Optically Detected Electron-Nuclear Double Resonance of As-Antisite Defects in GaAs

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This Letter reports on the first optically detected electron-nuclear double-resonance (ENDOR) measurements of a paramagnetic semiconductor defect in which ligand hyperfine interactions could be resolved. In semi-insulating GaAs:Cr the ENDOR lines of the first-shell ^{75}As neighbors of the regular tetrahedral $AsAs_4$-antisite defect could be detected and analyzed. The ENDOR investigation reveals that at least one other $AsAs_4$-antisite complex contributes to the same ESR spectrum.

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Antisite defects in III-V compounds give rise to deep levels in the gap and are thought to be responsible for limiting the performance of optoelectronic devices. In GaAs the anion antisite defect, where an As atom occupies a Ga site (As_{Ga}), is a double donor.[1] In the singly ionized state it is paramagnetic and can be observed by electron-spin resonance (ESR).[1,2] Recently, we have shown using optically detected electron-spin resonance (ODESR) that the spectrum observed with conventional ESR is indeed due to the antisite defect and not due to an As interstitial.[3] The ESR spectrum resolves the hyperfine (hf) interaction with the central As nucleus ($I=\frac{3}{2}$) but not the ligand hf interactions. Therefore, it could not be decided whether the central As atom in the antisite defect is always surrounded by four equivalent ligands or whether an impurity or vacancy is present in a higher shell, that is, whether several antisite defects with different structures exist. An anion antisite with a nearby impurity was discussed recently as a possible configuration for the dominant electron trap in GaAs, the so-called EL2 center, in order to explain its optical quenching behavior.[4] In plastically deformed GaAs, the ESR signals can be enhanced by an order of magnitude. However, one cannot say from ESR whether one really sees exactly the same defects as in the as-grown material. This is important to know for understanding the formation mechanism of the antisite defects, e.g., in order to decide whether their formation is due to stress alone during the post-growth cooling of the crystal or whether it is influenced by impurities.

Ligand hf interactions of an inhomogeneously broadened ESR line can be resolved by electron-nuclear double resonance (ENDOR).[5] In as-grown material the antisite defect concentration is approximately $10^{16}/cm^3$. The ESR signal-to-noise ratio is only about (2–3):1 due to the large linewidth and hf splitting and therefore too low for ENDOR measurements. In plastically deformed or neutron-irradiated GaAs all attempts made in our group to measure ENDOR failed since the ESR signal could not be saturated down to temperatures of about 3 K.

In this paper we report on ENDOR measurements of antisite defects using optical detection, a method which was also used to identify shallow In donors in ZnO.[6] However, to our knowledge this is the first optically detected ENDOR of a semiconductor defect in which ligand hf interactions could be resolved and analyzed. The method is based on the highly sensitive optical detection of the antisite defect ESR reported recently,[3] in which the microwave-induced change of the magnetic circular dichroism (MCD) of the absorption is monitored. The optically detected ENDOR experiment (ODENDOR) is a triple-resonance experiment in which in addition to the microwave an rf frequency is fed into the microwave cavity.

ESR transitions quench the MCD by equalizing the $m_s=\pm\frac{1}{2}$ population difference for only a specific nuclear m_I. The residual MCD is due to other spin packets with different m_I. In an ODENDOR experiment NMR transitions are detected by the more effective quenching of the MCD if they link additional $m_I\pm1$ spin packets to the ESR transitions. The spectra were measured at 1.4 K; the microwave field was 10^{-3} mT at 24 GHz. The rf could be varied between 5 and 100 MHz with an rf field of about 0.5 mT at the sample. Since the spin-lattice relaxation time was several seconds, no microwave or rf modulation techniques could be used.

Figure 1 shows a section of the ENDOR spectrum for an angle $\theta=3°$ ($\theta=0°$ for $B_0\parallel[110]$) of liquid-encapsulated Czochralski (LEC) as-grown, semi-insulating GaAs doped with Cr. It was mea-

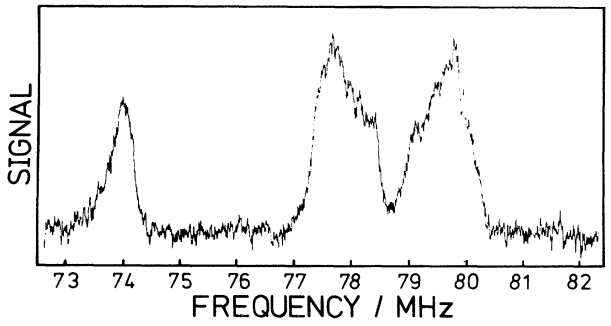

FIG. 1. Optically detected ENDOR (ODENDOR) of the As_{Ga}-antisite defect in semi-insulating GaAs:Cr. B_0 3° off [110]. $H = 989$ mT, $\nu = 24.1$ GHz, $T = 1.6$ K measured at $\lambda = 1320$ nm.

