

Optical Properties of As-Antisite and *EL2* Defects in GaAs

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This Letter reports the first application of an ESR-tagged magnetic circular dichroism measurement to a paramagnetic deep-level defect in a semiconductor. In semi-insulating GaAs two new absorption bands are found at 1.05 and 1.29 eV. Both bands are identified as intra-center electronic transitions of the As-antisite defect. The analysis of the absorption and concentration data implies that the "dominant electron trap" (*EL2*) in GaAs is not the As antisite.

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Antisite defects in III-V compounds are important intrinsic crystal perturbations. They give rise to deep levels in the gap and are considered to play a major role in limiting the performance of optoelectronic devices. The anion antisite, where a group-V atom occupies a group-III site, is a double donor. In its singly ionized charge state it is paramagnetic. Its electron spin resonance (ESR) was observed in as-grown GaAs,¹ and in plastically deformed,² electron-irradiated,³ and neutron-irradiated^{4,5} samples. In these ESR spectra only the hyperfine interaction with the central As nucleus was resolved. Therefore the possibility that the spectra may be due to As interstitials could not be excluded.

The dominant electron trap in GaAs is the so-called *EL2* center. This defect has a deep level at $E_c - 0.75$ eV, which is generally believed to cause the semi-insulating property of GaAs, and shows a characteristic optical excitation at 1.18 eV.^{6,7} The chemical identity of *EL2* has been a matter of intensive research. Recently it was suggested that *EL2* is the neutral charge state of the As antisite,^{2,8-10} or the antisite together with another nearby defect.⁷

In this paper we study the optical absorption and the magnetic circular dichroism (MCD) in the absorption of semi-insulating GaAs. The MCD found arises from a paramagnetic defect.¹¹ Monitoring of the microwave-induced changes of the MCD allows a highly sensitive measurement of the ESR of the defect.^{12,13} Further, we measured the dependence of these optically detected ESR transitions on the optical wavelength (MCD tagged by electron spin resonance). In this technique the magnetic field is

fixed to one particular ESR transition and the optical wavelength is varied through the absorption spectrum, while the optically detected signal of this ESR transition is monitored. Thus one measures only the MCD of those absorption bands belonging to the paramagnetic center and ESR spectrum, respectively. This study represents the first application of an ESR-tagged MCD measurement to defects in semiconductors. It demonstrates the high sensitivity and power of this method. Further details of the technique and the apparatus are described elsewhere.¹⁴

The measurements were done on liquid-encapsulated-Czochralski-grown GaAs samples, undoped as-grown samples, undoped plastically deformed samples, and chromium-doped samples. The key results are practically the same for all samples.

Figure 1 shows the optical absorption spectrum

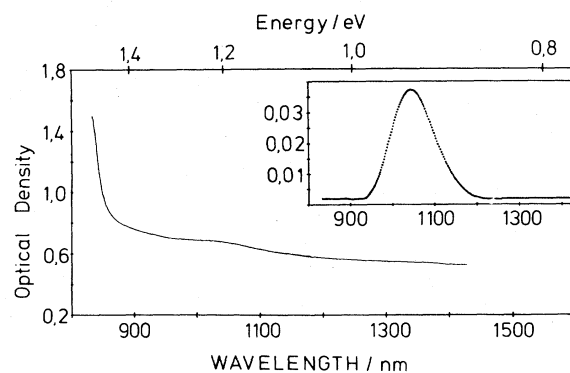


FIG. 1. Optical absorption of as-grown semi-insulating GaAs (crystal thickness $d = 0.3$ cm) at $T = 1.4$ K

for as-grown samples with a weak absorption band at 1.18 eV. In the inset this absorption is shown with enlarged scale after subtraction of a smooth background line. This band was studied in detail by Martin⁶ and Kaminska *et al.*,⁷ who identified it as an intracenter electronic transition of the *EL2* center.⁷ From the absorption data and concentration reported in Ref. 7, we determine the concentration of the *EL2* center in this sample as $5 \times 10^{15} \text{ cm}^{-3}$. The MCD, i.e., the difference of the absorption of left- and right-circular polarized light, of the same sample is shown in Fig. 2(b) (curve *a*). It could be measured up to $T = 20 \text{ K}$. Measurements as a function of field and temperature show that the MCD originates from a paramagnetic defect.¹¹ The integrated MCD corresponds to the absorption by this defect (see below). In it [see Fig. 2(a)] we identify two optical transitions at 1.05 ± 0.02 and $1.29 \pm 0.02 \text{ eV}$. Within experimental error the integral over the total MCD vanishes. Thus we have observed all transitions from the ground state to the nearby excited states.¹¹

