinated defect center [4]. The concentrations of the defects are determined by their equilibrium density near the glass transition temperature T_g because atomic diffusion essentially ceases for $T < T_g$. The law of mass action then yields [4,15]:

$$[D^-]\,[D^+] = N_A^{\,2} \exp\left(-E_{vap}/kT_g\right) = N_o^{\,2}/4 \tag{3}$$

N_A is the concentration of atoms capable of undergoing valence alternations. An appreciable density, $N_o \sim 10^{17}\,\mathrm{cm}^{-3}$, of intrinsic defects are therefore expected to exist even in well annealed glasses.

Since D^+ and D^- possess no unpaired spins, the model accounts for the absence of equilibrium spins. It also explains [3] the intricate photoluminescence (PL) properties [17] and the photo-induced ESR in chalcogenide glasses [18]. The D^- state is close to the valence band edge because it is a Coulomb trap for holes. Therefore light of energy near the absorption tail causes transitions of electrons from D^- states to the conduction band. A D°-e pair is formed with the electron trapped in a nearby conduction band tail state. At low temperatures, the probability that the electron drifts away is small and the optical transition from the relaxed D°-e state to the D^- state yields PL. The PL is Stokes shifted to about half the band gap energy because two relaxations occur, one of the D°-e state after excitation and the other of the D^- state after PL.

Some electrons manage to drift away from their D° and are captured by a nearby D^+, which turns into D° according to eq. (2). During extended light exposure the concentration of D° increases at low temperatures by these processes because reaction (1), which leads back to equilibrium, needs some thermal activation. As the D° centers are paramagnetic and do not contribute to luminescence, the PL intensity decreases during illumination (PL fatigue [19]) and the density of spin centers increases. When PL fatigue is complete the density of metastable spin centers N_s gives a measure of the defect concentration N_o. One finds $N_s \sim 10^{17}\,\mathrm{cm}^{-3}$ in vitreous As_2S_3 and As_2Se_3. The valence alternation model predicts that there can be two different kinds of D° centers in alloy glasses, originating from D^- and from D^+, respectively [15].

This admittedly simple description of the principle processes, which does not deal with several subtleties of the PL observations or alternative explanations [29], is sufficient for understanding what changes one should expect from doping.

III. Effects of Doping

Most elements added to the melt of chalcogenide glasses will seek their most stable bonding configuration. Ga in As_2Se_3, for instance, is likely to be four-fold coordinated, forming one coordinate bond with a neighboring Se or a GaAs bond as shown in Fig. 1(a). The center is neutral and thus relatively inactive electrically. The density of intrinsic defect centers $[D^+] = [D^-] = N_0/2$ remains unchanged. Entropy and the relatively low energy of creating charged defect pairs may favor the dissociation of a fraction x[A] of the foreign additives [20]. If this fraction is positively charged, as in the bonding configuration shown in Fig. 1(b), charge neutrality requires that

$$[D^-] = [D^+] + [A^+] \qquad (4)$$

because the concentrations of free electrons and holes can be neglected even at T_g where the equilibrium is established. Since the product $[D^-]\,[D^+]$ remains fixed according to eq. (3), the total density of defect centers $N = [D^-] + [D^+]$ must increase to [5,6]

$$N = (N_0{}^2 + [A^+]^2)^{1/2} \qquad (5)$$

Even though the A^+ centers form shallow donor states [6], the self-compensating increase in $[D^-]$ dictated by eqs. (3) and (4), is sufficient to accommodate all electrons donated by the charged dopants. Negatively charged dopants as the one illustrated in Fig. 1(c) act in a complementary manner with $[A^-]$ in eq. (5) and acceptor states A^- above the valence band.

