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Identification of a trigonal cation antisite defect in gallium arsenide

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We report on the identification of an intrinsic trigonal acceptor pair, which involves a cation antisite defect, in semi-insulating and *p*-type GaAs using magneto-optical and optically detected magnetic resonance techniques. Its possible role as a part of the $EL2$ defect configuration is discussed.

The electrical properties of semi-insulating (SI) GaAs are determined by the presence of the intrinsic midgap donor $EL2$ which compensates shallow acceptors. Therefore research has focused mainly on the role of $EL2$ and the compensation mechanism. Interest from a fundamental aspect was to obtain a microscopic model of the $EL2$ defect and to explain its mysterious properties such as metastable excited states. From a technological aspect the interest is to control and improve the properties of the SI substrate material. The $EL2$ structure model was determined from magnetic resonance techniques to be an arsenic-antisite–arsenic-interstitial (positively charged) pair defect.[1,2] Its midgap level causes problems in understanding the compensation mechanism. The concentrations of the paramagnetic singly ionized $EL2$ defect commonly observed are around 10^{16} cm^{-3}. Thus the compensation cannot be explained by extrinsic shallow acceptors like C and Zn,[3] which have much lower concentrations. Therefore it is apparent that intrinsic acceptors must play a key role. However, very little is known about their existence and structure in SI GaAs. In this paper we report on the identification of the dominant intrinsic acceptor in SI and slightly *p*-type Ga-rich GaAs using magneto-optical and optically detected electron-spin-resonance techniques; the acceptor involves a cation antisite defect Ga_{As}. This is the first time that the existence of a cation antisite defect has been proved experimentally. Its possible role as part of the $EL2$ defect configuration is discussed.

The samples used were grown by the horizontal Bridgman (HB) or by the liquid-encapsulated Czochralski (LEC) technique. Changes in the arsenic source temperature (HB) or the arsenic fraction (Ga-rich, As-rich) in the melt (LEC) determined whether the samples were SI, *n*-type, or *p*-type.

In SI samples the spectrum of the magnetic circular dichroism (MCD) of the absorption of the singly ionized $EL2$ defect usually dominates.[3] In order to identify possible contributions of an underlying MCD of other defects we made use of the fact that the dominant MCD can be persistently bleached.[4] The final excited metastable state is reached by the hole-ionization transition of $EL2^0$ ($EL2^+ \rightarrow EL2^0 + h_{VB}$) and subsequent transfer into the metastable state by optical excitation of $EL2^0$. Following the usual practice we denote the positively charged defect with the midgap level by $EL2^+$. The released holes can be captured by the acceptors, converting them into an ESR-active paramagnetic charge state.[5] Figure 1 (solid line) shows the MCD spectrum in SI LEC GaAs ([As]/[As+Ga]=0.5) obtained after $EL2$ bleaching. The optically detected ESR spectrum (ODESR) of Fig. 2, curve (a), is detected. It consists of at least 6 strongly overlapping lines, as seen from its analysis using digital filtering [Fig. 2, curve (b)] and deconvolution techniques [Fig. 2, curve (c)].[6] The angular dependence (Fig. 3) shows that the defect has trigonal symmetry with partly resolved hyperfine (hf) structure due to a nuclear spin of $I=\frac{3}{2}$. The value of the electron spin cannot be inferred from the ESR spectrum. A recently developed method for its determination using the temperature and magnetic field dependence of the MCD at $E=1.46$ eV yielded $S=\frac{1}{2}$.[7] The ODESR spectrum was analyzed with an axially symmetric spin Hamiltonian taking into account an axial *g* and hf anisotropy.[8] The result is

$$g_{\parallel}=1.96\,,\quad g_{\perp}=2.04\,,$$

$$A_{\parallel}=21\pm1\ \text{mT}\,,\quad A_{\perp}=12\pm1\ \text{mT}\,.$$

The principal axes of *g* and *A* are along a [111] direction. The theoretically calculated angular dependence with the above parameters (solid lines in Fig. 3) is in very good