In order to identify the defect responsible for this absorption we measured the microwave-induced change of the MCD at $\lambda = 1350 \text{ nm}$, $B_0 \parallel [100]$, $T = 1.4 \text{ K}$, and $\nu_{\text{ESR}} = 24.316 \text{ (K band)}$. The resulting ESR spectrum (see Fig. 3) is commonly as-

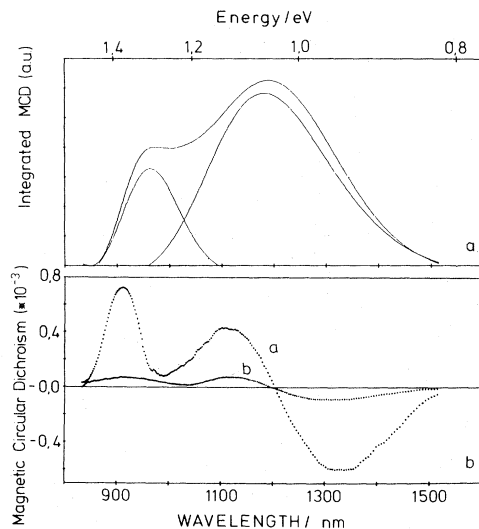


FIG. 2. (a) Integrated magnetic circular dichroism of as-grown semi-insulating GaAs and its decomposition into two Gaussian bands. (b) Curve *a*: Magnetic circular dichroism of the absorption of as-grown semi-insulating GaAs. $T = 4.2 \text{ K}$, $B = 2 \text{ T}$. Curve *b*: Excitation spectrum of the optically detected electron spin resonance lines of the As_{Ga} antisite defect (MCD tagged by spin resonance).

cribed to the As_{Ga} center.¹⁻⁵ The four-line structure, the g value, and the ^{75}As hyperfine-splitting parameters agree with those measured previously with conventional ESR.^{1,4} The weak lines between the ^{75}As hyperfine lines are due to forbidden transitions. To check if the total absorption of Fig. 2 is due to the antisite, we fixed the magnetic field to one of these ESR transitions. We then monitored this ESR line as a function of the optical wavelength. Thus we obtain the MCD tagged by spin resonance [see curve *b* in Fig. 2(b)]. Since this spectrum follows the shape of the original MCD, both transitions in Fig. 2(b) belong to the As_{Ga} ESR spectrum. This ESR spectrum is isotropic, which implies that the center has tetrahedral symmetry.

In a "rigid-shift" analysis¹¹ the MCD reflects the derivative of an absorption band, the peak-to-peak splitting of which is the spin-orbit splitting Δ of the excited state. Our results can be explained by a superposition of two such derivative structures due to two absorption bands, with excited states both split by spin-orbit interaction. This analysis gives $\Delta_1 = 0.23 \pm 0.02 \text{ eV}$ for the 1.05-eV transition and $\Delta_2 = 0.18 \pm 0.02 \text{ eV}$ for the 1.29-eV transition. These numbers lie between those of atomic arsenic and perfect crystalline GaAs.¹⁵ Since the absorption is unmeasurably weak a moments analysis could not be applied.¹¹ We therefore do not know whether these rigid-shift results for the spin-orbit splitting of the two states are very reliable. The orientation dependence of the MCD shows that the defect has tetrahedral symmetry and a perturbation in the neighboring shell of the central As atom can be ruled out. A perturbation farther away, for exam-

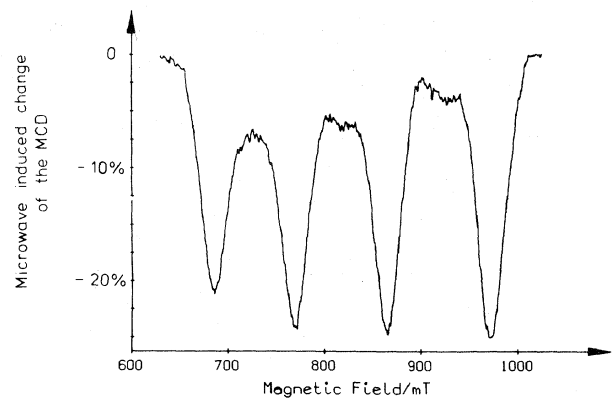


FIG. 3. Optically detected electron-spin-resonance spectrum of the As_{Ga} antisite defect in semi-insulating GaAs. $B_0 \parallel [100]$, $T = 1.4 \text{ K}$. $\nu_{\text{ESR}} = 24.31 \text{ GHz}$, measured at $\lambda = 1350 \text{ nm}$.

ple an interstitial, is, however, possible. The facts that the center of the defect is an As atom, that the defect has tetrahedral symmetry, and that the excited states are split by spin-orbit interaction imply that these excited states are p -like in character. Thus, they belong to the T_2 representation of the T_d point group. From the optical selection rules it follows that the deep level in the gap has A_1 symmetry. This result is also consistent with the fact that ESR shows a hyperfine splitting of the central As nucleus.

