PHYSICAL REVIEW B VOLUME 45, NUMBER 3 15 JANUARY 1992-I

Identification of the isolated arsenic antisite defect in electron-irradiated gallium arsenide and its relation to the *EL2* defect

K. Krambrock and J.-M. Spaeth
Fachbereich Physik, University of Paderborn, Warburger Strasse 100A, 4790 Paderborn, Federal Republic of Germany

C. Delerue, G. Allan, and M. Lannoo
Institut Supérieur d'Électronique du Nord, 90 rue Solferino, 50046 Lille, France

(Received 24 July 1991)

In semi-insulating GaAs, which was electron irradiated at 4.2 K and kept below 80 K, the isolated arsenic antisite As_{Ga} defect could be identified with optically detected magnetic resonance (ODMR). It decays at about 300 K while an additional As_{Ga} related defect is formed. Upon further heating to about 520 K this defect also decays and *EL2* is formed. The magnetic circular dichroism of the absorption (MCDA) of the isolated As_{Ga} defect has a simple derivativelike structure that is explained theoretically. Its MCDA and ODMR spectra are different from the corresponding *EL2* spectra indicating the different microscopic structures of the defects. The isolated As_{Ga} defect cannot be bleached into a metastable state at low temperature under the conditions where *EL2* is bleached completely.

The semi-insulating (SI) properties of undoped GaAs are caused by the dominant midgap level defect *EL2*. This deep donor has fascinating properties such as the fact that it can be photoexcited (bleached) at low temperature into a metastable state from which it returns to the ground state by thermal activation at 140 K.[1] The microscopic structure of the *EL2* defect is, however, still a matter of controversy (for a recent discussion, see Ref. 2). At present, mainly two distinct microscopic models are discussed. One is the isolated arsenic antisite As_{Ga} defect, which was proposed on the basis of piezospectroscopic studies of optical transitions of *EL2* (Refs. 3 and 4) and favored by theory to explain the metastable state.[5–7] The other model is an arsenic antisite-arsenic interstitial (As_{Ga}-As_i) pair defect, proposed first from electron paramagnetic resonance (EPR) studies[8] and supported further by optically detected electron-nuclear double resonance (ODENDOR).[9,10] In view of the ongoing controversy about the microscopic structure of *EL2* it seemed desirable and important to create and investigate the isolated As_{Ga} defect and to compare it with *EL2*.

In this paper we report on the formation of a new As_{Ga} defect by electron irradiation at low temperature. The properties of this defect, which according to our magneto-optical experiments most probably is the isolated As_{Ga} defect, are different from those of *EL2*. SI GaAs was irradiated at 4.2 K with 3-MeV electrons with a dose of 5×10^{17} cm^{-2} and kept below 80 K. At 1.5 K the magnetic circular dichroism of the absorption (MCDA) in the spectral range between 0.8 and 1.5 eV and optically detected EPR (ODEPR) (Ref. 11) of different defects were measured. One of these defects shows the characteristic four-line As_{Ga} defect spectrum due to the ^{75}As hyperfine (hf) interaction ($I=\frac{3}{2}$) (see, e.g., Ref. 2). Neither the g factor nor the ^{75}As hf splitting are different from those of *EL2* within experimental error.[9,10] Only the EPR linewidth is smaller (32 instead of 34 mT). However, with white light of 100 mW cm^{-2}, the EPR spectrum is hardly bleached at all within a time sufficient to bleach *EL2* completely (<1 min at 1.5 K). Much longer times (10–50 min) cause a small bleaching effect. The nature of this small effect is not clear. The MCDA excitation spectrum [MCDA tagged by EPR (Ref. 11)] belonging to this As_{Ga} defect shows a simple derivativelike structure [Fig. 1(a)], at variance with *EL2* (Ref. 12) [Fig. 1(b)]. Therefore, this new antisite defect must have a different structure compared to *EL2* in spite of its almost identical ODEPR spectrum. In addition, no MCDA of paramagnetic *EL2* ($EL2^+$) nor an optical transition of diamagnetic *EL2* ($EL2^0$) could be measured. $EL2^+$ and $EL2^0$ present prior to irradiation have disappeared, at least below 10% of the original values.

