Optical detection of electron nuclear double resonance on a residual donor in wurtzite GaN

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Optically detected electron nuclear double resonance (ODENDOR) was measured in the 2.2-eV yellow luminescence band associated with a residual donor in *n*-type unintentionally doped GaN. The ODENDOR lines are due to gallium and show a quadrupole splitting that can be described with an axial tensor. The quadrupole parameter was estimated to be $q(^{69}\mathrm{Ga})/h = \frac{1}{2}Q_{zz} = 0.22$ MHz. A hyperfine interaction for ^{69}Ga of approximately 0.3 MHz for the isotropic part and of approximately 0.15 MHz for the anisotropic part was estimated from the width of the ODENDOR lines. It is tentatively suggested that Ga interstitials are residual donors. [S0163-1829(96)53740-9]

Undoped metal-organic vapor phase epitaxy (MOVPE)—and halogen vapor phase epitaxy (HVPE)—grown GaN layers have high residual *n*-type conductivities typically with 10^{17} to 10^{19} cm^{-3} conduction electrons, which is above the impurity concentrations.[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.[1–3] Recently, Boguslawski *et al.* pointed out that Ga interstitials could be other candidates for native donors.[4] An EPR line with a halfwidth of approximately 0.5 mT was observed in nominally undoped, MOVPE-grown GaN and associated with the residual donor by correlated conductivity measurements.[5] The *g* values of the axial *g* tensor were determined to be $g_{\parallel} = 1.9515$ and $g_{\perp} = 1.9483$. No conclusion on the nature of the donor could be drawn from the structureless EPR line. Optically detected EPR (ODEPR) has also been observed via the so-called ''yellow'' luminescence band at 2.2 eV.[6] The origin of this luminescence is still under discussion.[6–10]

We report 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 signal at 893 mT (see Fig. 1) at 1.5 K. Glaser *et al.* [6] showed that the high field line is due to the residual donor. The other broader resonance was tentatively assigned to a deep double donor. We used a halogen lamp with filters as the excitation source for the yellow luminescence, which was detected with a photomultiplier with a long pass filter. ODENDOR was measured with cw microwave radiation and amplitude modulation (500 Hz) of the radio frequency.[11]

In Fig. 2 the ODENDOR spectrum is shown for $\vec{B} \| \vec{c}$. The relative ODENDOR effect with respect to the luminescence intensity was approximately 2×10^{-5}. We found ODENDOR signals only between 7 and 14 MHz. The recording time of the spectrum was approximately 10 h because of the extremely weak signals. The ODENDOR effect vanished for the magnetic field outside the donor ODEPR resonance indicating that it is connected with the residual donor. Since the ODENDOR lines are located near the Larmor frequencies of the two Ga isotopes corresponding to $\nu_{69} \approx 9.1$ MHz and $\nu_{71} \approx 11.6$ MHz, respectively (^{69}Ga and ^{71}Ga with abundancies of 60.1% and 39.9%, respectively, both with $I = 3/2$), it suggests that they are due to Ga interactions.

The angular dependence of the ODENDOR spectrum is shown in Fig. 3. The crystal was rotated from $\vec{B} \| \vec{c}$ to $\vec{B} \perp \vec{c}$ in steps of 15°. The peak positions of the rather broad ODENDOR lines were determined by a deconvolution of each spectrum with Gaussian lines. The squares in Fig. 3 represent the positions of the line peaks. The solid lines are calculated from the following nuclear spin Hamiltonian for the ODENDOR transitions:

$$\mathbf{H}_n = -\mu_n g_n \vec{B} \cdot \vec{\mathbf{I}} + \vec{\mathbf{I}} \cdot \underline{\underline{Q}} \cdot \vec{\mathbf{I}}. \tag{1}$$

The first term in Eq. (1) is due to the nuclear Zeeman energy, μ_n is the nuclear magneton, and g_n is the nuclear *g* factor. The second term is the quadrupole interaction energy. $\underline{\underline{Q}}$ is

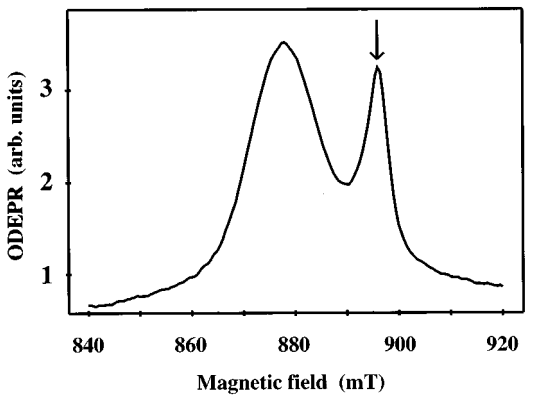

FIG. 1. ODEPR spectrum measured in the 2.2 eV luminescence; μW frequency 24.47 GHz, $T = 1.5$ K; the field position of the residual donor resonance where the ODENDOR was measured is marked with an arrow; $\vec{B} \| \vec{c}$ (wurtzite structure).

