PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

Unification of the properties of the *EL*2 defect in GaAs

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(Received 20 October 1988)

We provide experimental unification of the properties of *EL*2 in GaAs, linking the measurements of optical absorption, deep-level transient spectroscopy, electron paramagnetic resonance (EPR), magnetic circular dichroism (MCD), and optically detected electron-nuclear double resonance (ODENDOR). Results show that the *EL*2 defect has two energy levels, gives rise to the zero-phonon line in the neutral charge state, and gives rise to the EPR quadruplet, MCD, and ODENDOR signals in the singly ionized state. These manifestations disappear when *EL*2 is transferred to the metastable state. Any discussion of the properties of the *EL*2 defect must be consistent with these unified characteristics.

The midgap donor level *EL*2 in GaAs (Ref. 1) dominates the compensation mechanism in semi-insulating GaAs used for integrated circuits. This feature has generated an enormous practical interest in the *EL*2 defect. On the other hand, basic research has been attracted by the mystery of *EL*2 metastability which has been a driving force for many state-of-the-art theoretical calculations.[2–6] In a continuing search for the atomic structure of the *EL*2 defect in GaAs, models have been chosen considering at least one of the following *EL*2 features: (1) electronic levels, (2) optical transitions, (3) electron paramagnetic resonance signal (EPR), (4) magnetic circular dichroism (MCD) and connected with it optically detected electron-nuclear double resonance (ODENDOR) signals, and (5) the existence of normal and metastable states of the defect.

The total set of features mentioned above [(1)-(5)] should, in general, provide a unique means for linking experiment and theory. This has not become the common practice. Apparently conflicting interpretations of different experiments, many pitfalls and ambiguous results, combined with the equivocal character of the family of *EL*2-like defects,[7] and the family of paramagnetic arsenic antisite defects,[8,9] has generated uncertainty and raised a question as to which are the real features of the *EL*2 defect. As a result, many *EL*2 models are proposed considering only selected features while neglecting others.

Analysis of optical transitions, especially the 1.039 eV zero-phonon line (ZPL), provided the very first information on the tetrahedral symmetry of the occupied *EL*2 defect,[10] while a photo-EPR study linked ionized *EL*2 and the arsenic antisite EPR quadruplet signal.[11] The structurally most powerful MCD-detected ODENDOR technique identified a ⟨111⟩ distortion and C_{3v} symmetry of the paramagnetic state, and assigned the *EL*2 defect to the pair As_{Ga}-As_i.[8,12] The different *EL*2 defect symmetries, namely T_d and C_{3v}, as observed from the optical absorption ZPL and the combined MCD-ODENDOR technique, respectively, have generated the following questions. (1) Are these different experimental techniques probing the same defect? (2) What are the unified experimental features of the *EL*2 defect?

It is the intent of this work to provide the experimental evidence which unifies the properties of the *EL*2 defect as observed with optical absorption, EPR, deep-level transient spectroscopy (DLTS), and MCD-ODENDOR. However, it is not the intent of this work to assess the validity of previous conclusions, as to the exact microscopic structure of the *EL*2 defect, based on the interpretations of individual techniques reported previously.[8,10–12]

In 1987 we initiated a collaborative study designed to clarify existing uncertainties and verify relationships among the five features and their association with *EL*2. Preparation of special samples with properties tailored to the demands of different techniques was performed at MIT. The measurements of electronic levels and the zero-phonon absorption line were also made at MIT. An EPR and photo-EPR study, including quantitative determination of the spin concentration, was performed at the University of California, Berkeley, while MCD measurements were made at the University of Paderborn.

In undertaking the research, we realized the importance of the following experimental conditions: (a) the samples investigated should contain *EL*2 rather than other midgap levels occasionally present in melt-grown GaAs, (b) the concentration and the occupancy fraction must be varied and must be measured, (c) material incompatability between EPR and DLTS (which require high- and low-resistivity samples, respectively) must be overcome, and (d) the problem of the very low intensity of the EPR quadruplet in as-grown semi-insulating (SI) GaAs and the potential contributions from the family of arsenic antisite-related defects had to be resolved for a reliable determination of the spin concentration and a comparison between absolute concentrations of EPR centers and the *EL*2 defect.

To satisfy these conditions we employed a series of *n*-type, *p*-type, and semi-insulating thermally treated GaAs crystals. These crystals were annealed at 1200 °C for 12 h in an equilibrium As-ambient followed by a rapid quench to room temperature and then reannealed between 700 and 1000 °C. The 1200 °C annealing-quenching procedure [also referred to as the inverted thermal conversion (ITC) treatment] produces GaAs virtually free of the *EL*2 defect.[13] Such crystals contain deep acceptorlike native defects frozen in during the quenching. Subsequent annealing eliminates native acceptors and leads to controlled formation of *EL*2 at a concentration dependent on the annealing temperature and time. The formation rate has a maximum at about 850 °C, roughly corresponding to 10^{14} cm^{-3} *EL*2 defects formed per second at the initial annealing stages.