ODENDOR lines of nearest and second-nearest As

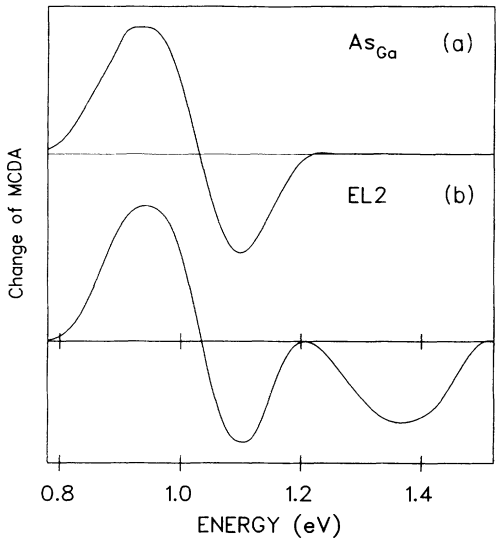

FIG. 1. MCDA excitation spectra (MCDA tagged by EPR) measured as a microwave-induced change of the MCDA at 1.5 K, 650 mT, and 23.83 GHz of (a) the isolated As_{Ga} defect and (b) the *EL2* defect.

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neighbors were measured, but none of Ga neighbors. The analysis of their angular dependence shows that the antisite defect has tetrahedral symmetry within experimental error. We cannot exclude a small deviation from the tetrahedral symmetry as long as its effect on the ENDOR line positions is hidden within the ENDOR linewidths of about 1 MHz. As in the case of $EL2$,[10] the ENDOR lines of the four nearest As neighbors of the new As_{Ga} defect are split by pseudodipolar couplings and therefore have a complicated angular dependence. Within experimental error their superhyperfine (SHF) and quadrupole interaction constants are identical to those of $EL2$ for ligands 2–4 given in Ref. 10. However, the lines ascribed to the As interstitial are missing. The fact that the new As_{Ga} defect has higher symmetry compared to $EL2$ is directly seen from the ENDOR lines of the 12 second-nearest As neighbors. They only have lines between 10 and 20 MHz for $B_0 \| [100]$ [Fig. 2(a)], while in the case of $EL2$ [Fig. 2(b)] they extend to 34 MHz. In the case of $EL2$ the presence of the As interstitial splits this shell into three subshells.[10,13,14] The three As next to the As interstitial have stronger interactions compared to the others [shell III_a between 25 and 35 MHz in Fig. 2(b)]. The isotropic and anisotropic SHF constants a and b, respectively, and the quadrupole constant q of the second As shell of the new As_{Ga} defect are very similar to the interactions of those As ligands of $EL2$, which are far away from the interstitial[10] (Table I). The results obtained for the new As_{Ga} defect are those one would expect from the As_{Ga}-As_i pair if the As_i is removed. Thus, the new As_{Ga} defect is a candidate for an isolated As_{Ga} defect, a far better one than $EL2$, for which this nature was often claimed. Whether or not the new As_{Ga} defect is "isolated" in the stringent sense, we cannot say, as long as a perturbance has a weak influence on the ENDOR line positions of the first and second shell. In that sense we henceforth call it isolated. Details of the analysis will be published elsewhere.[15]

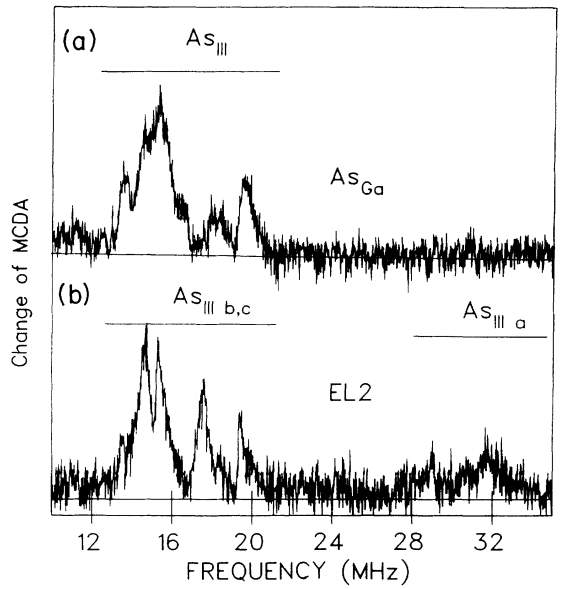

FIG. 2. ODENDOR spectra of the second-nearest As neighbors measured at 1.5 K and 23.83 GHz for $B_0 \| [100]$ of (a) the isolated As_{Ga} defect and (b) the $EL2$ defect.

TABLE I. Superhyperfine and quadrupole interaction parameters of second-nearest As neighbors of the As_{Ga} and $EL2$ defects. Angles θ_b and θ_q are measured from a [110] direction.

	a (MHz)	b (MHz)	θ_b	q (MHz)	θ_q
New As_{Ga}	21.5 ± 0.3	2.2 ± 0.3	30°	0.5 ± 0.3	28°
$EL2$: shell[a] $III_{c,b}$	19.5 ± 0.1	3.2 ± 0.1	15°	0.9 ± 0.1	32°
$EL2$: shell[a] III_a	35.2 ± 0.1	-1.3 ± 0.1	11°	2.8 ± 0.1	25°

[a]Following Refs. 10 and 13.