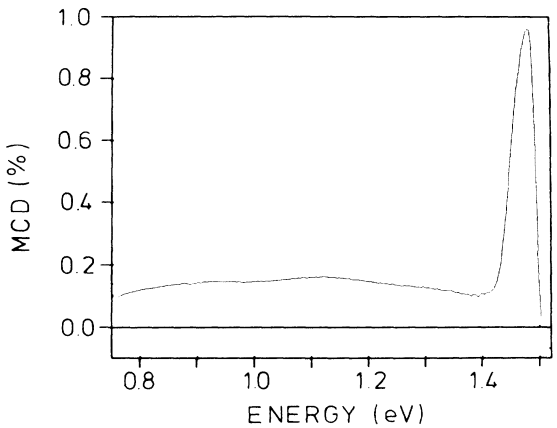

FIG. 1. Spectrum of the magnetic circular dichroism of the absorption of the trigonal acceptor pair in semi-insulating GaAs obtained after $EL2$ bleaching ($T=1.45$ K, $H=1$ T).

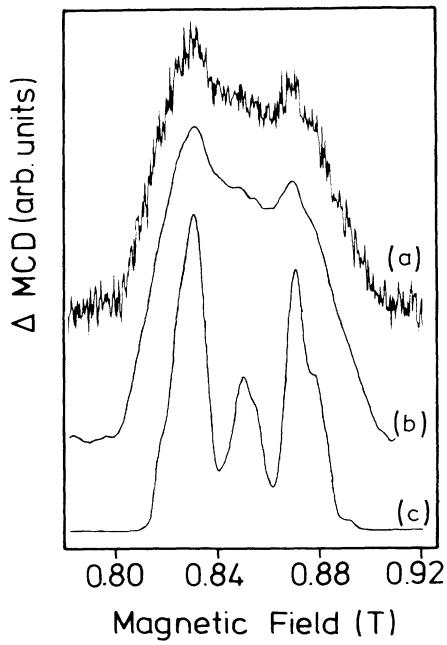

FIG. 2. Curve (a): optically detected ESR spectrum measured at $E=1.46$ eV for the magnetic field $\mathbf{B}_0 \| [1\bar{1}0]+10°$ in a (110) plane, $T=1.46$ K. Curve (b): after digital filtering (Ref. 6). Curve (c): after applying a deconvolution algorithm. The linewidth used for the deconvolution was 16 mT.

agreement with experiment, in view of the rather poor resolution of the ODESR spectrum. A trigonal acceptor in SI, GaAs has already been observed in photo-ESR investigations[9] and tentatively assigned to a Ga_{As}-B_{Ga} pair defect ($FR3$). The observed g factors ($g_\perp=2.89$, $g_\parallel=2.11$) are, however, different from the ones observed here. Since no hf interactions were resolved, the presence of Ga_{As} was only speculative. Assuming an intrinsic defect as the origin of the ODESR spectrum, the hf splitting can be either due to ^{75}As ($I=\frac{3}{2}$, 100% abundance) or due to the two Ga isotopes ^{69}Ga ($I=\frac{3}{2}$, 60% abundance) and ^{71}Ga ($I=\frac{3}{2}$, 40% abundance) with slightly different nuclear magnetic moments. A line-shape simulation of the ODESR spectrum for $\mathbf{B}_0 \| [100]$ is shown in Fig. 4. For the same linewidth as was used for the deconvolution (16 mT for each of the 4 hf lines), the spectrum was simulated for the hf splitting derived from the angular dependence. Assuming ^{75}As as central nucleus the line shape disagrees significantly with the experimental one [Fig. 4, curves (a) and (b)]. If the hf interaction was due to Ga isotopes, then the apparent splitting seen in the angular dependence is an average over the two isotopes. Assuming this and taking into account the abundances the line shape of Fig. 4, curve (c) is obtained (single hf linewidth again 16 mT). The agreement with the experiment [Fig. 4, curve (b)] is excellent. An impurity analysis rules out other nuclei, with $I=\frac{3}{2}$ and similar abundances and magnetic moments, respectively. Our analysis suggests that the unpaired electron is centered at a Ga nucleus.

