Insights into Metastable Defects in Semi-Insulating GaAs from Electronic Raman Studies of Nonequilibrium Holes

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We have analyzed the metastable defects in undoped semi-insulating GaAs from a new perspective, that of the electronic Raman scattering of holes generated on the compensated, residual shallow acceptors by cw neodymium-doped yttrium aluminum garnet laser radiation. The scattering results, when correlated with the several photoquenching phenomena, provide information on (i) the charge state of $EL2$ defects before they undergo the transition from a normal to a metastable state, and (ii) the relationship between $\mathrm{As_{Ga}}$ compensating centers and metastable $EL2$ defects.

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Mid-gap defects in undoped semi-insulating (si) GaAs have been of intense interest in this technologically important material. They are held to be responsible for the compensation of residual shallow acceptors which permits the production of semi-insulating material. The defects labeled $EL2$ are particularly intriguing for their ability to undergo transitions between a normal and a metastable state. The transition from a normal to a metastable state at low temperature is characterized by the photoquenching of a number of phenomena such as photocapacitance,[1-4] optical absorption,[5] and electron paramagnetic resonance (EPR).[6,7] The reverse transition, the recovery to the normal state,[1] is a thermal one occurring at $T > 120$ K. The identification of the defects is a problem of long standing. The only mid-gap defect that has been unambiguously identified is the arsenic antisite $\mathrm{As_{Ga}}$. It has been detected by EPR measurements[8] and shown[9] to be primarily responsible for the compensation. However, there is still contention about the identification of the metastable $EL2$ defects and their relation to the defects responsible for compensation. There have been various contending claims[4,9,10-16] arguing, on the one hand, that both the compensation and the metastability can be attributed to the $\mathrm{As_{Ga}}$ as isolated point defects, or, on the other hand, favoring the point of view that the metastability must be due to one or more complexes involving $\mathrm{As_{Ga}}$. The difficulty of the problem is further indicated by the fact that there does not yet exist any theoretical analysis which successfully identifies the metastable defects.[11,12]

Our purpose in this paper is to demonstrate how the results of a new experimental approach, electronic Raman scattering (ERS)[17] from nonequilibrium bound and free holes in undoped si-GaAs, can be correlated with the various photoquenching phenomena, and how this correlation provides some new insights into the relationship between the ability of defects to compensate residual shallow acceptors and their capability to undergo a metastable transition. We shall discuss what criteria this analysis imposes on theoretical attempts to determine what kind of defects can be metastable.

It has been demonstrated by Wan and Bray[17] by means of electronic Raman scattering (ERS) with low-power, cws Nd-doped yttrium aluminum garnet (Nd:YAlG) laser radiation, that there exists a very surprising, saturating population of holes, bound at low temperature on what should be the *compensated, residual shallow acceptors* present in undoped si-GaAs. Because of this effect, ERS spectra could be taken at ~15 K and used to identify and quantitatively to assess the acceptors.[17,18] Examples of such spectra, but now taken as a function of temperature, are presented in Fig. 1. Our Raman scans (~30 sec/point at intervals of 2 Å) were

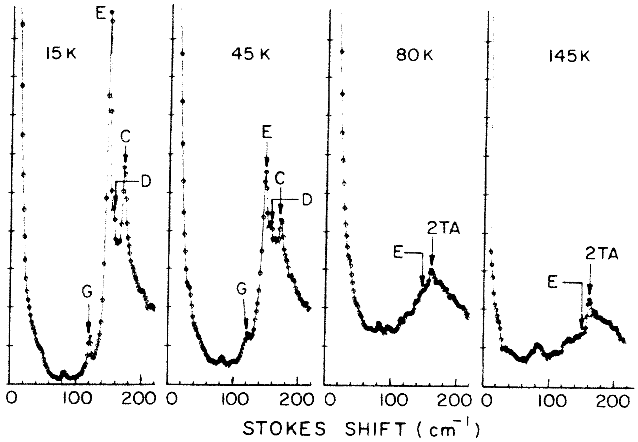

FIG. 1. Electronic Raman spectra in undoped semi-insulating GaAs, taken as a function of temperature. The sharp lines (G,E,D,C) represent transitions of *bound* holes between the $1S$ ground state and $2S$ and $2P$ excited states. Also visible are single-particle scattering contributions from *free* holes, and a weak background (seen isolated at 145 K) from two-phonon scattering in T_2 symmetry. The nonequilibrium hole populations are generated by the cw Nd:YAlG laser radiation used for the Raman scattering studies. The free holes increase with temperature at the expense of the bound holes; both vanish upon the thermal recovery of the $EL2$ defects (at $T > 120$ K) from the metastable state.