Upon warming the crystal to room temperature (RT) or slightly above (330 K) the signals of the isolated As_{Ga} defect disappear. A different four-line ODEPR spectrum with the same ^{75}As hf interaction but a different (tagged) MCDA spectrum appears which was found previously after RT electron irradiation of n-type and SI GaAs and called As_{Ga}-X_1.[2] Its level $+/++$ was shown to be at $E_{VB}+0.67$ eV. After warming to 300 K again neither $EL2^+$ nor $EL2^0$ was measured. Had $EL2$ still been present, it would have been seen because the Fermi level was now pinned at $E_{VB}+0.67$ eV or above. In the low-frequency ODENDOR spectrum of the As_{Ga}-X_1 lines were found due to ^{69}Ga and ^{71}Ga nuclei. The analysis of this defect is not yet complete, but it seems that a Ga_i is involved in this new As_{Ga}-related pair defect with lower than tetrahedral symmetry.[2]

Surprisingly, after heating the sample further to about 520 K, the MCDA of the As_{Ga}-X_1 defect disappeared and that of $EL2$ appeared [Fig. 1(b)]. Its MCDA could be bleached as easily as known for $EL2$ in SI GaAs. By ODENDOR it was established that indeed $EL2$ centers were measured. $EL2$ appears now in both charge states ($EL2^0$, $EL2^+$) with concentrations of 1.0×10^{16} cm^{-3} and 5.1×10^{16} cm^{-3}, respectively (before irradiation $EL2^0$ is 2.1×10^{16} cm^{-3} and $EL2^+$ is 0.5×10^{16} cm^{-3}). Thus the total concentration of $EL2$ is about a factor of 2.5 higher than it was before irradiation. From this and the failure to see $EL2$ before we conclude that $EL2$ was destroyed upon electron irradiation at low temperature and was formed at 520 K as another pair defect. Apparently, the isolated As_{Ga} defect is not stable at RT where Ga interstitials and Ga vacancies created by the electron irradiation become mobile.[16] It seems that between RT and 520 K the As_{Ga}-X_1 is thermally dissociated and $EL2$ can be formed at 520 K because As interstitials become mobile.[8,17] The disappearance of the isolated As_{Ga} above RT is not an effect of a Fermi-level change because the level of the isolated As_{Ga} can no longer be occupied by additional illumination after formation of As_{Ga}-X_1. The observation of a four-line conventional EPR spectrum after RT irradiation[18–20] was associated with the generation of an isolated As_{Ga} defect. Our results here show that this must have been the As_{Ga}-X_1 defect.

Now we present results of a Green's-function calculation of the MCDA of the isolated As_{Ga} defect. The MCDA spectrum $S(h\nu)$ can be related to the difference of the optical cross sections $\sigma^+(h\nu)$ and $\sigma^-(h\nu)$ for right and left circular polarized light, respectively. Following

Petit, Allan, and Lannoo[21] we obtain

$$\sigma^{\pm}(h\nu) \propto -\mathrm{Im}[1/h\nu\langle a_1|p^{\pm}G(E_{a1}+h\nu)p^{\mp}|a_1\rangle], \quad (1)$$

where a_1 is the wave function of the A_1 antibonding state of energy E_{a1}, G is the electronic Green's function, $p^{\pm}=p_x \pm ip_y$ is the momentum operator.[21] Im stands for the imaginary part. We get

$$S(h\nu) \propto -\mathrm{Re}[1/h\nu\langle a_1|p_yG(E_{a1}+h\nu)p_x - p_xG(E_{a1}+h\nu)p_y|a_1\rangle], \quad (2)$$