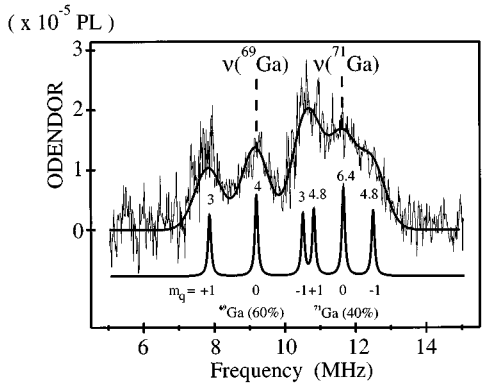

FIG. 2. ODENDOR spectrum for $\vec{B}\|\vec{c}$ measured in the 2.2 eV luminescence; $B=896$ mT, $T=1.5$ K; the Larmor frequencies for both Ga isotopes are marked; for the calculated spectrum (solid line) of the ODENDOR spectrum see text; the stick spectrum below represents the frequency positions of 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 line spectra are the relative transition probabilities, $q(^{69}\mathrm{Ga})=0.22$ MHz, $q(^{71}\mathrm{Ga})=0.14$ MHz.

the quadrupole tensor which is axial in this case and which can be described with the parameter q in its principal axes system,[11] whereby $q=\frac{1}{2}Q_{zz}$. The hyperfine (hf) interaction is neglected.

We analyzed our spectra with the assumption that they originate from one type of Ga nuclei with an axial quadrupole tensor oriented with its principal z axis along the $\vec{c}$ axis. The quadrupole interaction parameter was calculated to be $q(^{69}\mathrm{Ga})=0.22$ MHz, using Eq. (1). From the ratio of the nuclear quadrupole moments of ^{71}Ga and ^{69}Ga we inferred the quadrupole interaction of the isotope ^{71}Ga to be $q(^{71}\mathrm{Ga})=0.14$ MHz. The quadrupole splitting of the ^{69}Ga isotope is larger by approximately 60% than that of the ^{71}Ga. This can be clearly seen in Fig. 3. The fact that the splitting of the ODENDOR lines of both isotopes is the ratio of their quadrupole moments strongly suggests that the lines arise from Ga nuclei with quadrupole interaction. Had the splitting been caused by a hf interaction, it would be different. Since hf interactions scale like g_n values ($^{69}g_n=1.34\,439$, $^{71}g_n=1.708\,18$), the larger splitting would occur about the Larmor frequency of ^{71}Ga and not about the Larmor frequency of ^{69}Ga, as is observed in Fig. 2. Therefore, the hf splitting must be part of the linewidth of the relatively broad ODENDOR lines. Had the hf interactions been resolved, we would have seen a more complicated angular dependence consisting of more 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 0.65 MHz for ^{71}Ga ($\vec{B}\|\vec{c}$). The spectrum cannot be explained by larger hf interactions, irrespective of the assumed individual linewidths.

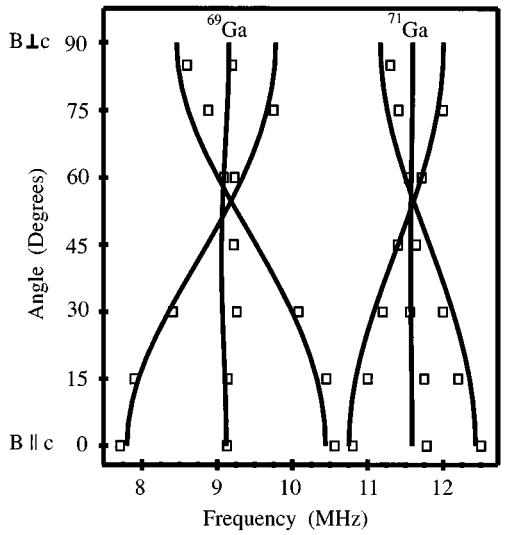

FIG. 3. ODENDOR angular dependence measured from $\vec{B}\|\vec{c}$ (0°) to $\vec{B}\perp\vec{c}$ (90°); the squares represent the ODENDOR line positions; the solid lines show the fit to the ODENDOR angular dependence with the assumption of a quadrupole interaction of Ga with axial symmetry about the $\vec{c}$ axis.

