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Relevance of persistent photoconductivity in semi-insulating and *n*-type semiconducting GaAs to the charge state of metastable *EL*2 defects

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We make use of persistent photoconductivity studies in GaAs to address the question of the charge state of *EL*2 defects which is a point of contention in current theories of their metastability. We first review conflicting interpretations of persistent hole photoconductivity in semi-insulating GaAs and then present new photoconductivity studies for *n*-type semiconducting GaAs to resolve residual points of conflict. We conclude that there is no evidence for a redistribution of charge in *EL*2 complexes during the metastable transition. Finally, further arguments based on experiment are presented against current models of a positively charged *EL*2 complex.

The photoinduced metastability of *EL*2 defects in semi-insulating (si) GaAs has aroused great interest and stimulated intense experimental and theoretical efforts over many years.[1] Although there has been much progress, the atomic configuration of the *EL*2 defects in the stable and metastable states remains controversial and elusive. It is now generally agreed that the *EL*2 defect contains the As antisite ($\mathrm{As_{Ga}}$), but there is still no consensus as to whether it is present in isolation or as part of a complex whose structure is itself a matter of contention.[2] The feature that is characteristic of the transition of *EL*2 to a metastable state is the photoquenching of its normal properties. The consequent experimental inaccessibility of the metastable state contributes to the difficulty of establishing the structure of the defect. However, it has not been sufficiently appreciated that some limited accessibility to the properties of metastable *EL*2 is provided by the onset of persistent phenomena[3-7] concomitant with the photoquenching effects. In this report, we shall discuss what information can be derived from persistent phenomena about the charge state of the metastable *EL*2 defects. Such information is particularly important for discriminating between current conflicting models of the *EL*2 defects.

We shall first review the persistent photoconductivity[3] and related phenomena[4-7] that have been reported for si GaAs, and attempt to clarify some conflicting interpretations. We shall then present photoconductive measurements for *n*-type semiconducting GaAs and show how they can resolve certain residual ambiguities and provide direct evidence that there is no observable change in net charge or in dipole strength of *EL*2 during its metastable transition. Finally, we shall summarize arguments in favor of a neutral charge state for the metastable *EL*2 defects, a conclusion that is in contradiction with some recent models.[8-11]

The stable *EL*2 defects are characterized by a subband-gap absorption band and an associated photoconductive spectrum[12] lying between 0.7 and 1.4 eV. The band is due to optically induced transitions between the defects and the valence and conduction bands. When the defects are driven into metastable states by intense or prolonged radiation in the range 1.0–1.3 eV,[13] both the photoconductive spectrum and the absorption band[12,14] are quenched. In their stead, a persistent *p*-type photoconductivity is generated[3] in si GaAs, along with a persistent nonequilibrium population of holes observed in electronic Raman[4-6] scattering and also in far-infrared[7] spectroscopic studies. The Raman studies[5] show that the holes are either bound on the residual shallow acceptors (e.g., carbon or zinc) or free, depending on the sample temperature. These results demonstrate that the presence of the nonequilibrium holes is clearly related to the presence of the normally compensated shallow acceptors, and not, as has been suggested,[3,15] to acceptor states on metastable *EL*2.

The generation of the holes and the relation of their persistence to the metastable transition of the *EL*2 defects has been previously explained.[5] In brief, the shallow acceptors in si GaAs are compensated by the midgap double donor As antisites when the latter are in their normal or stable state. This compensation is responsible for the formation of the (singly) positively charged fraction of the $\mathrm{As_{Ga}}$ which is identified by the electron paramagnetic resonance (EPR) spectrum.[16,17] The generation of nonequilibrium holes is a consequence of the excitation of electrons from the valence band to the $\mathrm{As_{Ga}}^+$ by the same radiation responsible for the metastable transition of the *EL*2. Ultimately, when the metastable transitions are complete, the channels for recombination of nonequilibrium holes with electrons on the $\mathrm{As_{Ga}}^+$ are blocked, leaving persistent nonequilibrium populations of both holes and the electrons. The former is observed in the photoconductivity and Raman spectra as noted above, and the latter is manifested in the quenching of the EPR spectrum of $\mathrm{As_{Ga}}^+$.[18] Thus it has been concluded[5] that the $\mathrm{As_{Ga}}^+$ defects become converted to neutral charge states, and that all the metastable $\mathrm{As_{Ga}}$ defects are maintained in the neutral charge state. However, this discussion does *not,* by itself, necessitate the neutrality of the

*EL*2 defect as a whole if it is a complex containing the $\mathrm{As_{Ga}}$. We shall return to this question at the end of the paper.