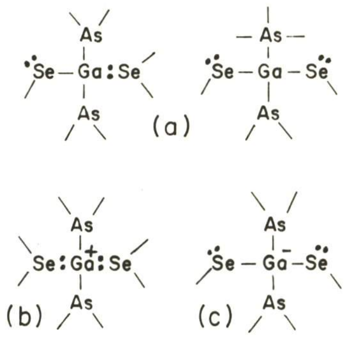

Fig. 1 Bonding configurations of trivalent atoms in As_2Se_3 (a) neutral configuration (b,c) charged configuration

The negative effective correlation energy of the defect centers and their interconversion property described by eq. (2) are normally interpreted as predicting a pinned Fermi level E_F even in the presence of charged dopants [21,6]. However, Okamoto et al. [22] and Uda et al. [8] pointed out that E_F moves gradually toward the valence band by an amount $\leq \Delta$ as the density of charged additives is increased above N_0 if the defect states have an energy distribution of width Δ. A calculation of the T-dependence of the hole concentration, p, for various $[A^-]/N_0$ is shown in Fig. (2). This calculation enjoyed some success in explaining transport measurements and has led to a reassessment of the simple defect model of section II.

We now turn to the experimental evidence of the doping effects. The gradual change in conductivity activation energy E_a of As_2Se_3 with increased Group III element doping observed by Ležal et al. [23] and shown in Fig. (3) is quoted [8] as support for the model of Fig. (2). The experimental points of the different Group III elements fall onto the same curve when the doping concentration is scaled relative to Ga as noted in Fig. (3). Tl, on the other hand, increases E_a [23], and it is therefore proposed that Tl introduces A^+ centers. Further evidence for doping comes from transit time measurements of holes in As_2Se_3 by Pfister et al. [9]. They find that additions of In and Ga between 10^{18} and $10^{20} cm^{-3}$ decrease the hole transit time by up to a factor 100, whereas Tl doping between 2×10^{16} and $10^{19} cm^{-3}$ increases the transit time by a similar

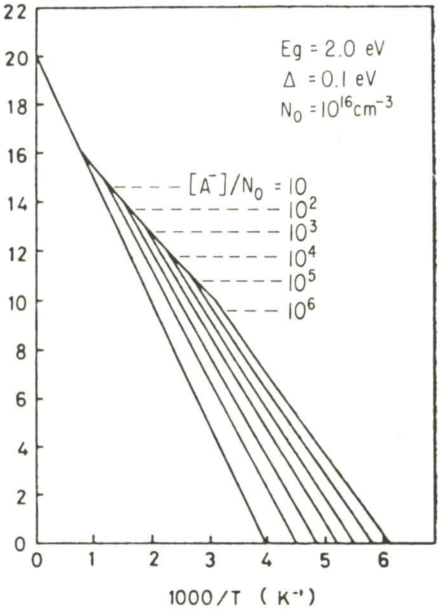

Fig. 2 Effect of negative dopants on hole concentration [8]

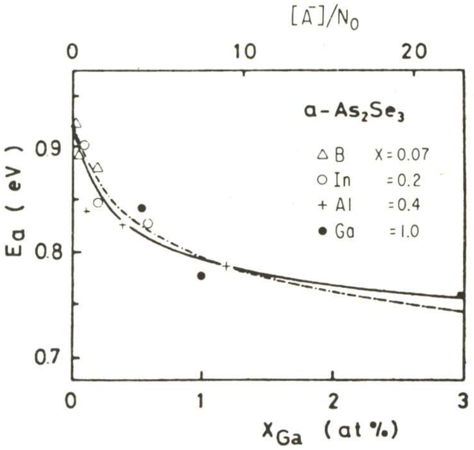

Fig. 3 Change of conductivity activation energy of As_2Se_3 with trivalent additives [8]

amount. This might be taken to imply that the effective D^- hole traps are decreased by Ga and In and increased by Tl additives. One is tempted to conclude that In and Ga introduce A^- centers and Tl introduces A^+ centers as in the interpretation of the experiments of Ležal et al. [23].