obtained with focused cw Nd:YAlG laser radiation ($\sim$few tenths of a watt in a 150-μm beam) at 1.17 eV. The weakly absorbed radiation permits the use of an in-bulk, 90° scattering configuration. The ERS spectra consist of four sharp lines labeled G, E, D, and C; these represent the transitions of bound holes from the ground state to the excited $2S$ and $2P$ states of the acceptors. The spectra were taken for T_2 symmetry to minimize the underlying contribution from the two-phonon spectrum. A line spectrum is unique to a particular acceptor and thus serves to identify it. The spectra in Fig. 1 can be attributed[17] to carbon acceptors. The dominant E line represents the allowed $1S$-$2S$ transition and its height provides a useful relative measure of the acceptor concentration. As is evident from Fig. 1, the bound-hole population decreases rapidly with increasing temperature. There appears to be a corresponding increase in free holes due to thermal liberation from the acceptors. This manifests itself in a growing single-particle scattering (SPS) contribution to the Raman spectrum in the wings of the laser line and possibly even further out in the continuum underlying the bound acceptor spectrum.[19] From the growth of the Rayleigh wing and the continuum underlying the ERS spectra in Fig. 1, there is reasonable qualitative evidence of the growth of the free holes at the expense of the bound holes as the temperature is increased. It is difficult, however, to make a quantitative analysis of the free holes because their SPS contribution in the Rayleigh wing competes with a bound-hole contribution from transitions of bound holes between the internally strain-split, degenerate ground states.[17] Finally, at $T = 145$ K, both the bound and free holes appear to have vanished; there remains only a residual structure from the very weak two-phonon Raman spectrum in T_2 symmetry.

Our main concern here is to analyze the surprising existence of the ERS spectra of the residual acceptors and its relation to the photoquenching phenomena and the metastability of the defects in this material. We shall first summarize the key, relevant characteristics of the ERS spectra, including their dependence on material, temperature, and laser intensity, and then discuss how these are connected to the metastable transitions of the deep donor defects. (1) With regard to the material aspect, the ERS spectra were obtained only in undoped si-GaAs. For cw radiation, they were not observed in the several Cr-doped si-GaAs and n-type semiconducting GaAs samples tested. (2) The large hole populations can only have been generated by the Nd:YAlG laser radiation itself, which happens to lie close to the peak of the band of radiation (1.0–1.4 eV) which is capable of inducing the transition of the defects to the metastable state.[1] (3) The bound and free holes behave like a persistent thermal-equilibrium population at $T < 100$ K, but disappear at 145 K. (4) The strengths of the ERS spectra (normalized for the laser intensity in the sample by the intrinsic Raman TO lines) were independent of intensity for a given sample and at a given temperature, even for reductions in laser intensity by a factor $> 100x$. Apparently, the total steady-state hole concentration is unaffected by the intensity of the laser radiation which generates it. (5) The bound-hole concentrations at the lowest temperatures were large, generally $> 10^{15}$ cm^{-3} and comparable to the total expected residual acceptor concentration.[17,18]

These results immediately indicate that the conditions for the appearance and disappearance of the nonequilibrium hole population correlate with the conditions for the transition of defects to the metastable state and their thermal recovery to the normal state. The further implications of these results are explored with the help of Fig. 2.

In Fig. 2(a) we review the picture of the compensation of residual acceptors (A) by the mid-gap double donor defects (D) in undoped si-GaAs. We consider the simplest case, where the concentration of D exceeds that of A and the concentration of shallow donors can be neglected.[10] The material is semi-insulating, not by virtue of high purity, but because the appreciable mid-gap donor defects (generally $\geq 10^{16}$ cm^{-3}) compensate the residual shallow acceptors (usually carbon in the 10^{15}–10^{16}-cm^{-3} range).[10] The resulting mixture of neutral (D^0) and singly positively charged defects (D^+) establishes the Fermi level close to the center of the gap and determines the semi-insulating character. From EPR studies,[9] the D^+ centers can be identified with positively charged antisites $\mathrm{As_{Ga}}^+$. The strength of the EPR signal has been found[10] to be correlated in different samples with the total carbon concentration (measured from far-infrared local-mode absorption). Thus we can take the concentrations of D^+ and A^- (representing ionized carbon) as equal, as depicted in Fig. 2(a).