The solid line drawn on the data in Fig. 2 shows the calculated ODENDOR spectrum for $\vec{B}\|\vec{c}$ assuming one type of Ga nuclei with quadrupole interactions. The hf interaction was neglected. A background linewidth of 0.85 MHz for ^{69}Ga was assumed. The difference in the width of the ODENDOR lines of both Ga isotopes due to unresolved hf interactions, because of the different nuclear g-values, with which the hf interaction scales, was neglected. This effect is of the order of the experimental error for the estimate of the ODENDOR linewidth. The lower portion of Fig. 2 shows the calculated ''stick'' spectrum. The relative probabilities of the ODENDOR transitions were taken into account as well as the relative abundances of both isotopes. Below the stick spectrum, the quantum numbers m_q of the ODENDOR transitions[11] are shown [$m_q=(m_I+m_I'/2)$]; the ODENDOR transitions occur between m_I and m_I'). It was assumed that the quadrupole parameter q is positive. The calculated spectrum agrees well with the measured one. Good agreement was also obtained for other orientations.

In wurtzite GaN, an axial electric field gradient is present at unperturbed lattice sites causing an axial quadrupole interaction. ENDOR lines with distant Ga nuclei (''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 Fig. 3). But in this case 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 ($m_q=\pm1$) 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 line shape of the ODENDOR lines for different crystal orientations. In Fig. 4 the line shapes of the hf transitions ($m_q=0$) for $\vec{B}\|\vec{c}$ and the superposition of both quadrupole lines ($m_q=\pm1$) with the hf line for 55° off the $\vec{c}$ axis is shown. For $\vec{B}\|\vec{c}$ a width of approximately (0.85 ± 0.1) MHz was estimated for the hf line. At 55°, the situation is more

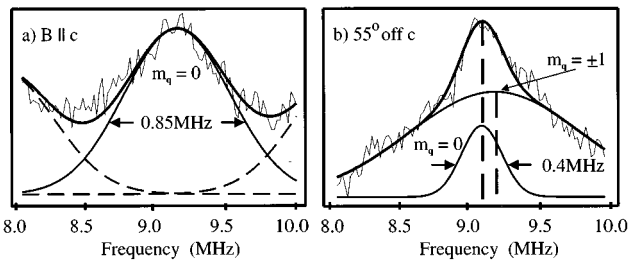

FIG. 4. (a) Line shape of the hyperfine (hf) transition ($m_q=0$) at 9.16 MHz for $\vec{B}\|\vec{c}$, at the flanks of the hf line the quadrupole lines ($m_q=\pm 1$, broken lines) located around 7.9 MHz and 10.4 MHz are superimposed (see also Fig. 2); (b) superposition of the hf and the quadrupole transitions for B 55° off $\vec{c}$, the solid lines show the fit to the ODENDOR lines, the linewidth estimated for the hf transition is (0.85 ± 0.1) MHz in (a) and (0.4 ± 0.05) MHz in (b).

complicated. Both quadrupole lines have the same frequency position. The hf line is separated by approximately 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. This broadening is especially observed if the angle θ between the z axis of the quadrupole tensor and the magnetic field is just 54.7°, where the quadrupole splitting following $(3\cos^2\theta-1)=0$ (see Fig. 3). The hf line is not sensitive to these fluctuations. We fitted the line shape 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 (0.4 ± 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 an N-site donor (such as the N vacancy or oxygen) showed that it is not possible to explain an angular dependent linewidth with four or more hf interacting 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 an 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 divided into the isotropic Fermi contact interaction a, and the anisotropic tensor which can be described with one interaction parameter b in the axial case.[11] For $\vec{B}\|\vec{c}$ the hf interaction would be $a+2b$ and for B 55° off $\vec{c}$ it would be a. We estimated the hf interaction parameters from the linewidths (Fig. 4) to be $a/h\approx 0.3$ MHz and $b/h\approx 0.15$ MHz for ^{69}Ga.