sured at $\lambda = 1300$ nm in the peak of the MCD (see Fig. 2 of Ref. 3) and by setting the magnetic field into the high-field flank of the high-field ESR line [$m_I(^{75}\mathrm{As}) = -\frac{3}{2}$] at 989 mT (see Fig. 3 of Ref. 3). The ENDOR signal height is dependent on the field position within an ODESR line. It is biggest relative to the ODESR effect when the field is nearly in the extreme flanks of the ESR lines and lowest at their peak. The ODENDOR effect is of the same order as the ODESR effect, which is never observed in conventional stationary ENDOR of solid-state defects. There the ENDOR effect is usually only at most a few percent of the ESR effect[7] so that a large number of defects and therefore rather large samples, of the order of 0.2 cm^3, are needed. Since the ODESR is more sensitive than conventional ESR (3 orders of magnitude for the As_{Ga} defect) and the ODENDOR effect is also relatively large, it should be possible to measure ODENDOR also in thin expitaxial layers. An ODESR spectrum of the As_{Ga} defect in an as-grown GaAs layer (concentration 10^{16} cm^{-3}) of 100-μm thickness was measured with a signal-to-noise ratio of $\sim 5{:}1$ with a bandwidth of 1 s^{-1}.

Applying the field shift method by measuring the ENDOR spectrum when setting the magnetic field into the other ESR lines, we established that all ENDOR lines are due to As ligands. Only lines for $m_s = +\frac{1}{2}$ were observed. Figure 2 shows the angular dependence of the ENDOR lines when the crystal is rotated in a [110] plane from [110] ($\theta = 0°$) towards [100]. As a result of the limited frequency range only lines up to 100 MHz could be detected.

The angular dependence was analyzed with the spin Hamiltonian

$$H = \tilde{g}_e \mu_B \vec{B}_0 \cdot \vec{S} + \sum_{\alpha=1}^{4} (\vec{I}_\alpha \cdot \tilde{A}_\alpha \cdot \vec{S} + \vec{I}_\alpha \cdot \tilde{Q}_\alpha \cdot \vec{I}_\alpha - g_{I\alpha} \mu_K \vec{B}_0 \cdot \vec{I}_\alpha).$$

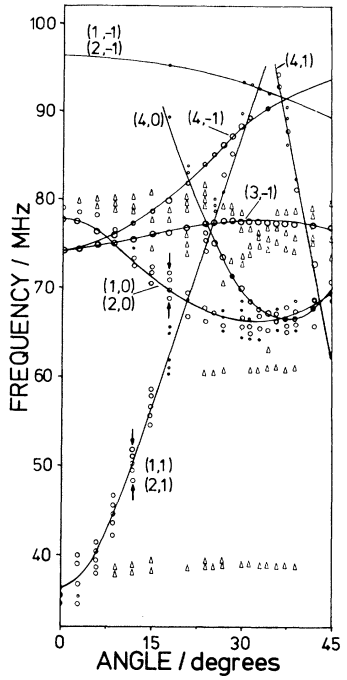

FIG. 2. Angular dependence of the ODENDOR lines for rotation of the crystal in a [110] plane from [110] $\equiv 0°$ towards [100]. Circles, regular antisite; triangles, additional antisites. Labeling of the drawn curves: nuclei (n_i, m_q), $i = 1$ to 4.

$\tilde{A}$ is the ligand hyperfine tensor, $\tilde{Q}$ is the ligand quadrupole tensor, and the sum runs over the four nearest As ligands. The Hamiltonian was diagonalized numerically and the ligand hyperfine and quadrupole interaction parameters were determined by fitting to the experimental line positions. The theoretical angular dependence, which extends up to 200 MHz, is the drawn curves in Fig. 2. The hf interactions have been calculated for an undistorted neighbor shell formed by four nearest [111] As neighbors (n_1, n_2, n_3, n_4). For rotation of the magnetic field in a [110] plane two As nuclei (n_1, n_2) are equivalent. Only the lines for these nuclei exhibit an additional splitting due to second-order hf or pseudodipolar coupling.[8] This gives a splitting into four lines for $m_q = 0$ [$m_q = (m_I + m_{I'})/2$ for a NMR transition $m_I \rightarrow m_{I'}$] and five lines for $m_q = \pm 1$ which is only slightly angularly dependent. This is indeed observed (see arrows in Fig. 2). The experimental data (circles in Fig. 2) are well explained by the calculated drawn curves which demonstrate that they are due to a regular $As_{Ga}As_4$ antisite. The results are in terms of the isotropic ligand hf constant a, the anisotropic hf constant b, and the quadrupole interaction constant q, which are related to the principal values of the respective

tensors for axial symmetry by

$$A_{zz} = a + 2b, \quad A_{xx} = A_{yy} = a - b,$$

$$Q_{zz} = 2q, \quad Q_{xx} = Q_{yy} = -q,$$

$$a = 155 \pm 0.2 \text{ MHz}, \quad b = 51 \pm 0.2 \text{ MHz},$$

$$q = 10.7 \pm 0.2 \text{ MHz}.$$

The interaction tensors have axial symmetry around the [111] connection line to the central As nucleus. There are, however, ENDOR lines which cannot be explained by the calculated angular dependence (triangles in Fig. 2). They can be measured within the same magnetic field range within all four ODESR lines as those belonging to the regular configuration. Thus in as-grown semi-insulating material, apart from the fully symmetrical $AsAs_4$ defect, at least one other probably more complicated defect contributes to the same ESR spectrum. From the signal height of the ENDOR lines one can estimate that the concentration of the latter must be of the same order as that of the regular configuration. An analysis of the additional antisite ENDOR lines is under way.