We now address the question of whether the ESR spectrum of Fig. 3 and the MCD (Fig. 2) are indeed due to the As antisite (As_{Ga}), or whether they arise from a tetrahedral As interstitial, which could give the same ESR spectrum. Self-consistent Green's-function calculations of the corresponding defects in GaP show that the anion antisite has a deep A_1 level in the gap, and the anion interstitial has a deep T_2 level.¹⁶ This result should also hold for GaAs. Because the above MCD results imply that the defect symmetry is T_d and that the deep level belongs to the A_1 representation, the anion interstitial is ruled out. Thus, the results of Figs. 2 and 3 are due to the As antisite.

The above absorption data of the antisite are summarized in Fig. 4. Theory shows that the anion antisite induces two localized states in the region of or close to the band gap.^{17,18} The energetically lower state belongs to the A_1 representation. Thus, its wave function at the central atom is built from As s orbitals. For the paramagnetic charge state, D^+ , this level is filled with one electron. Its energy is $E(D^+/D^{++}) = E_c - 1$ eV.² The other antisite-induced state is threefold degenerate (excluding spin) and transforms according to the T_2 representation. Thus, its wave function is p -like at the center. Calculations by Bachelet, Schlüter, and Baraff¹⁷ find this state as a sharp resonance at the

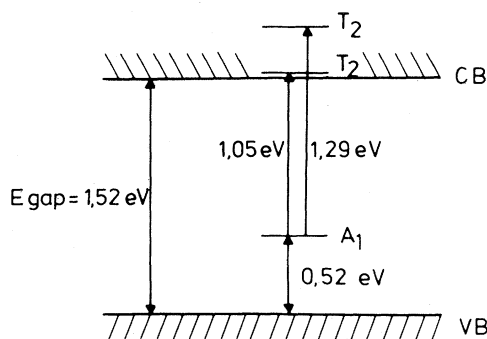


FIG. 4. Energy levels of the As antisite in semi-insulating GaAs.

bottom of the conduction band. Additional calculations show that its wave function has considerable weight in the immediate region of the As_{Ga} center similar to the A_1 bound state.¹⁹ The splitting between the deep A_1 level and this T_2 resonance state is calculated as 0.93 eV.¹⁷ A slight modification of this picture is necessary, because the experimental results require two localized excited states of T_2 symmetry. Calculations of the anion antisite in GaP indicate one possible explanation; the hybridization of the antisite-induced T_2 state with the T_2 conduction-band density of states can induce a double (or multiple) peak structure (see Fig. 8 in Ref. 18), which then could be consistent with the experimental results of the two intracenter transitions.

We now compare the D^+ state of As_{Ga} and the $EL2$ center. Kaufmann has measured the concentration of D^+ centers in one of our as-grown samples.²⁰ He determined the concentration as 1×10^{16} cm^{-3} . Together with the $EL2$ results of this sample we get the relative concentration of $EL2$ to D^+ centers as 1:2. The D^+ intracenter transitions are not visible in the absorption spectrum; therefore the cross sections of the intracenter excitations of $EL2$ and As_{Ga} are different. We estimate that $\sigma(EL2) \geq 10\sigma(D^+)$. This result is important in view of the recent suggestion that $EL2$ might be the neutral charge state of the As antisite.² The cross sections for the intracenter transitions of the D^0 and the D^+ centers should be similar. Because the wave functions of D^0 are slightly more extended, we expect $\sigma(D^0) < \sigma(D^+)$. The inconsistency of these two inequalities for the cross sections with the suggestion that $EL2$ and D^0 are identical implies that the $EL2$ center is most likely not the As antisite.

In conclusion, we report the first application of an ESR-tagged MCD measurement to a paramagnetic deep-level defect in a semiconductor. The study demonstrates also the high sensitivity of this technique for measuring ESR. The signal-to-noise ratio can be several orders of magnitude higher than that of conventional ESR—for the As antisite it is two orders of magnitude. Thus, it should be possible to study also thin epitaxial layers. The above analysis confirms the ESR-based identification of the As antisite in GaAs. Further, two electronic transitions are found at 1.05 and 1.29 eV. They are both identified as intracenter excitations of the antisite. The comparison of the results for the antisite with those for the $EL2$ center implies that the optical band assigned to the $EL2$ is most likely not due to the antisite.

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