The large changes in D^- and D^+ defect densities with doping needed to account for these transport results should have a profound effect on the PL intensity and the concentration of light-induced ESR centers. However, a detailed study [10] by Bishop et al. and Pfister et al. [24] revealed the surprising result that none of these impurities change the PL intensity or the density of ESR centers in any significant way. The near absence of an effect of Tl doping is shown in Fig. (4). To account for these PL and ESR results as well as for the doping dependent transport measurements within the doping model it has been proposed that the D^+, D^- centers fall into two categories: D^+ - D^- pairs with a limited spectrum of separations, which are associated by their Coulomb interactions, and isolated D^- and D^+ defects. The isolated defects change their concentrations according to the doping theory. They do not yield PL and metastable ESR, according to this proposal, but affect the transport properties as explained above. If PL and photo-induced ESR are solely related to associated pairs, the problem appears to be solved, because their concentration is known to be independent of the density of charged additives [15]. In fact, arguments favoring associated pairs for PL had been presented even before the results of the doping experiments were known [25].

This more intricate defect model rests entirely on the doping dependence of transport properties mentioned earlier. I question the validity of interpreting the transport measurements in terms of the doping theory. First, there is no direct evidence that any of the additives are incorporated as charged species in the experiments quoted. The decrease in E_a shown in Fig. (3) is in fact approximately equal to the decrease in the optical gap (see Fig. (5)) due to the impurities [23], with Ga causing a larger decrease than B. Furthermore, according

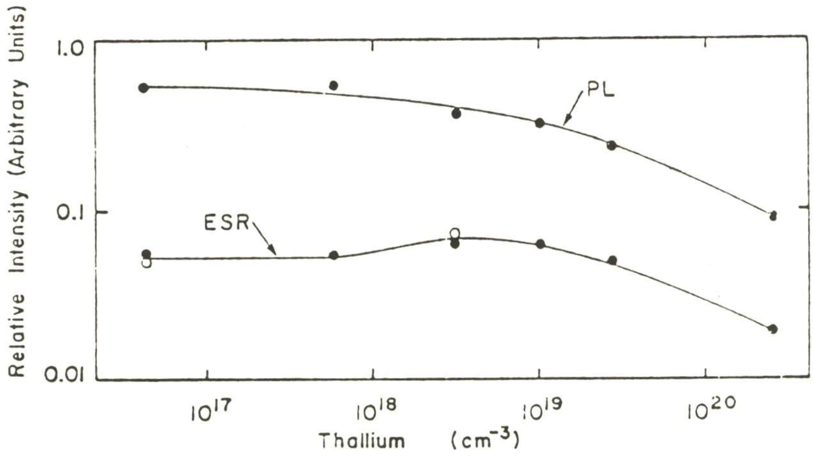

Fig. 4 ESR and PL intensities in As_2Se_3 as a function of Tl content[24]

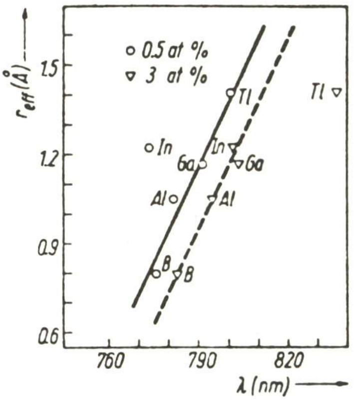

Fig. 5 Shift of optical gap of As_2Se_3 with trivalent additives [23]

to Lezal et al. [23], Tl initially increases E_a. This result does not agree with the doping theory because E_F is expected to drop slightly for both A^+ and A^- additives when the width Δ of the defect states is finite. Finally, Tl is a very good glass former and high concentrations can easily be incorporated. Since Tl begins to affect the hole transit time near 2 X 10^{16} Tl/cm^3, they must do so in their lowest energy bonding configuration, which is neutral when the nearest neighbors are included. Associated Tl^+ D^- pairs are possible. The transit time is very sensitive to changes in the band tail states and additional traps produced by overall neutral alloying additives [9]. The present transport measurements therefore give no cause to modify the original models for intrinsic defects which explain PL and photo-excited ESR.

