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Optical Detection of Electron Nuclear Double Resonance on the Residual Donor in GaN

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Abstract

Optically detected electron nuclear double resonance (ODENDOR) was measured in the 2.2 eV ‘yellow’ luminescence band associated with the residual donor in n-type undoped GaN. The ODENDOR lines are due to gallium and show a quadrupole splitting which can be described with an axial tensor. The quadrupole parameter was estimated to be q(^{69}Ga) = 1/2 Q_{zz} = 0.22 MHz. A hyperfine interaction for ^{69}Ga of about 0.3 MHz for the isotropic and of about 0.15 MHz for the anisotropic part was estimated from the width of the ODENDOR lines. It is tentatively suggested that a Ga interstitial is the residual donor.

Application of gallium nitride for optical devices in the near UV region requires a control of the native and extrinsic defects. Undoped MOVPE- and HVPE-grown GaN layers have high residual n-type conductivities with typically 10^{17} cm^{-3} to 10^{19} cm^{-3} conduction electrons, exceeding the concentrations of impurities [1] [2]. This strongly suggests that the conductivity is due to native defects. The nature of the responsible residual donor has not been identified. It is often believed to be the N vacancy [1] [2] [3]. An EPR line with a halfwidth of about 0.5 mT was observed in nominally undoped, MOVPE-grown GaN and associated with the residual donor by correlated conductivity measurements [4]. The g values of the axial g tensor were determined to be $g_{\|}$ = 1.9515 and $g_{\wedge}$ = 1.9483. But no conclusion could be drawn from the structureless EPR line on the nature of the donor which was also observed with optically detected EPR (ODEPR) via the so called ‘yellow’ luminescence band at 2.2 eV [5].

We report on the first optically detected electron nuclear double resonance (ODENDOR) measurements on the residual donor in GaN. The nominally undoped GaN layers were grown on sapphire with MOVPE. The ODENDOR spectra were measured in the yellow luminescence as an intensity change of the ODEPR line of the donor at 1.5 K. ODENDOR was measured with cw microwave radiation and amplitude modulation (500 Hz) of the radio frequency [6].

In Figure 1 (upper trace) the ODENDOR spectrum is shown for B || c. The relative ODENDOR effect with respect to the luminescence intensity was about 2 X 10^{-5}. We found ODENDOR signals only between 7 MHz and 14 MHz. The recording time of the spectrum was about 10 hours because of the extremely weak signals. The ODENDOR effect vanished for the magnetic field outside the sharp donor ODEPR resonance. Since the ODENDOR lines are centered about the Larmor frequencies of the two Ga isotopes (^{69}Ga and ^{71}Ga with abundancies of 60.1% and 39.9%, respectively, both with I = 3/2) it can be concluded that they are due to Ga interactions. The angular dependence of the ODENDOR spectrum is shown in Figure 2. The crystal was rotated from B || c to B ^ c in steps of 15 degrees. The peak positions of the rather broad ODENDOR lines were determined by a deconvolution of each spectrum with Gaussian lines. The squares in Figure 2 represent the positions of the line peaks. The solid lines are calculated from the spin Hamiltonian for the ODENDOR transitions including the nuclear Zeeman energy and a quadrupole interaction. We analyzed our spectra with the assumption that they originate from Ga nuclei with an axial quadrupole tensor $\underline{\underline{Q}}$ oriented with its principal z axis along the c-axis. The quadrupole interaction parameter q = 1/2 Q_{zz} was calculated to be *q*(^{69}Ga)/h = 0.22 MHz. From the ratio of the nuclear quadrupole moments of ^{71}Ga and ^{69}Ga we inferred the quadrupole interaction of the isotope ^{71}Ga *q*(^{71}Ga)/h = 0.14 MHz. The quadrupole splitting of the ^{69}Ga isotope is larger by about 60% than that of the ^{71}Ga. This can be clearly seen in Figure 2. The splitting of the ODENDOR lines of both isotopes follows exactly to the ratio of their quadrupole moments which proves that the lines arise from Ga nuclei with quadrupole interactions and not from hyperfine (hf) interactions which would cause a different splitting pattern. The hf interaction must be hidden in the linewidth of the relatively broad ODENDOR lines. An estimate of an upper limit of the hf interaction from the width of the ODENDOR lines gives 0.5 MHz for ^{69}Ga and 0.64 MHz for ^{71}Ga (B || c). The spectrum cannot be explained for larger hf interactions irrespective of the assumed individual line width. Figure 1 (solid line) shows the calculated ODENDOR spectrum for B || c assuming a quadrupole interaction of one type of Ga nuclei with axial symmetry. An individual linewidth of 0.6 MHz (including hf interactions) was assumed. The calculated ‘stick’ spectrum is also shown. The relative probabilities of the ODENDOR transitions were taken into account as well as the relative abundances of both isotopes. The quantum numbers m_q ($m_q = 1/2 (m_I + m_I´)$) of the ODENDOR transitions between m_I and $m_I´$ [6] are indicated for q > 0. The calculated spectrum agrees well with the measured one. A similarly good agreement was obtained for other orientations.

