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Magnetic characterization of conductance electrons in GaN

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New electron paramagnetic resonance (EPR) measurements in hexagonal and cubic GaN intentionally doped with silicon are presented. In both type of samples the well-known EPR resonance of the dominant shallow donor is observed, whereby the g-tensors are determined to $g_{||} = 1.9512$, $g_{\perp} = 1.9485$ (free-standing hexagonal GaN) and $g = 1.9533$ (cubic GaN layer grown on 3C-SiC substrate). The spectra show an exceptionally small line width below 0.4 mT and contain no further signature. As a result, beside the line width itself, the EPR line is characterized by its g-tensor exclusively. With the help of a qualitative analysis of the Si donor wave function within effective mass theory (EMT) and a followed up calculation of the hyperfine (HF) splittings in the framework of density functional theory (DFT) the characteristic shape of the EPR lines can be explained by an enhanced delocalization of the unpaired electrons of shallow Si donors at the gallium sublattice due to overlapping impurity and conduction bands.

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1 Introduction The nature of defects in cubic and hexagonal GaN causing unintentional conductivity has been controversially discussed since more than a decade and is still a subject of challenging experimental and theoretical work (e.g., [1, 2]). Although there is no direct proof until now, oxygen or auto-doping by nitrogen vacancies is assumed to be responsible for unintended n-type background doping, whereas silicon, the donor with the lowest binding energy in GaN [3, 4], is used for intentional doping that allows a variation of the doping concentration. The most powerful tools to investigate the electronic and microscopic structure of the dopants are magnetic resonance methods like electron paramagnetic resonance (EPR).

In nominally undoped material an EPR-signal was tentatively assigned to the residual donor, however, apparently the same signal was found after silicon doping [1, 3, 5–14]. In some samples the signal has an unexpected small line width. In all samples the signal contains no further signature. As a result, beside the line width itself, the EPR line is characterized by its g-tensor exclusively, preventing further insight into the microscopic structure. Although the signal indeed varies with the Si doping concentration, an indirect effect via a shift of the Fermi level (and, by this, residual donors as an origin) cannot be excluded.

In this work, we propose that the EPR-signals are due to electrons located in joint impurity bands. This is supported by new EPR measurement with exceptionally small line widths in hexagonal and cubic GaN, intentionally doped with silicon. With the help of a qualitative analysis of the Si donor wave function within effective mass theory (EMT) and a following calculation of the HF splittings in the framework of density functional theory (DFT) the shape of the EPR lines can be explained by an enhanced delocalization of the unpaired electrons of shallow Si_{Ga} donors due to overlapping impurity and conduction bands.

2 Experimental The samples investigated in this work were commercial n-type samples from Cree, a free-standing bulk GaN sample and an 1 μm thick cubic GaN layer MBE-grown on 3C-SiC substrate [15]. The two latter samples were intentionally doped with silicon, whereby the carrier concentration N_D in both cases was about 1×10^{18} cm^{-3}. All samples were investigated with electron para-magnetic resonance (EPR). The EPR measurements were performed

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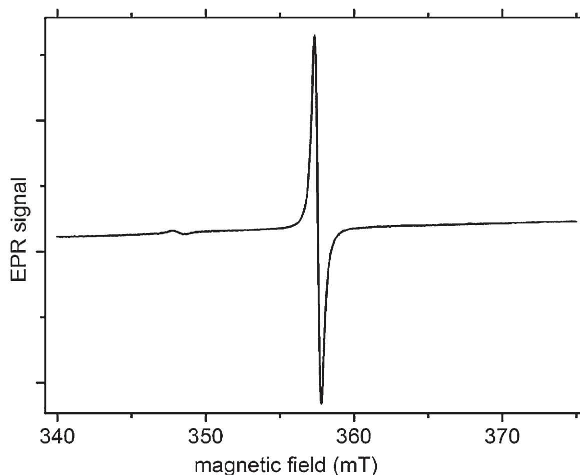

Figure 1 EPR spectrum of silicon doped hexagonal GaN measured at 6 K in X band (9.8 GHz). The signal with small intensity at around 348 mT is due to the magnetic field marker (DPPH). For details see text.