where Re stands for the real part. We use a semiempirical tight-binding formalism with two s and six p orbitals per atom including spin. The matrix elements of $p^{\pm}$ were calculated as in Ref. 21. The Green's functions of the perfect crystal were calculated with the parameters of Ref. 22 slightly modified to include spin-orbit coupling. The spin-orbit couplings for Ga and As atoms were fitted to account for the experimental VB splitting (e.g., $\Gamma_8-\Gamma_7=0.35$ eV). The As_{Ga} defect is created by replacing the s and p energies of a Ga atom by those of an As atom. We also adjust the potential on the antisite and on its first neighbors to get local neutrality of charge which is usually a good approximation of the true potential.[23] The advantage of our calculation in comparison to that of Ref. 24 is that it takes into account realistic calculated wave functions, the full band structure and resonances induced in the bands by the defect. We find the A_1 antibonding state in the gap with the levels $+/0$ at $E_{VB}+1.29$ eV and $+/++$ at $E_{VB}+0.90$ eV, respectively. The A_1-T_2 splitting is 0.9 eV and the s density on the As_{Ga} atom is about 16% in good agreement with other calculations[25,26] and experiment.[10] It is interesting to note that the calculated levels are higher than those measured for $EL2$ ($E_{VB}+0.54$ eV and $E_{VB}+0.74$ eV). The MCDA spectra for a transition from the $++/+$ $(+/0)$ to the CB (VB) is calculated neglecting the electron-phonon coupling for simplicity and assuming that the defect is at $T=0$ K, i.e., only $m_s=-\frac{1}{2}$ is occupied. The MCDA for the A_1-VB transition has always the same sign in contradiction to experiment and to the results of Kaufmann and Windscheif[24] (Fig. 3, dashed line). We explain this difference by the simplified p band structure used in Ref. 24 which does not properly include the mixing between bands. The use of the true antibonding wave function is probably also very important. For the A_1-CB transition the MCDA shows a strong A_1-T_2 transition near 0.9 eV, i.e., a positive peak followed by a negative from the transitions to the spin-orbit split $J=\frac{1}{2}$ and $\frac{3}{2}$ T_2 states, respectively (Fig. 3, solid line). The contribution of the X minimum (>1.3 eV) is small. Furthermore, the amplitude of the A_1VB spectrum is considerably smaller than that for the A_1-T_2 (see relative scale in Fig. 3) supporting the A_1-T_2 interpretation of the MCDA. The A_1-T_2 transition is strongly allowed because the two states are antibonding and localized in the same space region as was already pointed out by Dabrowski and Scheffler.[5] The calculated spectral shape of the MCDA as a simple derivative structure agrees well with the experiment [Fig. 1(a)]. Due to the neglect of electron-phonon coupling it cannot be expected that both the peak separation and the bandwidth can be reproduced. In Ref. 27 it is shown that strong phonon coupling with nonsymmetrical vibrational modes causes the $J=\frac{3}{2}$ and $J=\frac{1}{2}$ states to repel each other. It also broadens the transitions.

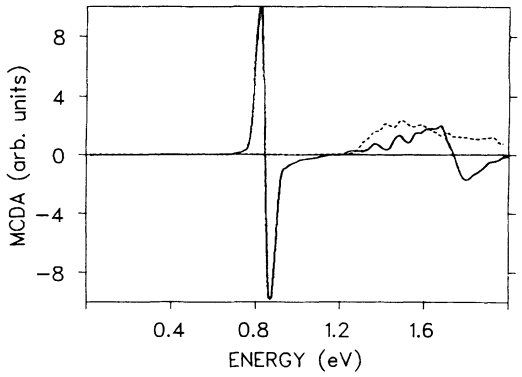

FIG. 3. Results of a full Green's-function calculation of the MCDA of the isolated As_{Ga} defect MCDA for the A_1-VB transition (dashed line) (the oscillations come from the computation and have no physical meaning) and MCDA for the A_1-CB transition (solid line), which shows a strong A_1-T_2 transition [the contribution of the X minimum of the CB ($E>1.3$ eV) is small].

In a simple model for $EL2$ (As_{Ga}-As_i pair defect) the C_{3v} symmetry splits the $J=\frac{3}{2}$ states in two Kramers doublets (some mixing with the $J=\frac{1}{2}$ state also occurs). In the MCDA this may result in the splitting of the negative peak into two peaks as is actually observed [see Fig. 1(b)].

From ODENDOR, MCDA, and its theoretical explanation we conclude that we have identified an As_{Ga} defect in electron-irradiated GaAs kept below 80 K which has within experimental error tetrahedral symmetry and which we associate with an isolated As_{Ga} defect. In particular, the As_{Ga} defect is not bleachable under the bleaching conditions for the $EL2$ defect. However, our experiments show that the nature of $EL2$ as a pair defect favors the transition into a metastable state compared to an isolated As_{Ga} defect. Whether the model of a split interstitial for the metastable state[28] or a modified version of the currently proposed vacancy-interstitial model[5-7] could explain the results is still an open question. The As_{Ga} is apparently able to lower its total energy by forming pairs with native defects such as interstitials. This may be an explanation why this defect could not yet be observed in as-grown SI GaAs, where many As interstitials are present. Further work is necessary to investigate the mechanism of the production of the isolated As_{Ga}.

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