Optical absorption experiments were performed with a dual beam spectrometer with a liquid-helium cold-finger cryostat allowing for variable temperature operation between 4 and 300 K. EPR measurements were carried out using an *X*-band spectrometer interfaced to a computer. The sample temperature was controlled and varied between 4 and 300 K with a helium-gas-flow cryostat. The apparatus had provisions for illumination of the sample in the cavity with either monochromatic or white light. The EPR quadruplet spin concentrations were determined by comparing the area under the microwave absorption curve (doubly integrated quadruplet) with the area under the microwave absorption curve of phosphorus-doped silicon samples with known phosphorus concentration. Signal intensity versus microwave power characteristics were performed to insure that saturation effects were negligible during spin-concentration determinations. MCD measurements were done at 1.6 K with a *K*-band computer controlled spectrometer; the experimental procedure is discussed in Refs. 8 and 12.

DLTS measurements on *n*-type GaAs samples which have been annealed at 1200 °C and rapidly quenched to room temperature and then reannealed at 800 °C for 1 h and rapidly quenched to room temperature (this annealing sequence is hereafter referred to as ITC+800) have shown that this thermal treatment produces only one midgap level with the electron emission rate $e_n(\mathrm{s}^{-1}) = [T^2(3.53\times10^{-8})]\exp[-0.815(\mathrm{eV})/kT]$ and a characteristic 1.039-eV zero-phonon line. The electron-capture cross section of *EL*2 is thermally activated with an activation energy of 66 meV, so that the energy level as measured by Hall effect is at $E_c-0.75$ eV.[1] Both features are signatures of the true *EL*2 defect[7,10] in its filled, neutral charge state (i.e., $EL2^0$). DLTS measurements on similarly treated *p*-type GaAs showed that the *EL*2 formation was manifested by the formation of a trap at 0.54 eV above the valence band which corresponds to the second level of the *EL*2 defect.[7,11] Thus, the levels at $E_c-0.75$ eV and $E_v+0.54$ eV, respectively, seem to be the only levels of the *EL*2 defect in the GaAs energy gap.

In semi-insulating as-grown and ITC+800 GaAs samples, the EPR quadruplet and the MCD signal (previously assigned[12] to the As_{Ga}-As_i defect) were examined. Both features were measured in exactly the same as-grown and ITC+800 samples. Results are given in Table I. The relative intensities of the MCD and EPR signals indicate that both techniques are sensing one and the same defect. Detailed analysis of the MCD lines has shown that the strong signal in the ITC+800 samples corresponds to only one defect. No other MCD signals were found in this sample. We therefore infer that the EPR quadruplet signal in the ITC+800 samples examined in these studies does not contain any hidden components. This conclusion is very important since it eliminates ambiguities related to the "family of arsenic antisite defects" occasionally found in as-grown liquid-encapsulated Czochralski- (LEC) grown GaAs. As conclusively demonstrated below, the defect which gives rise to both the EPR quadruplet and the MCD signal in the samples employed in these investigations is the ionized charge state of *EL*2. Though there is no unambiguous experimental determination of the total charge states involved in the midgap level at $E_v+0.75$ eV and the level at $E_v+0.54$ eV, we follow common practice and call the filled midgap level $EL2^0$.

Quantitative measurements correlating the ZPL and EPR quadruplet were performed on a series of ITC+800 samples. The experimental approach was to obtain quantitative changes, brought about by low-temperature optical illumination and recovery cycles, in both the EPR quadruplet concentration and optical absorption ZPL. The quantitative relationship between the ZPL and DLTS *EL*2 signal was previously demonstrated by Skowronski, Lagowski, and Gatos[14] using *n*-type GaAs. In *n*-type GaAs, all *EL*2 defects are occupied and are therefore neutral (i.e., $EL2^0$). This previous work thereby provided calibration for determining the $EL2^0$ concentrations from ZPL intensities in semi-insulating GaAs. Thus, high-resolution ZPL measurements performed on conducting as well as semi-insulating material were used as a common element linking *EL*2-related DLTS and EPR measurements. The ITC+800 samples were particularly suitable for quantitative correlations between the ZPL and the EPR quadruplet since they exhibited a high EPR quadruplet concentration before illumination with only a small ZPL absorption, while after illumination and recovery there was a small quadruplet concentration and a large ZPL. In other words, large changes in both the EPR quadruplet and ZPL absorption were brought about by the illumination and thermal recovery cycles. Special attention was placed on making the experimental conditions of EPR measurements (at Berkeley) and optical ab-

TABLE I. Comparison of MCD and EPR signal intensities measured on the same as-grown and ITC+800 GaAs samples.