If we compare the measured hf interactions with the corresponding values of the free Ga atom in a simple linear combination of atomic orbitals picture we find about 6% of the unpaired spin located in $4s$ orbitals and about 46% in $4p$ orbitals at the Ga nucleus. This is what one expects for a deep localized acceptor Ga_{As} with the unpaired electron in a T_2 orbital. For an interstitial Ga atom the unpaired electron is in an A_1 state. There the hf interaction is dominated by a large isotropic part as observed by Kennedy *et al.*[10] About one-half of the electron is located at the ligands. If the delocalized electron resides mainly on the four nearest Ga neighbors one can estimate their ligand hf interaction by assuming an sp^3 character in their orbitals. From such an estimate it follows that 26 ligand lines cause a total linewidth of 15 mT

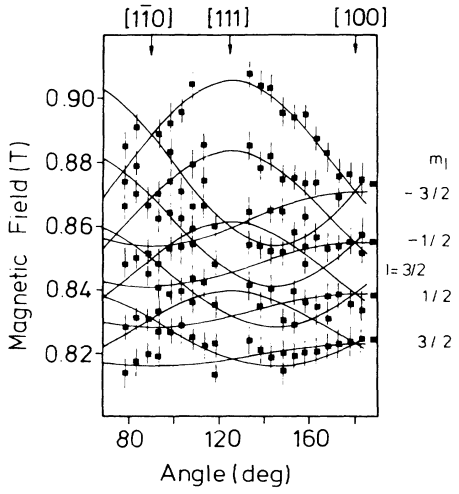

FIG. 3. Angular dependence of the optically detected ESR lines for a rotation in a (110) plane from [1$\bar{1}$0] to [100]. The ■ mark the line peak positions.

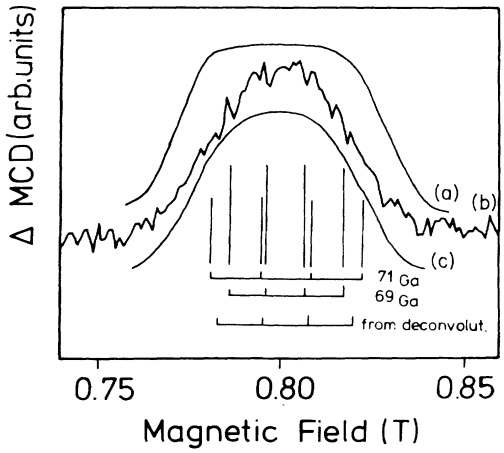

FIG. 4. Curve (a): optically detected ESR spectrum for $\mathbf{B}_0 \| [100]$. Curve (b): simulated ESR spectrum assuming the hyperfine interaction with a nucleus $I=\frac{3}{2}$ and 100% abundance (i.e., ^{75}As). Curve (c): simulation for Ga nuclei with $I=\frac{3}{2}$ and two isotopes, ^{69}Ga and ^{71}Ga, with 60% and 40% abundances, respectively.

for each hf line, which is consistent with the experimentally determined linewidth. Due to the many lines the ligand hf interactions are not resolved.

From analysis of the ODESR spectrum the origin of the trigonal symmetry of the Ga_{As} defect cannot be determined and it remains open to speculation. However, the defect must be a pair defect, of which one member is Ga_{As}; the other, X, is unknown. The possibility that it is a Jahn-Teller-distorted isolated Ga_{As} is excluded, since the energy levels of the defect are not consistent with the ones ascribed to the isolated Ga_{As} defect (78 and 203 meV) on the basis of many experiments[11,12] (see below). We have observed this specific defect in seven different samples in LEC- as well as in HB-grown material from stoichiometric and nonstoichiometric melts. It is thus very likely that an intrinsic defect is involved in this cation-antisite-X defect pair. X must, however, be diamagnetic if nearby; the ESR spectrum would have shown a fine-structure splitting greater than 50 mT if it was a paramagnetic nearest neighbor.