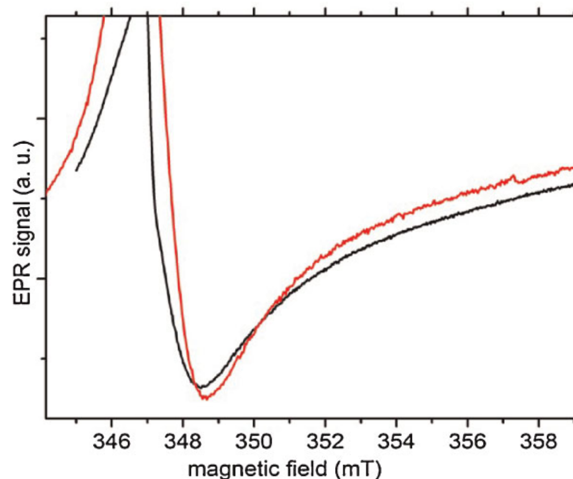

Figure 2 (online color at: www.pss-b.com) EPR spectrum of Si-doped cubic GaN measured at 6 K in X band (9.8 GHz). The black trace is due to the 3C-SiC substrate, while the red one shows the additional signal from the 1 μm thick cubic GaN MBE layer. For details see text.

on a home-made X band (9.87 GHz) spectro-meter with a cylindrical TE_{011} cavity and a He gas flow cryosystem allowing temperatures between 3.5 K and 300 K. A 100 kHz field modulation in combination with lock-in detection has been applied for signal improvement. During the EPR measurements the samples were cooled down to 6 K. Field calibrations were done using a DPPH standard for an accurate g-factor determination.

3 Results

As an example Fig. 1 shows a typical EPR spectrum of the silicon doped free-standing hexagonal GaN sample. The g-tensor was determined as $g_{||} = 1.9512$ and $g_{\perp} = 1.9485$ ($\pm$0.0001) with respect to the hexagonal crystal axis. No hyperfine (HF) splitting was observed, although the line width was only about 0.4 mT. The same spectrum was observed in the commercial Cree sample. For the MBE-grown cubic GaN layer the signal-to-noise ratio was drastically reduced by several orders of magnitude due to the layer thickness below 1 μm being close to the sensitivity limit of the spectrometer in X band. Figure 2 shows two spectra, one reference spectrum of the 3C-SiC substrate revealing the EPR spectrum of the shallow nitrogen donor (black trace in Fig. 2) and the second spectrum (red trace in Fig. 2) showing an additional signal at $g = 1.9553$ with a line width below 0.3 mT. This signal was observed only after silicon doping and shows no additional HF structure. The intense EPR signal in the left part of the spectrum is well known to originate from the nitrogen donor in the 3C-SiC substrate. It was, thus, used as a reference for an accurate g-factor determination for the additional EPR signal coming from the cubic GaN layer.

4 Discussion

In Table 1 the EPR parameters of our measurements are compiled together with those formerly reported in the literature for intentionally silicon doped GaN [15, 16]. Most of the data stems from hexagonal thin films, whereby our hexagonal sample provides uniquely a free-standing bulk sample. Almost all of the spectra show an anisotropy $g_{||} - g_{\perp}$ of about 0.0027. The absolute values, however, differ by up to 0.001. If not completely being due to some uncertainties in the experimental error bars, we believe that the observed variation of the g-tensor is most probably due to variations in doping concentration. At least in the cubic polytype a slight shift of the g-values toward lower

Table 1 Experimentally determined EPR parameters (principal values of the g-tensor and linewidth of the resonance curve) for various Si-doped GaN-samples (upper part: hexagonal GaN, lower part cubic GaN). The values are ordered with respect to increasing carrier concentration N_D.

reference	N_D (cm^3)	$g_{\|\|}$	$g_{\perp}$	linewidth (mT)
hexagonal GaN				
[1]	3×10^{16}	1.9510	1.9483	0.4–0.5
[6]	5×10^{16}	1.9503	1.9483	0.9
[7], ODMR	1×10^{17}	1.9515	1.9485	13.0
[9]	1×10^{17}	1.951	1.948	0.5
[10]	$< 10^{17}$	1.9514	1.9486	1.0
[11]	1×10^{17}	1.9514	1.9487	5.0
[12]	1×10^{18}	1.9510	1.9483	1.0
this work	1×10^{18}	1.9512	1.9485	<0.4
[13]	7×10^{18}	1.9503	1.9476	3.0

reference	N_D (cm^3)	g	linewidth (mT)
cubic GaN			
this work	$<10^{18}$	1.9533	0.3
[14]	1×10^{18}	1.9533	1.8–3.2
[12]	$<10^{19}$	1.9475	0.8