With this background, we can turn to the photo-Hall measurements in si GaAs which show that there is an increase in Hall mobility along with the generation of the persistent hole photoconductivity.[3] The increase in mobility, which implies a decrease in ionized impurity scattering, was observed to be correlated with the increase in hole population.[19] The most obvious explanation for the decrease in concentration of ionized impurities is the conversion of $\mathrm{As_{Ga}}^+$ to a neutral metastable state, as discussed above.

However, an alternative suggestion[3] has been made that the increase in mobility and decrease in ionized impurity scattering can be due to the configurational change of *EL*2 complexes. It was argued that if the defect complexes consist of charged constituents that are driven closer together by their Coulomb attraction,[8,20] their scattering power would be decreased. We note that this suggestion can be tested experimentally. We require a situation where the metastable transition can occur without involving the masking effects due to the presence of compensating $\mathrm{As_{Ga}}^+$ defects and their neutralization.

Such a situation exists in *n*-type semiconducting GaAs, where compensation of minority shallow acceptors is taken care of not by the $\mathrm{As_{Ga}}$ defects, but by the majority shallow donors. The $\mathrm{As_{Ga}}$ defects are thus always neutral.[21] The *EL*2 defects in this material still undergo the metastable transition, as is demonstrated by the photoquenching of their characteristic absorption spectrum.[22,23] The only difference from si GaAs is that the thermal recovery temperature is lowered from ~ 120 K to ~ 40 K.[23] Thus, if there is any change either in net charge or in spatial redistribution of charges associated with configurational changes of *EL*2 defect complexes, it can be expected to provide the sole contribution to persistent photoconductive and photo-Hall effects.

Accordingly, we looked for the possible onset of a persistent photoconductivity when the absorption of *n*-type semiconducting GaAs was photoquenched. In Fig. 1, we present the time dependence of both the conductivity and the absorption at $T=45$ K (Ref. 24) during prolonged irradiation of the sample by a halogen tungsten lamp, whose radiation was passed through a 1.17-eV filter with a 50-Å band pass. We find no observable change in conductivity to accompany the quenching of the absorption.

The failure to see any effect could not have been due to insufficient sensitivity for observing photoconductive effects. Since there are some $2.4\times10^{16}\ \mathrm{cm^{-3}}$ *EL*2 defects in the sample (as estimated from the magnitude of the absorption quench) compared to a free carrier concentration of $2.1\times10^{15}\ \mathrm{cm^{-3}}$ at $T=45$ K (as obtained from Hall measurements), any changes in carrier concentration or mobility associated directly with the metastable transition of all the *EL*2 defects should have given detectable effects.

From the failure to observe detectable changes in carrier concentration or mobility, we can conclude that there are no detectable changes in charge or scattering strength for the *EL*2 defects associated with their metastable transition in *n*-type semiconducting GaAs. Hence, the observed persistent increase in hole population and in mobility in si GaAs has to be associated solely with the persistence of the neutralization of the compensating $\mathrm{As_{Ga}}^+$ defects and not with charge redistribution effects associated with lattice configurational changes of the *EL*2 defects.

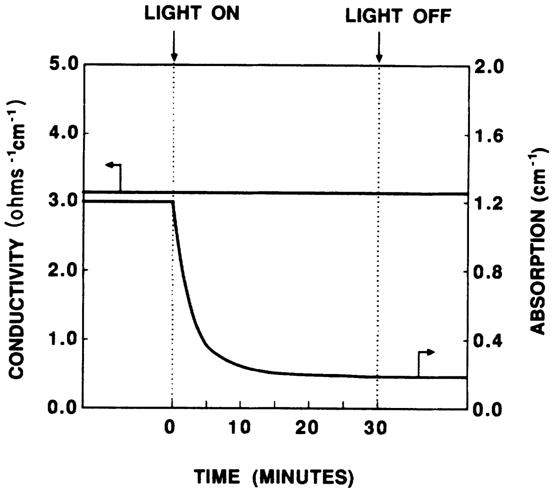

FIG. 1. The conductivity and subband-gap optical absorption at 1.17 eV of *n*-type semiconducting GaAs is shown before, during, and after irradiation of the sample with 1.17 eV light at 45 K. The photoquenching of the absorption commences with the onset of the light, but no corresponding change in the conductivity of the sample was observed. The absorption measurements before and after irradiation were made with very weak light not capable of photoquenching of the absorption.