With the assumption that we have measured a central Ga atom of the donor, we can interpret the results of the line shape analysis. Two types of simple defects exist with one central Ga atom, the Ga interstitial and the Ga antisite defect. Boguslawski *et al.*[4] calculated that the Ga antisite is a deep defect and the Ga interstitial acts as a shallow donor. Therefore, we exclude a Ga antisite defect. Thus a candidate for the residual donor is the Ga interstitial. (We disregarded more complicated configurations involving several equivalent Ga atoms along $\vec{c}$.) There are two different types of positions for interstitial Ga atoms in wurtzite GaN. Both sites have C_{3v} symmetry. Without lattice distortion there would be no quadrupole interaction on either site. Boguslawski[4] found that there were lattice relaxations for both interstitials. A crude estimate of the quadrupole interactions for both sites was calculated within a simple point charge model where the electric field gradient is produced by the nearest neighbors of the relaxed interstitial, whereby the relaxation was taken from.[4] For both sites we obtained $q(69\text{ Ga})/h\approx 0.6$ MHz, which is the order of magnitude observed. Because of the C_{3v} symmetry at both interstitial sites, it cannot be decided by symmetry which of the two 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 approximately 10 eV for n-type GaN by Neugebauer *et al.*[12] 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. During epitaxial growth, especially under Ga rich conditions, it is imaginable that Ga atoms trapped at the surface acts as precursors for the interstitial. A Ga interstitial would need a barrier of approximately 5 eV to be stable at the growth temperature of approximately 1300 K, a value which seems compatible with a formation energy of the order of 10 eV. For the N vacancy, Neugebauer *et al.*[12] calculated the formation energy to be approximately 4 eV in n-type GaN. This would also be too large to result in measurable concentrations if growth is performed under thermal equilibrium conditions.

The electric field gradient at the regular Ga lattice positions 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.[13] This value comes very close to the field gradient calculated from the quadrupole parameter q estimated from the angular dependence (Fig. 3): $V_{zz}=(6.5\pm 0.2)\times 10^{20}$ 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 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.[14] An 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.

Finally, we would like to speculate about the mechanism of the yellow luminescence. According to Boguslawski,[4] both Ga interstitials have deep levels in the band gap in addition to the levels resonant with the conduction band. One could imagine that the broad resonance in the ODEPR spectrum (see Fig. 1), which was tentatively assigned to a deep double donor,[6] could be caused by the paramagnetic charge state associated with a deep level of the Ga interstitial. In this

model, both resonances would be produced by the same defect in different charge states. This would explain why the resonances always appear in tandem. It is possible to see the same defect in different charge states in ODEPR because the excitation light drives the population of the levels from thermal equilibrium. The electron transfer from Ga_i^0 to Ga_i^{2+} would be spin dependent and seen in ODEPR. Therefore, it is possible that the levels of two charge states of the Ga interstitial are involved in the recombination leading to the yellow luminescence. Whether the yellow luminescence is between Ga_i^0 and Ga_i^{2+} or between Ga_i^+ and an acceptor, is not clear at present.

In conclusion, we tentatively suggest the model of the Ga interstitial for the residual donor. The angular dependence of the ODENDOR linewidth is in favor of 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.

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[1] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett. **15**, 327 (1969).
[2] M. Ilegems and M. C. Montgomery, J. Phys. Chem. Solids **34**, 885 (1973).
[3] P. Perlin *et al.*, in 22nd International Conference on the Physics of Semiconductors, edited by D. J. Lockwood (World Scientific, Singapore, 1995), p. 2383.
[4] P. Boguslalwski, E. L. Briggs, and J. Bernholc, Phys. Rev. B **51**, 17 255 (1995).
[5] W. E. Carlos, J. A. Freitas M. Asif Khan, D. T. Olson, and J. N. Kuznia, Phys. Rev. B **48**, 17 878 (1993).
[6] E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, M. Asif Khan, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, Phys. Rev. B **51**, 13 326 (1995).
[7] T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2395 (1980).
[8] D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, Phys. Rev. B **52**, 16 702 (1995).
[9] F. K. Koschnick, J.-M. Spaeth, E. R. Glaser, K. Doverspike, L. B. Rowland, D. K. Gaskill, and D. K. Wickenden, *18th International Conference on Defects in Semiconductors* [Mater. Sci. Forum **196-201**, (1) 37 (1995)].
[10] T. Suski, P. Perlin, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, M. Bockowski, S. Porowski, and T. D. Moustakas, Appl. Phys. Lett. **67**, 2188 (1995).
[11] J.-M. Spaeth, J. R. Niklas, and R. H. Bartram, *Structural Analysis of Point Defects in Solids*, Springer Series in Solid-State Sciences Vol. 43 (Springer-Verlag, Berlin, 1992).
[12] J. Neugebauer and Ch. G. Van de Walle, Phys. Rev. B **50**, 8067 (1994).
[13] O. H. Han, Hye Kyung, C. Timken, and E. Oldfield, J. Chem. Phys. **89**, 6046 (1988).
[14] G. Denninger, R. Beerhalter, D. Reiser, K. Maier T. Detchprohm and K. Hiramatsu, Solid State Commun. (to be published).