Hole Transport, Photoluminescence, and Photoinduced Spin Resonance in Thallium-Doped Amorphous As_2Se_3

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Thallium in a-As_2Se_3 reduces transient hole transport but has no effect upon the photoluminescence and photoinduced ESR. The results are discussed in terms of the recent models of charged defects in chalcogenides.

The concept of paired electronic states which lie within the forbidden energy gap[1] has provided an extremely useful framework for describing many experimental observations in amorphous solids. In particular, recent models[2,3] for amorphous chalcogenide semiconductors ascribe to specific "defect" such universally observed features as the pinning of the Fermi energy, the absence of paramagnetism,[4] and the existence of traps as inferred from various transport,[5] photodarkening,[6] photoluminescence (PL), and photoinduced electron spin resonance (ESR)[7] experiments. These defects, which are considered to be highly localized and intrinsic are diamagnetic in their ground-state configuration, but some of them are postulated to be metastable at low temperature in an excited paramagnetic state. In the simplest model description, these defects occur on chalcogen atoms and are charged when isolated. They consist of deviations from the normal twofold coordination such that one obtains equal numbers of singly coordinated, negatively charged chalcogen "dangling bonds" and triply coordinated, positively charged chalcogens. In the literature[2,3] the positively and negatively charged states of the defects have been variously named C_3^+ or D^+ and C_1^- or D^-, respectively. The metastable paramagnetic state has been referred to as D^0, D, or C_3^0, and there is some discussion[2,8] as to whether the coordination of the chalcogen atom in this state is onefold or threefold. Initially only isolated defects were invoked to explain the PL, ESR, and transport data, but recently it has been suggested[9] that the PL is associated with (neutral) close pairs.

The defect chemistry proposed for chalcogenide glasses had led to the prediction that electropositive or electronegative impurities should alter the density of specific defects in a controlled fashion.[10,11] We have performed transport, PL, and photoinduced ESR measurements as a function of impurity content in order to probe the defect models further and to correlate specific defects with photoelectronic properties. The first results of such studies are described in this Letter. We show that, in the model binary chalcogenide a-As_2Se_3 doped with thallium, the defect centers associated with PL and photoinduced ESR are *different* from the trapping centers which limit transient hole transport.

The doped As_2Se_3 films were prepared by first mixing the appropriate amounts of Tl and As_2Se_3 glass and sealing the mixtures in evacuated quartz ampoules. The ampoules where then heated for 24 h at 750°C in a rocking furnace. The melt was quenched in water and the bulk glass was milled to a grain size appropriate for evaporation. Films of 10–20 μm thickness were deposited by flash evaporation at a rate of ~ 0.1 μm onto aluminum substrates held approximately at the glass transition temperature (~ 180°C). Aluminum was used as the top electrode for the time-of-flight measurements. The compositions of the alloyed materials and films were analyzed by atomic absorption spectroscopy.

Figure 1 shows the dependence of the hole transit time t_T in amorphous As_2Se_3 upon Tl concentration, N_{Tl}, at room temperature and fixed $E/L = 0.5$ V/μm^2, where L is the sample thickness and E the (uniform) applied electric field. Similar data symbols identify samples obtained from the same preparation run. With increasing Tl concentration, in the range 10^{17}–10^{19} Tl/cm^3, the hole transit time t_T increases approximately as $N_{Tl}^{0.8}$ such that at 10^{19} Tl/cm^3 transport is about two orders of magnitude slower than in undoped amorphous As_2Se_3. In this concentration range, both the activation energy Δ and the field dependence of t_T are independent of N_{Tl}, i.e., $\Delta \approx 0.60 \pm 0.05$ eV and $n \simeq 1.85 \pm 0.10$ where $t_T \propto E^{-n}$ for $E < 10$ V/μm.[5] The hole current pulse remains dispersive as is typical of undoped As_2Se_3