Finally, we turn to the consideration of very recent specific proposals that the *EL*2 complexes are positively charged, consisting of a neutral $\mathrm{As_{Ga}}$ and a positively charged As interstitial ($\mathrm{As}_i{}^+$).[8–11] The positive charge for the As_i is needed to explain the absence of any unpaired spin contribution from As_i to the EPR spectrum. We argue below that this charge state for the *EL*2 defect is not consistent with the available experimental evidence either for *n*-type semiconducting material or for si GaAs.

Consider first *n*-type semiconducting material, and the possible circumstances in which the As interstitials could be positively charged.

(i) Their donor levels might be shallower than those of the ordinary shallow donors. However, this would permit freeze-out to occur at low temperatures and render the interstitials neutral. But when we see substantial freeze-out of free electrons at $T<30$ K, we find no impairment of the photoquenching of the absorption. The metastable transition of *EL*2 still occurs at low temperature, when the As_i, *if present*, is presumably neutral. Also metastable *EL*2 undergoes thermal recovery at $T>50$ K when the As_i would presumably be positively charged. These facts are completely inconsistent with the proposed model.

(ii) It might still be argued that the As_i defects are positively charged at all temperatures because they have very shallow donor levels which are all compensated by acceptors. However, there is no evidence that the requisite high concentration of compensating acceptors (at least equal to the *EL*2 concentration) is universally present in *n*-type semiconducting samples.

Next we consider si GaAs. If an $\mathrm{As}_i{}^+$ component is present in *EL*2 complexes in si material, the donor level of the As interstitials would have to lie well above those of the As antisites, and compensation by the shallow acceptors would be required for it to be unoccupied. The shallow acceptor concentration would thus have to be large enough in all si samples to compensate all the As_i defects, and also to provide for the $\mathrm{As_{Ga}}{}^+$ component observed in the EPR spectrum. The acceptor concentration would thus have to be rather narrowly restricted to a concentration range lying between 1 and 2 times the concentration of the *EL*2 defects. It would be very difficult to produce si GaAs consistently if the ratio of *EL*2 defects and residual shallow acceptors accidentally present, were thus restricted. But also, the available experimental evidence contradicts such a possibility. It has been observed that the EPR signal strength of $\mathrm{As_{Ga}}{}^+$ correlates fairly well with the far-infrared local-mode absorption measurements of the concentration of carbon.[17] There is no evidence in that data of the presence of an additional large carbon concentration equal to that of the required concentration of As interstitials. Thus, we believe that there are fundamental difficulties with a positively charged *EL*2 complex consisting of $\mathrm{As_{Ga}}$-$\mathrm{As}_i{}^+$ and that the preponderance of the experimental evidence favors a neutral charge state for the metastable *EL*2 defect.

In conclusion, we have presented arguments against both a charged *EL*2 complex and a complex in which the metastable transition involves a rearrangement of charge on its constituent parts. It is worth noting that much of the theoretical motivation for postulating complex structures for the *EL*2 defect was the difficulty[25] with understanding how isolated $\mathrm{As_{Ga}}$ can have a metastable state. However, new theoretical arguments[26,27] have provided for the first time a basis for the existence of a metastable configuration for the isolated $\mathrm{As_{Ga}}$ defect. Such a model would be consistent with the arguments presented in this paper.

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[2] For the most recent presentation of conflicting models of *EL*2, see *Proceedings of the 14th International Conference on Defects in Semiconductors, Paris, August 18-22, 1986*, edited by H. J. von Bardeleben (Trans Tech, Switzerland, 1986), pp. 247-371.

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