In Wurtzite GaN an axial electric field gradient is present at unperturbed lattice sites causing an axial quadrupole interaction. Distant ENDOR lines would be split by this interaction. The angular dependence of distant ENDOR lines would produce the same pattern as we measured (see Figure 2). But then it is not expected that the width of the *central* ENDOR line labeled with the quantum number $m_q = 0$ (hf line) is angular dependent. Distant ENDOR lines are not broadened by unresolved hyperfine interactions with angular dependence. The widths of the quadrupole lines ($m_q = \pm 1$) may change with the orientation of the crystal because of strain and crystal imperfections causing additional field gradients. To check whether we have measured distant ENDOR or not we analyzed the lineshape of the ODENDOR lines for different crystal orientations. In Figure 3 the lineshapes of the hf transitions ($m_q = 0$) for B || c and the superposition of both quadrupole lines ($m_q = \pm 1$) with the hf line for 55^0 off c is shown. For B || c a width of about (0.55 ± 0.05) MHz was estimated for the hf line. At 55^0 the situation is more complicated. Both quadrupole lines have the same frequency position. The hf line is separated by about 0.1 MHz from the quadrupole lines. Therefore, all three lines are superimposed. The quadrupole lines are broadened because of fluctuations of the electric field gradient produced, for example, by strain. This broadening is especially observed when the angle Φ between the z-axis of the quadrupole tensor and the magnetic field is just 54.7^0, where $3\cos^2\Phi - 1 = 0$. The hf line is not sensitive to these fluctuations. We fitted the lineshape with two Gaussian lines centered around the calculated frequency positions of the quadrupole and hf transitions. The linewidth of the hf line was estimated to be (0.3 ± 0.05) MHz. Because of the difference in the linewidths of the hf lines for both orientations we think that we did not measure distant ENDOR. We assume now that the width of the ODENDOR lines is mainly determined by an unresolved hf interaction with one type of Ga nuclei. Calculations of the linewidth assuming hf interactions with four Ga ligand nuclei assuming a N-site donor showed that it is not possible to explain an angular dependent linewidth with four or more Ga neighbor nuclei. In such a case the superposition of the hf lines of all neighbors produces a nearly constant linewidth for different crystal orientations. An angular dependent linewidth can be explained by a hf interaction with a shell consisting of one Ga nucleus. That would mean that the quadrupole interaction we measured is caused by only one Ga nucleus for each donor. Because of the axial symmetry of the quadrupole tensor we expect that the hf tensor has the same symmetry with its principal z-axis parallel to the c-axis. The hf interaction can be devided into the isotropic Fermi contact interaction a and the anisotropic tensor $\underline{\underline{B}}$ which can be described with one interaction parameter b in the axial case [6]. For B || c the hf interaction would be a + 2b and for B 55^0 off c it would be a. We estimated the hf interaction parameters from the linewidths (figure 3) to be $a/h \approx 0.3$ MHz and $b/h \approx 0.15$ MHz.

With the assumption that we have measured a central Ga atom of the donor we can interpret the results of the lineshape analysis. Two types of defects exist with a central Ga atom, the Ga interstitial and the Ga antisite defect. Boguslawski *et al.* [7] calculated that the Ga antisite is a deep defect and the Ga interstitial acts as a shallow donor. Therefore, we can exclude the observation of a Ga antisite defect. Thus, a candidate for the residual donor is the Ga interstitial. There are two different positions for an interstitial Ga atom in wurtzite GaN, the T site and the O site [7]. Both sites have C_{3v} symmetry. Without lattice distortion there would be no quadrupole interaction on either site (T and O). After Boguslawski [7] there are lattice relaxations for both interstitials. A crude estimate of the quadrupole interactions for both sites was calculated within a simple of point charge model where the electric field gradient is produced by the nearest neighbors of the relaxed interstitial, whereby the relaxation was taken from [7]. For both sites we obtained $q(^{69}\mathrm{Ga})/h \approx 0.6$ MHz which is the right order of magnitude. Because of C_{3v} symmetry in both interstitial sites it cannot be decided by symmetry which of the interstitial sites is occupied by the donor. The estimate of the quadrupole interaction is not precise enough to decide on the basis of the magnitude of the quadrupole interaction.