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values can be observed. With 0.4 and 0.3 mT for hexagonal and cubic GaN, respectively, our new measurements provide the narrowest EPR lines measured so far for the shallow donor in Si-doped GaN. Nevertheless, no additional HF structure due to the magnetic interaction of the unpaired electron and the nuclear spins can be observed. The central line covers only HF splittings below 10, 6, and 4 MHz for Si, N, and Ga nuclei, respectively. As a consequence we can exclude that intrinsic defects like nitrogen vacancies or silicon interstitials (contributing to a rather localized defect state) are found by chance close to the conduction band.

The shallow donor in Si-doped hexagonal GaN provides a donor level 22 [3] to 27 meV [4] below the conduction band. Assuming a rather delocalized unpaired electron, the wave function of the shallow level can be qualitatively analyzed within EMT. Using an angular averaged dielectric constant $\varepsilon_r = 9.8$ [17] we obtain an effective mass $m^* = E_D/E_H\,\varepsilon_r{}^2 m_0$ between 0.16 and 0.19 m_0, that allows us to estimate the effective Bohr radius $r_{B^*} = m_0/m^*\ \varepsilon_r\ r_B$ of the donor electron ranging from 26.8 to 33.5 Å. For the lowest concentration (slightly above $1 \times 10^{16}\,\text{cm}^{-3}$), the mean distance between donors is, thus, with 315 Å about 10 times the effective Bohr radius. For moderately Si doped sample (e.g., slightly below $1 \times 10^{18}\,\text{cm}^{-3}$) the mean distance is reduced, but with 90 Å, most of the donors should still have only few spatial overlap. Note that 50% of the unpaired donor electron are found within a sphere with radius r_{B^*}. For concentrations above $7 \times 10^{18}\,\text{cm}^{-3}$ as in the case of the samples of Kim et al. [13] the mean distance approaches the order of magnitude given by the Bohr radius (48 Å in comparison with $r_{B^*} = 30$ Å). As a consequence the coupling between the donors becomes more and more critical leading to a broadening of the EPR lines. Note that the spectra reported by Kim et al. [13] provides exactly the same *g*-tensor as observed in this work, but with a 10 times larger line width corresponding to the higher carrier concentration. This explanation is also in qualitative agreement with the observation of Palczewska et al. [10]: in their samples, above a concentration of some $10^{18}\,\text{cm}^{-3}$ the EPR lines are broadened before becoming undetectable for concentrations above $6 \times 10^{18}\,\text{cm}^{-3}$. Along the same arguments we can now explain the variation of the *g*-values: the coupled donors lead to defect bands whereby the dispersion of the bands increases with increasing carrier concentration. As a consequence, an admixture of the tails of the conduction bands and by this a change in the *g*-tensor becomes more and more probable.

Last but not least we want to investigate via total energy calculation in the framework of DFT if the observation of very narrow EPR-lines with no additional HF structure is really consistent with an assignment to Si donors. The atomic structure is given by a silicon atom incorporated substitutionally at the Ga-sublattice. Due to the EMT-like delocalization of the wave function an *ab initio* treatment of the Si_{Ga} donor within a supercell approach is a prehibitive, perhaps also in future too demanding task. Assuming $r_{B^*} = 30$ Å, supercells including at least 2500 atoms would be necessary to model a complete donor electron appropriately. Furthermore, in order to take into account admixed contributions from the conduction bands large k-point samplings are necessary to describe the metallic-like electronic structure of the unpaired donor electron. In order to allow an approximative calculation of the HF splittings we model the ionized Si_{Ga}^+ donor together with 10% of the unpaired electron in a comparatively small supercell with 96 atoms in connection with a $16 \times 16 \times 16$ k-point mesh. Further standard details of the computational setup can be found elsewhere [18, 19]. For the HF splitting due to the central Si nucleus a value of 2.5 MHz is predicted. Moreover, all HF splittings due to the N and Ga nuclei are below 5 and 7 MHz, respectively. By this, the calculated HF splittings for the shallow Si donor level about 25 meV below the conduction band is consistent with the observed narrow EPR lines without additional HF structure. As a result, the shape of the EPR lines can be explained by an enhanced delocalization of the unpaired electrons of substitutional Si_{Ga} donors due to overlapping impurity and conduction bands.

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