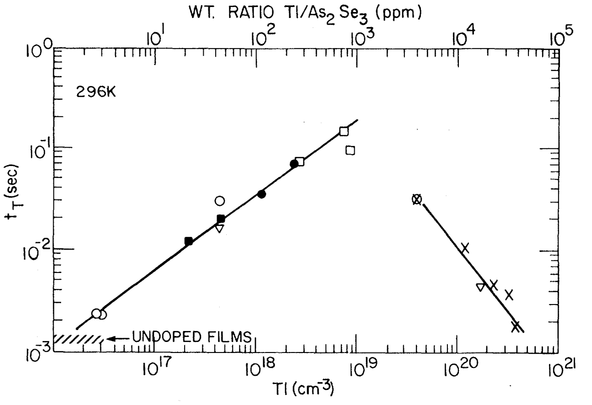

FIG. 1. Hole transit time as a function of Tl concentration in a-As$_2$Se$_3$. $T = 296$ K, $E/L = 0.5$ V/μm^2, where L is the sample thickness and E the applied electric field. Different symbols pertain to different preparation runs.

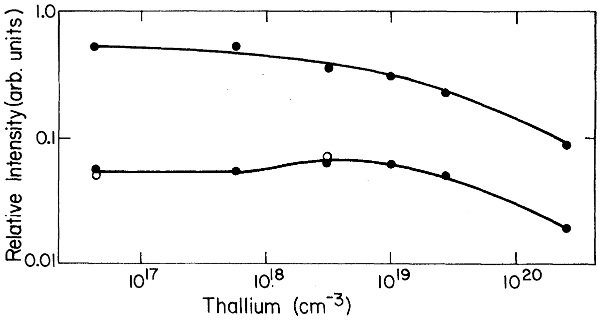

FIG. 2. Relative PL (top curve) and ESR (bottom curve) intensities as functions of thallium concentration. Solid circles were taken on bulk starting material and open circles were taken on films. ESR data were taken at 4.2 K and PL data at 77 K.

using aluminum electrodes.[5] As N_{Tl} increases beyond ~5×10^{19} Tl/cm^3, t_T becomes shorter again and Δ and n assume values distinctly lower than in the undoped material. We find $\Delta \approx 0.52 \pm 0.05$ eV and $n \simeq 1.45 \pm 0.10$. The hole current pulses appear less dispersive and exhibit a "plateau" preceding t_T. For the intermediate concentrations, $(1\text{-}5)\times10^{19}$ Tl/cm^3, the current pulses are so featureless that no t_T can be extracted from the signal even if techniques developed for the analysis of dispersive transport are used.[5]

PL and photoinduced ESR measurements were performed on the same films used for the transport studies and on the bulk starting material used to make the flash-evaporated films. No differences in the PL or ESR results were detected between bulk and thin-film samples. Figure 2 shows the PL and photoinduced ESR intensities as functions of Tl content. It is clear from this figure that there is esentially no dependence of either measurement on N_{Tl}. In addition to the intensities, other pertinent characteristics of the ESR and PL, the ESR line shape and inducing rate and the PL spectral width, fatiguing rate, and excitation spectrum were essentially independent of Tl content. These results are in marked contrast to those of the transport measurements and establish unambiguously that *in these doped samples there is no direct connection between the defects which generate the PL and ESR signals and the traps that limit transient hole transport.*

Although we have concentrated here on the results of thallium doping, similar measurements on a-As$_2$Se$_3$ doped with iodine lead to identical results. In this case, iodine greatly improves hole transport such that at ~0.53 at.% I the reduction of the transit time is about a factor of 20.[12] Hence, by doping with Tl or I the hole drift mobility in a-As$_2$Se$_3$ can be varied by more than three orders of magnitude while for the same samples the PL and the photoinduced ESR remain essentially unchanged. Preliminary measurements on Mn-, Ni-, and Cu-doped a-As$_2$Se$_3$ show similar results but the conclusions to be drawn from these measurements are not straightforward since the transport activation energy depends on the dopant and its concentration.