In the *normal* state, the optical absorption of subband gap, cw laser radiation at 1.17 eV is attributable to the two processes shown in Fig. 2(b), the excitation of electrons from the valence band to D^+ (via σ_p), and from D^0 to the conduction band (via σ_n). The threshold energies for both of these transitions are believed to be close to 0.7 eV.[7] Free holes are generated in the valence band and

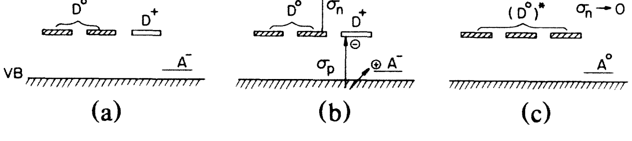

FIG. 2 (a) Compensation of shallow acceptors (A^-) by mid-gap defects (D^+). (b) Normal-state excitation of free electrons and bound holes by Nd:YAlG laser radiation. (c) Change of charge status of compensating shallow acceptors and defects preceding transition of the latter from the normal D^0 to the metastable state $(D^0)^*$. The state of compensation is metastably reversed and all defects and acceptors are locked into the neutral state.

they can freeze out on the acceptors at sufficiently low temperature. However, efficient, direct recombination of the holes with the free electrons that are also generated should prevent the buildup of a very large hole population. Moreover, the dependence of the balance of generation and recombination processes on light intensity should make such a hole population increase with light intensity. These features of the two-step excitation process are, however, not compatible with our ERS observations.

To build up an intensity-independent, saturating hole population on the acceptors, the recombination of the holes must be suppressed. This has two requirements: (a) The normal-state, optical excitation of electrons from *all defects* to the conduction band must be cut off, i.e., the optical excitation cross section σ_n must vanish (at least at 1.17 eV), and (b) the direct recombination of electrons on neutral defects with bound holes, and particularly with free holes which can migrate to their vicinity, must also be quenched. These requirements are just compatible with the observed photoquenching of the absorption,[5] and hence the quenching of the generation and recombination processes. We have confirmed that the quenching of the absorption occurs in all our undoped si-GaAs samples. It has been suggested recently[4,8,13] that the optically induced metastable transitions are low-probability events, preceded by an internal excitation of an electron on a neutral defect. We can expect therefore that, as the metastable conversion proceeds, the normal recombination processes diminish and eventually cease. The laser intensity simply determines the speed of the process, but not its final state. We see that the Nd:YAlG laser radiation has several tasks in addition to being the source for the Raman scattering: (i) the generation of the holes by the excitation of electrons from the valence band to the D^+ defects, thereby converting them to the neutral state, and (ii) the inducing of the metastable transition of *all the neutral defects* to quench the recombination of electrons and holes.

The final stage, where all the defects have undergone transitions from the normal state D^0 to the metastable state $(D^0)^*$, is depicted in Fig. 2(c). The defects are all in their neutral state and nonequilibrium holes are stored on all the now neutral acceptors. The acceptors and metastable defects form two systems which are isolated from each other and thus achieve a metastable reversal of their initial, equilibrium state of compensation. Only as many holes (free or bound) can be stored as the number of nonequilibrium electrons that can be excited to and metastably trapped on the defects. This explains the saturation of the ERS.

The conversion of defects from D^+ charge states to neutral D^0 states and ultimately to metastable neutral states is also consistent with the observed quenching of the EPR.[6,7] We can exclude the suggestion[4,15] that the D^+ defects may undergo a separate direct transition to a metastable state. This would be inconsistent with the buildup of the ERS signal.

The correlation of the results of ERS, EPR, and absorption measurements has provided information on how the holes are distributed on the acceptors and the compensating defects and in the valence band, and thus permits us to draw certain conclusions about the nature of the metastable transition. The metastable transitions of the defects must occur only from the neutral charge state of the defects, and they must occur without change in charge status. This conclusion was also reached from photocapacitative experiments.[1,4] The present analysis not only confirms it in a completely different but more direct way, but broadens it by requiring the prior normal conversion of defects in the D^+ state to the D^0 state.

Furthermore, we can draw interesting conclusions about the relation of the metastable $EL2$ defects to the compensating defects. Consider the consequences for the possibility that compensating but nonmetastable defects are present. Suppose that they were only a fraction of the total defect population, but still comparable to the smaller acceptor population. In that case, it is obvious that they would substantially suppress both the storage of holes (hence of the ERS signal) and the quenching of the EPR. Yet the quench of the absorption would be diminished only partially, by the fraction of nonmetastable defects in the total defect population. No evidence of such disparity in the quenching effects has been cited. The available evidence[17,18] suggests that the buildup of ERS is substantially complete. Therefore, it follows that no substantial fraction of compensating but nonmetastable defects is present in most of the samples tested.