Sample	Signal intensity (arbitrary units) MCD	EPR
As-grown	1	1
ITC+800°, 1 h	5	5

sorption measurements (at MIT) as similar as possible.

Quantitative results are given in Table II. They were also used to construct and plot the intensity of the EPR quadruplet signal versus the intensity of the ZPL. This plot shown in Fig. 1 demonstrates the one-to-one correlation between a decrease in spin concentration and an increase in the concentration of the neutral $EL2$. The data in Table II show that the correlation remains valid during the photoionization of $EL2$ (0.9-μm illumination), during the photopopulation of $EL2$ by photoexcitation of holes to the valence band (1.3-μm illumination), as well as upon recovery of $EL2$ from the metastable state. It is also seen that the transfer of $EL2$ to a metastable state (by white-light illumination) eliminates both the ZPL and EPR quadruplet, confirming that the metastable state is not paramagnetic and is not optically active. With the exception of steps (2) and (6), the concentration of the $EL2^0$ (determined from the ZPL) plus the EPR quadruplet concentration remains constant; $N_{EL2^0}+N_{\rm quad} = (2.5\pm0.4)\times10^{16}$ cm^{-3}. The experimental uncertainty of $\pm0.4\times10^{16}$ cm^{-3} originates from uncertainties of about 2×10^{15} cm^{-3} for N_{EL2^0} and about 20% for the spin concentration.

The complementary behavior of the concentration of the EPR quadruplet and the $EL2^0$ concentration (determined from the ZPL) indicates that the entire EPR signal arises from the singly ionized charge state of $EL2$, i.e., $EL2^+$. There is, however, the possibility that a fraction of the EPR quadruplet in these ITC+800 samples arises from paramagnetic arsenic centers which do not exhibit typical $EL2$ properties as observed for instance in plastically deformed GaAs.[15] This possibility is most unlikely since both the EPR quadruplet and the ZPL are totally quenched upon white-light illumination, which is not the case in plastically deformed GaAs.[15] Furthermore, the relationship, $N_{EL2^0}+N_{\rm quad}=2.5\times10^{16}$ cm^{-3} remains valid after $EL2$ is brought back out of the metastable state after warming to 150 K. Therefore, if such paramagnetic arsenic centers are present in these ITC+800 samples which are not $EL2$, they must therefore be optically quenchable and also return from the metastable state at 150 K along with the quadruplet signal component which is related with $EL2^+$. In consideration of these factors, we conclude that all of the quadruplet in the ITC+800 samples arises from only the $EL2^+$ defect.

Thus, the optical absorption ZPL and the DLTS $EL2$ signal had previously been quantitatively correlated by Skowronski, Lagowski, and Gatos.[14] In this work, the

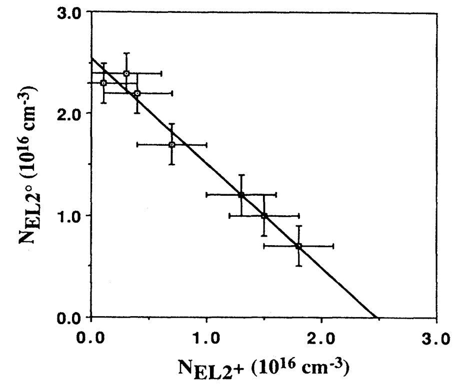

FIG. 1. The concentration of $EL2^0$, determined from the ZPL absorption coefficient, is plotted against the concentration of $EL2^+$, determined from the EPR quadruplet spin concentration.

TABLE II. Sequence of illumination and thermal recovery steps employed for quantitatively correlating the ZPL absorption coefficient with the EPR quadruplet concentration. The ZPL detects $EL2^0$ while the EPR quadruplet detects $EL2^+$. $\alpha_{\rm ZPL}=1.0\times10^{-2}$ cm^{-1} corresponds to 0.9×10^{16}-cm^{-3} $EL2^0$ defects as determined previously (Ref. 13).