IV. Photodarkening and Photodoping

Photodarkening [11] involves the reversible red-shift and broadening of the optical absorption-edge upon exposure to band gap and higher energy photons, besides reversible changes in other properties. Biegelsen and Street recently demonstrated [26] that the creation and infrared bleaching of photodarkening centers is associated with the creation and bleaching of new defect centers which exhibit photo-induced ESR at low T. These observations confirm earlier speculations that photodarkening is due to defect pairs created by light, a certain fraction of which are likely to be less stable defect pairs which annihilate in infrared bleaching light. It is not certain yet whether the photo-created defect pairs have the same microscopic structure as the equilibrium D^-, D^+ defects. If they do, then the observed reduction of PL by light-created defect pairs rules out associated pairs as the main source for PL, as originally suggested by Hudgens and Kastner [25].

The photo-induced paramagnetic centers in $As_{43}S_{57}$ (slightly As-rich relative to stoichiometry) were recently identified by Gaczi [13] as two-fold coordinated As free radicals, P_2^0 in our defect notation. Figure (6) shows a comparison of the ESR data taken at 12K with a calculated one which is an orientational average of an individual center whose structure arises from the anisotropic principal axis components of the g-tensor and of the hyperfine tensor. The two-fold bonded neutral pnictide centers P_2^0 ($N_s \sim 5 \times 10^{17} cm^{-3}$) may either be photodarkening centers created by the high energy 5145 Å light used in Gaczi's experiment or previously existing D^- and D^+ centers rendered neutral by photo-excitation. Figure (7) shows a possible photo-creation mechanism. The diamagnetic D^- and D^+ centers are probably P_2^- and $(P_3 + C_3)^+$ or $(P_4^+ + P_3^0)$, respectively. It is interesting that no sulfur ESR signal was detectable in As-rich alloy glasses. The photo-induced (or created) ESR line in sulfur rich $As_{35}S_{65}$ could tentatively be identified [27] as the $\bullet S\text{-}S\text{-}As\leftrightarrows$ radical. This is a neutral dangling chalcogen bond stabilized by π-bonding to the second chalcogen atom [28] and not the neutral three-fold chalcogen atom suggested earlier [4]. More work is required to identify the radicals in nearly stoichiometric glasses in which signals from As and S atoms are superimposed.

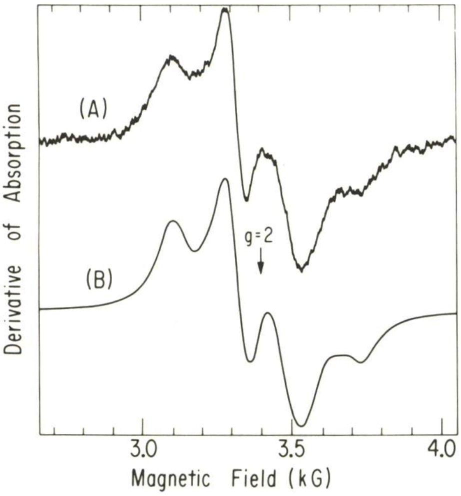

Fig. 6 a) Photo-induced ESR in $As_{43}S_{57}$ at 12K b) Calculated spectrum for two-fold bonded As radical [13]

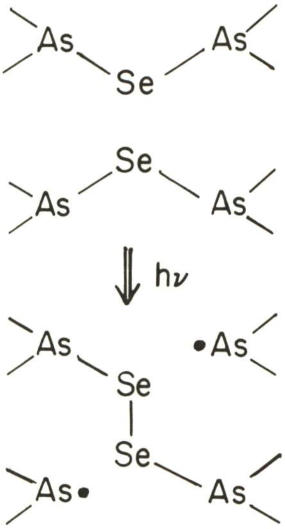

Fig. 7 A mechanism for photo-creation of two doubly bonded As radicals

The new results of Biegelsen et al. [26] may also explain photodoping [12] which is the light-induced diffusion of Ag in chalcogenide glasses. In the dark and at room temperature, the ionization of Ag is limited by the equilibrium concentration of intrinsic defect centers and diffusion of Ag^+ is hindered by the Coulomb potentials of D^-. The abundance of electron-hole pairs and of defect centers created by strong illumination simulates a high effective temperature. Except for a cooler phonon population the situation under strong illumination is similar to that at higher temperatures where Ag diffuses and is dissolved easily in chalcogenide glasses. This high effective temperature of charge carriers and defects enables the reactions of the defect and doping chemistry to act and to promote Ag diffusion even at low phonon temperatures.