The change of the signal height of one ENDOR line belonging to the regular $AsAs_4$ center was monitored during change of the optical wavelength, that is, one measures a kind of optical-excitation spectrum of the ENDOR line. Figure 3 shows that both optical transitions as discussed in Ref. 3, which were found from the ESR tagging to belong to the As_{Ga} ESR spectrum, also belong to the ENDOR line of the regular configuration. It can therefore be excluded that one of the two optical transitions belongs to a perturbed center and that the other belongs to the regular configuration. This is the first experiment in which the optical-absorption

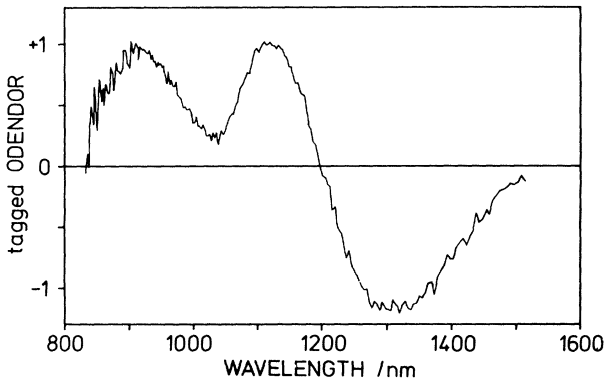

FIG. 3. Excitation spectrum of the optically detected ENDOR lines of the As_{Ga}-antisite defect (MCD tagged by ENDOR).

bands of a defect are directly correlated to an ENDOR line and therefore to a structural detail of a defect.

First experiments with plastically deformed undoped GaAs gave very surprising results. Upon plastic deformation the conventional As_{Ga} ESR increases by a factor of 10.[1] This ESR signal enhancement is, however, not observed in the MCD measurements in the same sample. The strength of the MCD is within the range of the As_{Ga} concentration fluctuations for undeformed and deformed samples the same. Thus the additional As_{Ga} defects produced by deformation must have different optical properties such that their MCD is not observable in the optical range between 0.7 and 1.5 eV. The antisite defects seen by MCD and ODESR in deformed material are probably those contained in the material before deformation. The ODENDOR lines, however, differ significantly in frequency position and angular dependence from those shown in Fig. 2. This indicates that the antisite structure may be strongly influenced by plastic deformation. A further detailed ENDOR investigation is under way.

The different nature of As_{Ga} defects in deformed material is corroborated by the observation that their spin-lattice relaxation time is so short that the conventional ESR spectrum could not be saturated at 3 K with a microwave power of the order of 10 mW ($Q = 14000$). T_1 for the regular and additional $AsAs_4$ defects in undeformed GaAs was found to be 6 s at 1.4 K and 980 mT.

Analyzing the ligand hyperfine data of the $AsAs_4$ defect with a simple linear combination of atomic orbitals approach as was done for the PP_4 antisite defect in GaP,[9] we find that 17% of the unpaired electron resides on the central As nucleus while 66% resides on the four nearest As ligands, where the As atomic values were taken from Morton and Preston.[10] This is similar to the PP_4 analysis where the respective values are 26% and 66%. Therefore 83% of these unpaired electrons are in the $AsAs_4$ cluster, 92% in the PP_4 cluster. The quadrupole interaction found for the As ligands is surprisingly large. One would expect the dominant quadrupole interaction to be due to a point charge at the central nucleus, for which one obtains only $q = 3.61$ MHz assuming a Sternheimer antishielding factor γ_∞ of 30.[11] Apparently, the covalent bonding to the four As ligands has a large influence on the quadrupole interaction.

Recent calculations of the distortion around the antisite defect show only a very small distortion which is unlikely to cause such a large electrical

field gradient.[12]

In conclusion, we report the first optically detected ENDOR measurements of a point defect in a semiconductor in which ligand hyperfine interactions were resolved and analyzed. We also report on the first ENDOR-tagged MCD measurements in which a direct correlation between an optical-absorption band and an ENDOR line is established, which with high precision resolves the structural details of a defect. The method is several orders of magnitude more sensitive than conventional ENDOR and makes possible the study of structures in low-concentration samples or thin layers. When lasers are used as light sources, a high spatial resolution for such a structural investigation could also be achieved.

The results on the As_{Ga}-antisite defects in semi-insulating GaAs and in plastically deformed GaAs show that although the regular tetrahedral $AsAs_4$ complex exists, there are several other $AsAs_4$-antisite complexes hidden under the same ESR spectrum. They are either deformed by stress or complexed with additional impurities. This should be taken into account when one discusses the possible relation between the EL2 defect and the antisite defects.

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