A Ga_{As} defect would be a double acceptor, of which the singly ionized state A^- is paramagnetic, while the two charge states A^0 and A^{2-} are diamagnetic. In SI material the Ga_{As}-X pair defect can be detected before $EL2$ bleaching in the dark. The transfer of $EL2$ to the metastable state and the subsequent hole capture by the acceptors results in an increase of its MCD signal by a factor of 2–3. This is thought to be due to a hole capture which converts the Ga_{As}-X pair from the diamagnetic to the paramagnetic charge state. The shift in the Fermi level closer to the valence band after $EL2$ bleaching could also account for this observation. The coexistence of the MCD spectrum of the Ga_{As}-X pair with the MCD spectrum of $EL2^+$ before bleaching indicates that one of its energy levels is close to the $EL2^+$ level, i.e., at $E_v+0.54$ eV. The trigonal pair defect is also present in Ga-rich samples (LEC: [As]/[As+Ga] $=0.475$; HB: $T_{As}=613$°C) which again points to an acceptor with its energy levels in the lower half of the band gap. Upon irradiation of the sample with a second monochromatic light source the MCD band at $E=1.46$ eV always decreases as a function of the exciting photon energy by $\sim 10\%$ (photon flux $\approx 10^{16}$ s^{-1}) with a sharp decrease between 1.5 and 1.4 eV and 1.3 and 1.4 eV, respectively (Fig. 5). The photoquenching experiments can be explained by assuming two energy levels in the lower half of the gap (see inset in Fig. 5). The energetically lower level, when occupied by one electron, gives rise to the paramagnetic MCD transitions. The MCD band at $E=1.46$ eV is interpreted as being due to the photoionization transition to the conduction band (σ_{n_1}). The band shape (onset, peak maximum) is very similar to the ionization transitions of transition metals in GaAs studied with the MCD-ODESR technique, one example being Mn^{2+} in GaAs with its level 117 meV above the valence band.[13] The onset of the band (see Fig. 1) at 1.425 eV would locate the lower level at $E_v+(0.1\pm0.01)$ eV. The second level (one additional electron) can be estimated from the photoquenching of the MCD (Fig. 5). It is around $E_v+(0.5\pm0.1)$ eV. The capture of a second electron converts the paramagnetic to the diamagnetic charge state (process σ_{p_2}) which could dominate up to

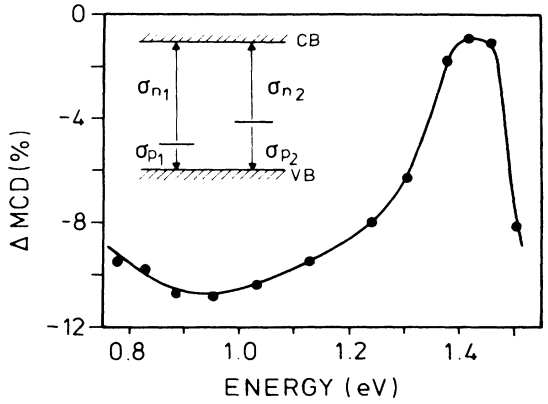

FIG. 5. Spectral dependence of the quenching of the magnetic circular dichroism of the absorption at 1.46 eV. Inset: energy levels and ionization transitions for a double acceptor in GaAs.

that photon energy where the electron ionization transition σ_{n_2} starts at $E=1.1$ eV. The drop in the quenching curve (Fig. 5) indeed starts at around 1 eV. The efficiency of the quenching process (σ_{p_2}) is reduced due to the back conversion (σ_{n_2}) towards the paramagnetic charge state. The ionization process (σ_{n_1}) from the lower level starts just below the band gap energy. It quenches the MCD and accounts for the observed sharp MCD decrease at $E>1.4$ eV. This gives further evidence to attribute the MCD band at $E=1.46$ eV to an electron ionization transition of the Ga_{As}-X pair defect.