The foregoing results may be used to differentiate between the defect models proposed for chalcogenide glasses by Mott, Davis, and Street (MDS)[2] and Kastner, Adler, and Fritzsche (KAF).[3] Both models associate the isolated negatively charged defect (C_1^-, or D^-) with the trap that limits hole transport. Also, both models predict that impurities entering the glass in a charged state are being compensated by the defect center of opposite charge. Within this framework one may argue that Tl, an electropositive element, is incorporated as a positively charged impurity and hence the C_1^- (or D^-) density increases in a manner approximately proportional to N_{Tl}. Alternatively iodine is expected to assume a negative charge which is compensated by C_3^+ (or D^+) and therefore, by the law of mass action, the C_1^- (or D^-) density decreases.[10,11] It is apparent that the time-of-flight data for a-As$_2$Se$_3$ containing low impurity concentrations can be explained in these terms, the main evidence being that the activation energy and the field dependence of the transit time remain unchanged. If one accepts this interpretation, one has to conclude that the PL and the photoinduced ESR are not associated with isolated defect centers. This conclusion is generally consistent with the recent suggestions of Kastner and Hudgens[9] but does not appear to support the original interpretation of MDS.[2] The former authors[9] attribute PL to paired defect centers ($C_1^- - C_3^+$), the density of which is asserted to be insensitive to doping,[8] while the latter authors[2] suggest that close pairs are unstable and recombine and therefore they associate all photoelectonic properties with isolated charged defect centers, in particular the D^-.

There is little detailed information on Tl bonding in amorphous chalcogenides, but several experimental facts point to the following speculation. From an x-ray structure determination in crystalline TlSe the thallium is thought to exist in two valence states: tetrahedrally coordinated Tl^{3+} and Tl^{1+} in eightfold coordination.[13] The Tl-Se bonds have more covalent character at Tl^{3+} sites than at the largely ionic Tl^{1+} sites. From nuclear magnetic resonance (NMR) measurements of ^{205}Tl chemical shifts in Tl-As-Se it has been suggested[14] that Tl goes in as Tl^{1+} for $\lesssim 30\%$ Tl. This evidence suggests that the thallium sites in Tl-doped As_2Se_3 probably consist of ionic Tl^{1+} with a high degree of coordination to nearest-neighbor (presumably Se) atoms.

Although the present results may be interpreted as being more consistent with the KAF model, several problems remain. (i) The intrinsic densities of traps as inferred from transport and ESR measurements in As_2Se_3 are not accurately known but fall in the range $10^{16}-10^{17}$ cm^{-3} and $10^{17}-10^{18}$ cm^{-3}, respectively. Because the equilibrium concentrations of isolated charged defects and close pairs of defects are governed by different activation energies,[8] it is unlikely that they would occur in the same concentration. (ii) It is expected that the highly localized *isolated* defect centers would contribute to the photoinduced ESR and therefore the ESR intensity should increase with thallium concentration. (iii) Assuming that the proposed law of mass action holds, the positively charged isolated thallium defects should reduce the density of the electron traps, viz. D^+ (or C_3^+).[10,11] Strong support for this mechanism would be the observation of an increased electron range in the doped samples but no electron displacement was noted in our experiments.

Future experiments may resolve these problems but we suggest that an alternative explanation is also plausible given our present level of understanding. One may speculate, for example, that the ESR, PL, and optical absorption processes are due to isolated D^- (or C_1^-) traps and that Tl introduces a trap different from D^- (or C_1^-) which has a similar cross section and release energy for hole capture. Furthermore, the trap would have to be neutral since otherwise (by arguments based on the law of mass action) the density of isolated charged defects would change. While for band transport these conditions can hardly be satisfied simultaneously, for hopping transport a trap with these properties is indeed conceivable as we shall illustrate in the following paragraph.