The formation energy of the Ga interstitial was recently calculated to be in the order of 10 eV for n-type GaN by

Neugebauer *et al.* [8]. Such a high formation energy makes it rather improbable to observe the Ga interstitial with appreciable concentrations in material grown under thermal equilibrium. However, epitaxial growth (MBE, MOVPE, HVPE) is performed far from thermal eqilibrium.

The electric field gradient at the unperturbed Ga nuclear position was determined to be $V_{zz} = 6.75 \times 10^{20}$ V/m^2 with magic angle sample-spinning nuclear magnetic resonance measurements (MASS-NMR) on GaN powder [9]. This value comes very close to the field gradient calculated from the quadrupole parameter q estimated from the angular dependence (Figure 2): $V_{zz} = (6.5 \pm 0.2) \times 10^{20}$ V/m^2 . It is a serious problem to understand with our tentative model of a Ga interstitial why the field gradients at the interstitial position and at the regular unperturbed Ga lattice site should be so similar. On the other hand a very similar electric field gradient ($V_{zz} = 6.45 \times 10^{20}$ V/m^2) was reported from Overhauser shift double resonance experiments on the donor [10]. A hf interaction is necessary to produce the Overhauser shift of the EPR line. Therefore, with Overhauser shift experiments nuclei of the defect or nearby the defect are measured.

In conclusion we tentatively suggest the model of the Ga interstitial for the residual donor. The angular dependence of the ODENDOR linewidth is in favour for this model. On the other hand, the electric field gradient estimated from the quadrupole interaction is similar to the gradient at an unperturbed Ga lattice site which is not easily understood.

Acknowledgments

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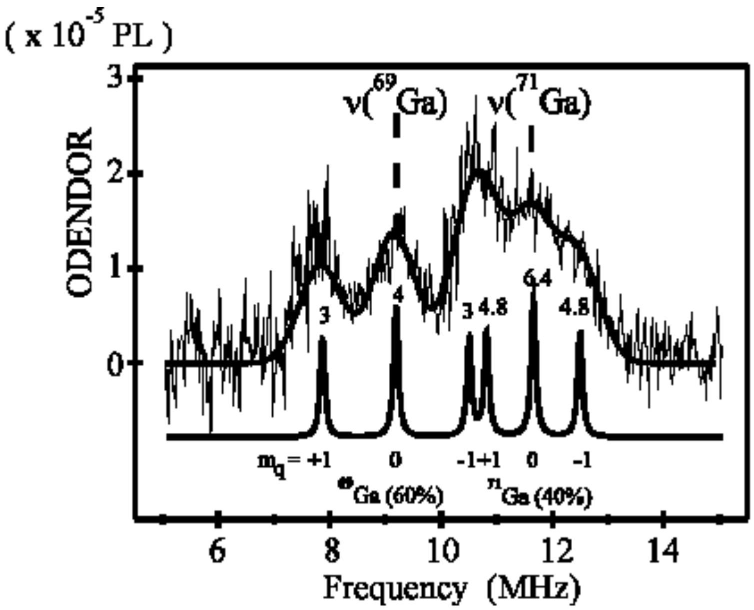

Figure 1. ODENDOR spectrum for B || c measured in the 2.2 eV luminescence; B = 896 mT, T = 1.5K; the Larmor frequencies for both Ga isotopes are marked; for the calculated spectrum (solid line) of the ODENDOR spectrum see text; the stick spectrum below represents the frequency positions of the calculated ODENDOR lines with their relative intensities; the frequency positions of the lines are characterized by the m_q quantum numbers of the quadrupole transitions; the numbers on top of the stick spectrum are the relative transition probabilities.