As to the energy levels of the isolated cation antisite defects in GaAs two different results are under consideration. In LEC crystals grown from gallium-rich melts a native double acceptor with energy levels 78 and 203 meV above the valence band is found and assigned to Ga_{As}.[11,12] In liquid-phase epitaxial GaAs as well as in bulk crystals grown from gallium-rich solutions (traveling heater method) a hole trap with energy levels $E_v+0.4$ eV and $E_v+0.7$ eV is commonly found.[14,15] The levels are due to native defects and also assigned to Ga_{As}. Theoretical calculations are more consistent with this assignment.[16] Whether the isolated Ga_{As} is present in SI stoichiometric GaAs in a concentration range of relevance for the compensation mechanism is not clear. The new ESR lines observed after $EL2$ bleaching with conventional detection of ESR [labeled $FR1$ or $BE1$ (Refs. 15 and 17)] show a complex substructure. Neither defect can be identified with the trigonal Ga_{As}-X pair defect observed in ODESR because the following properties are different: The ESR transitions of $BE1$ and $FR1$ are at least partly due to electrical dipole transitions as seen from the temperature dependence of the ESR signal and its sensitivity to the electrical field distribution in the microwave cavity. Upon annealing under As equilibrium pressure at 1200 °C and rapid quenching (inverted thermal conversion treatment) the intensity of $BE1$ increases by two orders of magnitude,[17] which was not observed for the Ga_{As}-X pair. The trigonal Ga_{As}-X pair is stable when annealed at high temperatures (500 °C, 1 h) while $FR1$ and $BE1$ are thermally destroyed at 450 °C. Neither $FR1$ nor $BE1$ can therefore

be the major compensating acceptors because of their thermal destruction at 450 °C, upon which the sample does not change its SI character.

The concentration of the paramagnetic $EL2^+$ defect is 10^{16} cm^{-3} while that of the extrinsic shallow acceptors (C, Zn) is of the order of $(1-2)\times10^{15}$ cm^{-3}. The dominant intrinsic acceptor in high-resistivity SI material should be in the concentration range of 10^{16} cm^{-3} and could well be the trigonal acceptor pair observed here. Unfortunately, no concentrations can be determined from the MCD since the optical cross sections of the trigonal pair are not known. However, the fact that it was observed with about the same signal intensity in so many different SI samples suggest that this defect is not a result of a particular thermal treatment but a major intrinsic defect as is $EL2$.

The trigonal distortion on the Ga_{As}-X pair is either due to X being a gallium vacancy or due to X being an interstitial As_i or Ga_i at the nearest [111] site (a near site is assumed due to the significant influence of X on the g value). The triple acceptor Ga_{As}-V_{Ga} (Ref. 17) would be the stable configuration of an arsenic vacancy V_{As} as was calculated in Ref. 18 and would nicely fit with the stoichiometry dependence of the $EL2$ formation.[19] An As_i would be favored in SI As-rich material. Moreover, the creation of a cation antisite Ga_{As} may leave the replaced As atom nearby as As_i^+ bound by Coulomb attraction, the positive charge being required for As_i to be diamagnetic. The midgap $EL2$ defect is singly positively charged due to the positive charge of the As interstitial.[2] Charge neutrality would require an additional negatively charged defect close to it. An acceptor like a Ga_{As}-related defect could fulfill this requirement. Also the high mobility in SI GaAs could be explained by the formation of close donor-acceptor pairs leading to a dipolar scattering mechanism.[20]

The question arises whether the trigonal acceptor and the As_{Ga}-As_i pair are both parts of a larger linear complex along the [111] direction, possibly the complete $EL2$ structure. The As_i would be two bond lengths away from As_{Ga} and one from Ga_{As} on the opposite side. In the optically detected electron-nuclear double-resonance experiments of the As_{Ga}-As_i pair the Ga_{As} could not be seen, since Ga is 7.37 Å away from the As_{Ga} and no nuclei beyond the *2nd* As shell (4.67 Å away) could be detected.[2]

The binding of the As_i to the As_{Ga} is not understood at present.[21] The presence of the nearby Ga_{As} may modify the picture and lead to a better understanding of the As_{Ga}-As_i pair.

We have identified for the first time a cation antisite defect in GaAs and its energy levels. The trigonal acceptor pair Ga_{As}-X is probably the long-sought major compensating partner of the As_{Ga}-As_i $EL2$ pair defect.

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