Hole transport in a-As_2Se_3 has been proposed[5] to be a trap-limited hopping motion with an average hopping distance $r_h \sim 40-50$ Å and a trap density $N_t \sim 10^{17}$ cm^{-3}. The trapping level in the undoped material was tentatively associated with the D^- center. We define r_c as the radius beyond which the attractive force due to a Coulomb center is negligible. Now, for $r_c/r_h > 1.5$ the probability p that the hopping site next to a trap lies within r_c exceeds 0.9, hence most carriers are trapped under the influence of the Coulomb attraction. However, for $r_c/r_h < 0.5$, $p < 0.1$ in which case most trapped carriers did not experience the Coulomb force on the nearest-neighbor site. The case for a-As_2Se_3 lies in between these two extremes: $r_c/r_h \sim 1.0$ for which $p \sim 0.5$. Clearly, an extensive mathematical formulation of the trap-controlled hopping process would be desirable. A specific possibility for such a trap may be a dipole consisting of a Tl^+ close to a C_1^-. A trapped hole converts the C_1^- into a neutral paramagnetic atom which upon relaxation remains either singly coordinated (D) or, perhaps more likely, undergoes bond switching resulting in a threefold-coordinated neutral center, C_3^0, which is removed from the thallium site by at least one twofold-coordinated chalcogen atom. It is possible that the release energy from this trap is similar to that from an isolated neutral chalcogen because the lone pairs effectively shield the positive charge on the thallium ion, and the C_3^0 has been removed from the positive Coulomb center via a bond-switching process.

The fact that no photoinduced ESR associated with the dipole trap is observed may be due to the influence of the nearby thallium, but clearly this point merits further clarification.

The transport measurements for Tl concentrations exceeding $\sim 5 \times 10^{19}$ cm^{-3} suggest the onset of a new transport channel. It is proposed that, in addition to being incorporated as a positive defect with a singly coordinated chalcogen as a compensating center, some fraction of the thallium atoms introduces a shallow trapping level approximately 0.1 eV above the hole hopping states, N_h. While at lower concentrations the shallow traps do not contribute to the measured transit time, direct charge displacement through these traps will begin to dominate the intrinsic transport channel if their concentrations exceed the hopping density $N_h \approx 10^{19}$ cm^{-3}. This density is in numerical agreement with the observed transition at $\sim(1-5)\times 10^{19}$ Tl/cm^3 (Fig. 1). The changes of the transport properties (field dependence and activation energy of t_T and transient current shape) further support the argument that a new mechanism begins to dominate transport for $N_{\mathrm{Tl}} \gtrsim 5\times 10^{19}$ Tl/cm^3.

In summary, we have shown that thallium added to a-As$_2$Se$_3$ in concentrations 10^{17}–10^{19} cm^{-3} significantly reduces transient hole transport but that it has no effect on photoluminescence and photoinduced ESR. Although our results can be explained in terms of the specific defect chemistry originally proposed by MDS and modified by KAF which invokes the existence of close defect pairs, several difficulties remain with that interpretation. We have proposed an alternative explanation which is generally consistent with the proposed defect models but which, in our opinion, may provide a more satisfactory explanation.

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Excitations in a Random Ferromagnetic-Antiferromagnetic Alloy

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A study is presented of elementary excitations of an unfrustrated system which can exhibit frozen magnetism without average long-range order. In three dimensions long-wavelength excitations are quasipropagating with linear dispersion and quadratic damping in accord with hydrodynamic speculations and computer studies, but high-energy modes may be localized. In lower dimensions the modes are overdamped even in a linearized equation-of-motion approximation.

There is growing interest in the low-temperature elementary excitations of alloys with strong quenched ferromagnetic-antiferromagnetic exchange disorder; such systems can exhibit frozen (or quasifrozen) magnetism without average long-range order. Spin-glass systems[1] with frustrated[2] exchange are complicated by the difficulty of microscopically specifying the classical ground or low-lying metastable states, necessitating poorly controlled[3] approximations in analytic studies of their excitations. There exist, however, unfrustrated models which can exhibit frozen magnetism without long-range order but have microscopically specifiable classical ground states. In this Letter I consider the excitations of the simplest such model with nontrivial dynamics, the Heisenberg-Mattis[4] model. Its classical thermodynamics is trivial, but its excitation