Sequence of experiment steps	Optical absorption 1.039-eV ZPL $\alpha_{\rm ZPL}$ (10^{-2} cm^{-1})	N_{EL2^0} (10^{16} cm^{-3})	EPR quadruplet N_{EL2^+} (10^{16} cm^{-3})	$N_{EL2^0}+N_{EL2^+}$ (10^{16} cm^{-3})
(1) Cooled from 300 K in the dark	0.75	0.7	1.8	2.5
(2) White-light illumination transfer to metastable state	0.0	0.0	0.0	...
(3) 10-min recovery at 150 K transfer out of metastable state	1.9	1.7	0.7	2.4
(4) 30 min of 0.9-μm illumination $EL2$ photoionization	1.3	1.2	1.3	2.5
(5) 10-min recovery at 150 K	1.1	1.0	1.5	2.5
(6) White-light illumination transfer to metastable state	0.0	0.0	0.0	...
(7) 10-min recovery at 150 K transfer out of metastable state	2.6	2.4	0.3	2.7
(8) Illumination with 2.5-μm light	2.4	2.2	0.4	2.6
(9) Illumination with 1.3-μm light	2.5	2.3	0.1	2.4

ZPL has been quantitatively correlated with the EPR quadruplet. In addition, the EPR quadruplet has been correlated with the MCD signal. This MCD signal is the identical signal which has previously been used in ODENDOR studies. The significance of these correlations is that they bridge together the experimental results of optical absorption, DLTS, EPR, MCD, and ODENDOR in regards to the $EL2$ defect in GaAs.

Based on these observations, the following unified view on $EL2$ properties can be deduced:

(1) The $EL2$ defect has two levels in the gap at $E_c - 0.75$ eV and $E_v + 0.54$ eV, respectively.

(2) The $EL2$ defect in the normal state has the following manifestations: a 1.039-eV ZPL, an EPR quadruplet (with the hyperfine splitting constant the same as that of the As_{Ga^+} signal reported previously[16]), and the MCD and ODENDOR signals described in Ref. 12. The ZPL corresponds to neutral $EL2$ (i.e., $EL2^0$), while the EPR quadruplet and the MCD signal originate from the ionized $EL2^+$ defect.

(3) None of the above features is observable when the $EL2$ defect is in the metastable state. It is probable that other defects in GaAs (such as antisite related defects) can have manifestations similar to some of the above features. We are, however, unaware of any other defect having all these manifestations.

At present there seems to be an important inconsistency in the unified $EL2$ properties. Namely, different $EL2$ manifestations indicate different symmetries. The ZPL implies tetrahedral symmetry[10,17] while ODENDOR clearly shows a trigonal symmetry.[12] This inconsistency may be an indication that the symmetries of $EL2$ in the neutral and ionized states are different. More difficult to reconcile is the discrepancy between the charge states of $EL2$ (0/+ for $E_c - 0.75$ eV and +/++ for $E_v + 0.54$ eV) and the presence of an arsenic interstitial as a constituent of the defect, for which the midgap level should be of +/++ double donor character.[2] Further studies, both experimental and theoretical, are evidently needed to solve the continuing $EL2$ puzzle.

M.H., E.R.W., and W.W. are supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76-SF00098. J.L., M.M., and H.C.G. are grateful to the U.S. Air Force Office of Scientific Research for financial support.

[1]G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semi-Conductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 399.

[2]G. A. Baraff, M. Lannoo, and M. Schluter, Mater. Res. Soc. Symp. Proc. **104**, 375 (1988).

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

[4]C. Delevue, M. Lannoo, D. Stievenard, H. J. von Bardeleben, and J. C. Bourgoin, Phys. Rev. Lett. **59**, 2875 (1987).

[5]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).

[6]J. Dabrowski and M. Scheffler, Phys. Rev. Lett. **60**, 2183 (1988).

[7]H. C. Gatos and J. Lagowski, Mater. Res. Soc. Symp. Proc. **46**, 153 (1985).

[8]J. M. Spaeth, A. Gorger, D. M. Hofmann, and B. K. Meyer, Mater. Res. Soc. Symp. Proc. **104**, 363 (1988).

[9]E. R. Weber and P. Omling, in *Festkörperprobleme: Advances in Solid State Physics,* edited by P. Grosse (Vieweg, Braunschweig, 1985), Vol. 25, p. 623.

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

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

[12]B. K. Meyer, D. M. Hofmann, J. R. Niklas, and J. M. Spaeth, Phys. Rev. B **36**, 1332 (1987).

[13]J. Lagowski, H. C. Gatos, C. H. Kang, M. Skowronski, K. Y. Ko, and D. G. Lin, Appl. Phys. Lett. **49**, 892 (1986).

[14]M. Skowronski, J. Lagowski, and H. C. Gatos, J. Appl. Phys. **59**, 2451 (1986).

[15]P. Omling, E. R. Weber, and L. Samuelson, Phys. Rev. B **33**, 5880 (1986).

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

[17]Tetrahedral symmetry has recently been confirmed by uniaxial stress ZPL measurements by K. Bergmann, P. Omling, L. Samuelson, and H. G. Grimmeis, in *Proceedings of the Fifth Conference on Semi-Insulating III-V Materials, Malmö, Sweden, 1988,* edited by G. Grossmann and L. Ledebo (Hilger, Bristol, 1988), p. 397.