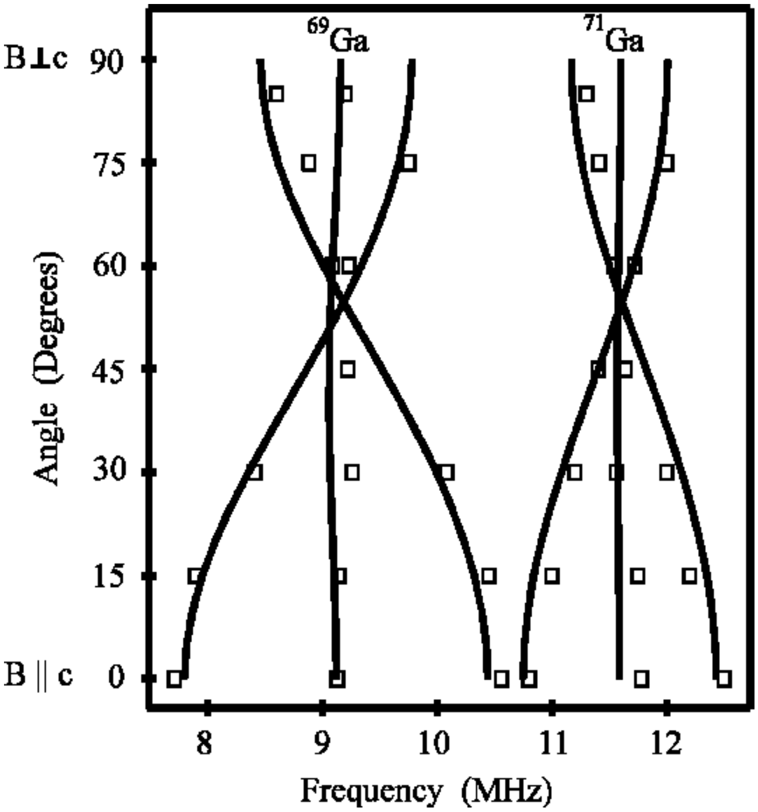

Figure 2. ODENDOR angular dependence measured from B || c (0 degrees) to B ^ c (90 degrees); the squares represent the ODENDOR line positions; the solid lines show the fit to the ODENDOR angular dependence with the assumption of a quadrupole interaction of one shell of Ga nuclei having on Ga nucleus in each shell.

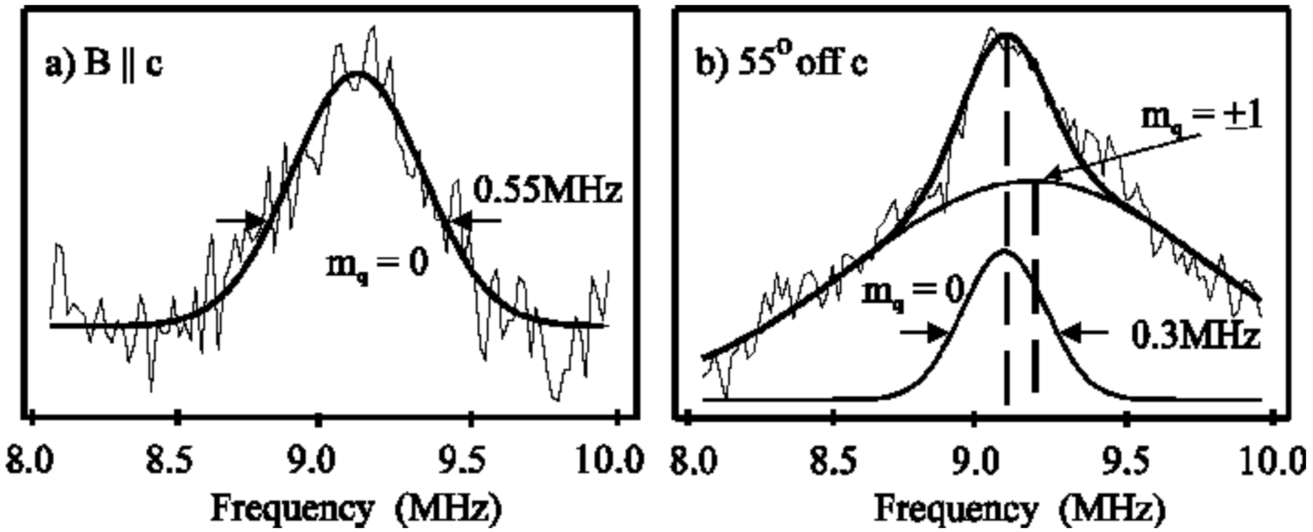

Figure 3. a) Line shape of the hyperfine (hf) transitions (m_q = 0) for B || c and b) for the superposition of the hf and the quadrupole transitions (m_q =±1) for B 55^0 off c, the solid lines show the fit to the ODENDOR lines, the linewidth estimated for the hf transition is 0.55 MHz in Figure 3a and 0.3 MHz in Figure 3b.

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