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1) S. C. Agarwal: Phys. Rev. B7 (1973) 685.
2) R. A. Street and N. F. Mott: Phys. Rev. Lett. 35 (1975) 1293.
3) N. F. Mott, E. A. Davis, R. A. Street: Phil. Mag. 32 (1975) 861.
4) M. Kastner, D. Adler, and H. Fritzsche: Phys. Rev. Lett. 37 (1976) 1504.
5) N. F. Mott: Phil. Mag. 34 (1976) 1101.
6) H. Fritzsche and M. Kastner: Phil. Mag. B37 (1978) 285; H. Fritzsche, P. Gaczi, and M. Kastner: Phil. Mag. B37 (1978) 593.
7) M. Kastner: Phys. Rev. Lett. 28 (1972) 355.
8) T. Uda and E. Yamada: J. Phys. Soc. Japan 46 (1979) 515.
9) G. Pfister and M. Morgan: Phil. Mag. B41 (1980) 209.
10) S. G. Bishop, U. Strom, E. J. Friebele, P. C. Taylor: J. Non-Cryst. Solids 32 (1979) 359; G. Pfister and P. C. Taylor: ibid 35/36 (1980) 793.
11) Y. Ohmachi and T. Igo: Appl. Phys. Lett. 20 (1972) 506; J. P. de Neufville: Optical Properties of Solids – New Developments, edited by B. O. Seraphin, North Holland, Amsterdam (1976) p. 437.
12) I. Shimizu, H. Sakuma, H. Kokado, E. Inoue: Photogr. Sci. Eng. 16 (1972) 291; K. Chatani, I. Shimizu, H. Kokado, and E. Inoue: Japan J. Appl. Phys. 16 (1977) 389.
13) P. J. Gaczi and H. Fritzsche: to be published.
14) P. W. Anderson: Phys. Rev. Lett. 34 (1975) 34.
15) M. Kastner and H. Fritzsche: Phil. Mag. B37 (1978) 199.
16) R. A. Street and G. Lucovsky: Solid State Commun. 31 (1979) 289.
17) R. A. Street: Adv. in Physics 25 (1976) 397.
18) S. G. Bishop, U. Strom, and P. C. Taylor: Phys. Rev. Lett. 34 (1975) 1346; 36 (1976) 543.
19) J. Cernogora, F. Mollot, C. a la Guillaume: Phys. Stat. Solidi (a) 15 (1973) 401.
20) M. Kastner: Phil. Mag. B37 (1978) 127.
21) D. Adler and E. J. Yoffa: Can. J. Chem. 55 (1977) 1920.
22) H. Okamoto and Y. Hamakawa: Solid State Commun. 24 (1977) 23.
23) D. Ležal, V. Trkal, I. Srb, S. Dokonpil, V. Šmid, and V. Rosicka: Phys. Stat. Solidi (a) 12 (1972) K39.
24) G. Pfister, K. S. Liang, M. Morgan, P. C. Taylor, E. J. Friebele, S. G. Bishop: Phys. Rev. Lett. 41 (1978) 1318.
25) S. J. Hudgens and M. Kastner: Amorphous and Liquid Semiconductors, edited by W. E. Spear, Centre for Industrial Consultancy and Liaison, Edinburgh (1977) 622.
26) D. K. Biegelsen and R. A. Street: Phys. Rev. Lett. 44 (1980) 803.
27) P. J. Gaczi: to be published.
28) D. Vanderbilt and J. D. Joannopoulos: Phys. Rev. Lett. 42 (1979) 1012; ibid Solid State Commun. to be published.
29) M. Kastner and S. J. Hudgens: Phil. Mag. 37 (1978) 665.