This analysis has interesting consequences on points of contention in the literature. Undoped si-GaAs is now believed to contain a family of $\mathrm{As_{Ga}}$-related defects, including isolated point defects and various complexes. The identification of isolated $\mathrm{As_{Ga}}$ point defects as the metastable $EL2$ defects has been frequently questioned,[11,12,15] although the identity of the specific complexes that undergo such transitions has not yet been determined.[11] Our analysis suggests that *any* compensating defects *normally present* as a substantial fraction of the number of residual shallow acceptors must be able to undergo metastable transitions. Specifically, then, the isolated antisites, *if they are normally present in sufficient concentration in as-grown material,* must be capable of undergoing the metastable transition.

Our failure to observe ERS in Cr-doped si-GaAs samples provides an interesting counterexample. If the optical transition of electrons from the Cr impurities to the conduction band is not quenchable, then strong buildup of holes on the shallow acceptors cannot occur because they would recombine with the free electrons optically excited from the Cr to the conduction band. This could leave excess holes bound on the Cr impurities instead of on shallow acceptors. In *n*-type semiconducting GaAs, free electrons are always available to recombine with nonequilibrium holes and thus prevent the buildup of an ERS signal from the compensated acceptors.

In summary, the ERS studies not only emphasize the important role of the compensated shallow acceptors in determining the characteristics of undoped si-GaAs, but they also help to interpret the photoquenching of the EPR and optical absorption of the defects. In this respect, we also note the relevance of the ERS studies to another mysterious observation, that of persistent *p*-type photoconductivity.[20] The latter can now be attributed to the nonequilibrium free holes associated with the residual acceptors. These should be present at temperatures above which the holes freeze out on the acceptors, and below which the metastable transition is annealed. Finally, the analysis of the ERS studies establishes intimate connections between *EL*2 and compensating defects.

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[1] G. Vincent and D. Bois, Solid State Commun. **27**, 431 (1978); G. Vincent, D. Bois, and A. Chantre, J. Appl. Phys. **53**, 3643 (1982).

[2] A. Mitonneau and A. Mircea, Solid State Commun. **30**, 157 (1979).

[3] P. Omling, L. Samuelson, and H. G. Grimmeiss, Phys. Rev. B **29**, 4534 (1984).

[4] M. Skowronski, J. Lagowski, and H. C. Gatos, Phys. Rev. B **32**, 4264 (1985).

[5] G. M. Martin, Appl. Phys. Lett. **39**, 747 (1981).

[6] E. R. Weber, H. Ennen, U. Kaufman, J. Windscheif, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982).

[7] M. Baeumler, U. Kaufman, and J. Windscheif, Appl. Phys. Lett. **46**, 781 (1985).

[8] R. J. Wagner, J. J. Krebs, G. H. Stauss, and A. M. White, Solid State Commun. **36**, 15 (1980).

[9] K. Elliott, R. T. Chen, S. G. Greenbaum, and R. J. Wagner, Appl. Phys. Lett. **44**, 907 (1984).

[10] M. Kaminska, M. Skowronski, J. Lagowski, J. M. Parsey, and H. C. Gatos, Appl. Phys. Lett. **43**, 302 (1983).

[11] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 2340 (1985).

[12] G. B. Bachelet and M. Scheffler, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 755.

[13] M. Kaminska, M. Skowronski, and W. Kuszko, Phys. Rev. Lett. **55**, 2204 (1985).

[14] M. Deiri, K. P. Homewood, and B. C. Cavenett, J. Phys. C **17**, L627 (1984).

[15] B. M. Meyer and J.-M. Spaeth, J. Phys. C **18**, L99 (1985).

[16] M. Taniguchi and T. Ikoma, Appl. Phys. Lett. **45**, 69 (1984).

[17] K. Wan and Ralph Bray, Phys. Rev. B **32**, 5265 (1985).

[18] J. Wagner, H. Seelewind, and U. Kaufman, Appl. Phys. Lett. **48**, 1054 (1986).

[19] Diego Olega, Manuel Cardona, and Ulrich Rössler, Phys. Rev. B **22**, 1905 (1980). This work describes some complexities in the single-particle scattering spectrum for holes in GaAs; however, for much higher hole concentrations ($\approx 10^{19}$ cm^{-3}) than in our case.

[20] J. Jiménez, M. A. Gonzalez, P. Hernandez, J. A. deSaja, and J. Bonnafe, J. Appl. Phys. **57**, 1152 (1985). The authors observed a metastable increase in photoconductivity at 80 K and regarded it as "opposite to the expected optical quenching." In fact, as we demonstrate in this paper, the generation of a persistent population of free holes at 80 K is consistent with the metastable transition of the defects and fully compatible with the various quenching effects. See also J. Jiménez, P. Hernandez, J. A. deSaja, and J. Bonnafe, Solid State Commun. **55**, 459 (1985).