Direct experimental evidence of impurity decoration of Ga vacancies in GaN

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Positron annihilation spectroscopy, supported by ab-initio theory, has been applied to verify the decoration of Ga vacancies in GaN by oxygen and hydrogen. Our results indicate that the Doppler broadening measurement of electron momentum distribution is sensitive enough to distinguish even between N and O atoms neighboring the Ga vacancy. We identify isolated V_{Ga} in electron irradiated GaN and V_{Ga}-O_N complexes in highly O-doped high-purity GaN. Evidence of H decoration of Ga vacancies is obtained in epitaxial GaN grown by metal-organic chemical-vapor deposition.

Gallium nitride (GaN) is an important wide band-gap semiconductor for optoelectronic and electronic applications. It can be grown by several methods, each of which have partially different impurity and defect characteristics. The interaction of impurities and defects have been often suggested by correlative studies [1, 2], and also directly observed e.g. in the case of dislocations [3], pyramidal defects [4] or N vacancies [5].

The oxygen and silicon impurities dope GaN to n-type semiconductor. The conductivity of n-type GaN is partly compensated by Ga vacancies, which are formed as dominating negative defects independently of the growth method. V_{Ga} forms an energy level in the forbidden energy gap, which can lead to undesired optical properties of GaN such as the yellow luminescence [6]. The irradiation with > 1 MeV electrons produces Ga vacancies artificially by removing Ga atoms from the lattice site to the interstitial site [7]. The annealing experiment at 500-600K shows that Ga vacancy formed with electron irradiation starts to migrate, whereas V_{Ga} formed in growth is much more stable in annealings up to 1300-1500 K [8]. This suggest that the Ga vacancy formed in growth is complexed with an impurity atom with a high binding energy.

The improved quality of GaN enables now to perform more exact and quantitative studies of defects. Especially the GaN grown by hydride vapor phase epitaxy (HVPE) has low (10^{16} cm^{-3}) residual impurity concentration and dislocation density ($< 10^8$ cm^{-2}). In such material the relation between intentional doping and defects can be systematically studied. Furthermore, intrinsic defects can be produced by electron irradiation at concentrations much higher than that of the residual impurities.

In this work we study the vacancy defects in GaN formed in growth as well as in electron irradiation with positron annihilation spectroscopy [9]. Positrons are sensitive for neutrally and negatively charged defects, especially vacancies, at which they get trapped. In a vacancy the electron density is decreased which makes the positron lifetime longer and narrows the positron-electron momentum distribution. The defect identification can be reached by recording the Doppler broadening of the energy spectrum of the annihilation radiation. This experiment gives information about the chemical environment of an annihilation site. We show that the isolated Ga vacancy formed by electron irradiation is indeed distinguishable from V_{Ga}-O_N and V_{Ga}-H complexes formed during growth. The result thus provides direct experimental evidence of impurity decoration of native Ga vacancies in GaN.

The positron lifetime spectra were measured with a spectrometer having a time resolution of 240 ps. The lifetime spectrum is a superposition of exponential decay components $n(t) = \sum_i I_i \exp[-t/\tau_i]$. The positron in the state i will annihilate with the lifetime of τ_i and the intensity of I_i. The average lifetime $\tau_{ave} = \sum_i I_i \tau_i$ will increase with increasing positron trapping into vacancies. The Doppler broadening of the annihilation radiation was measured with a Ge-NaI coincidence equipment having an energy resolution of 1.35 keV.

We modeled positron annihilation parameters using electronic-structure calculations. Valence electron densities were calculated self-consistently using the local-density approximation (LDA) employing the projector augmented-wave (PAW) method [10] and a plane-wave code VASP [11, 12]. The ionic structures found for V_{Ga}^{3-} and $(V_{Ga} - O_N)^{2-}$ are in a good agreement with Ref. 13. The ensuing positron states and annihilation characteristics were calculated using the LDA [14] and the state-dependent scheme for electron-positron correlation [15]. Momentum distributions were calculated using the all-electron valence wave functions of the PAW method and convoluted with the resolution of the Doppler experiment [16]. The Doppler spectra were calculated in the direction of the c-axis of the wurtzite GaN. For asym-

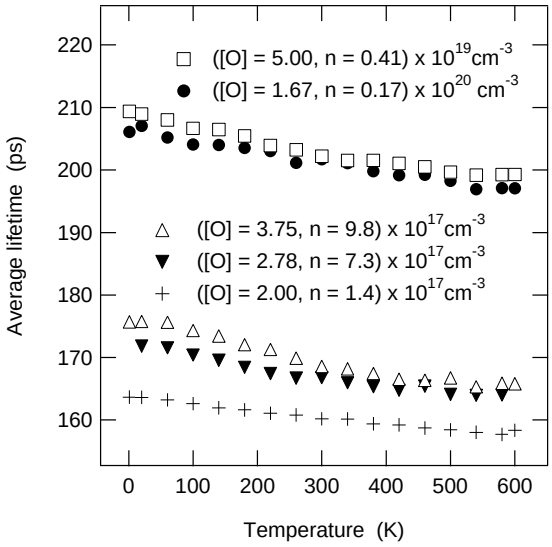

FIG. 1: The average positron lifetime as a function of measuring temperature. The first number in the parentheses stands for O concentration and the second one indicates the free carrier concentration.

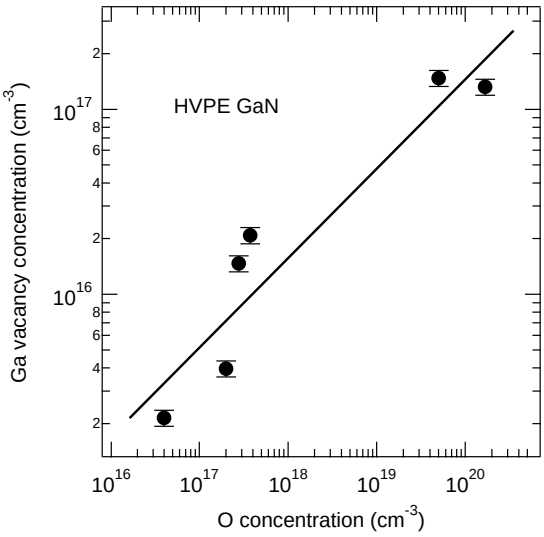

FIG. 2: Gallium vacancy concentration as a function of doping. The solid line is guide to the eye. The results in the sample with the lowest O concentration have been taken from Ref. 19.

metric defects we considered different configurations and used a properly weighted average to account for their random orientation. For H-containing systems we used the configurations given in Ref. 17 and placed H atoms in the vacancy ignoring further ion relaxations.

The measured free-standing n-type GaN samples with different level of intentional oxygen doping were grown by the hydride vapor phase epitaxy (HVPE). The free electron and oxygen concentrations were measured with Hall experiments and secondary ion mass spectroscopy (SIMS), respectively, and they can be found in the legends in Fig. 1. The thicknesses of samples varied between 350-810μm. To create a reference sample with isolated Ga vacancies, we irradiated an undoped GaN sample with 2 MeV electrons at 300 K to a dose of $5\times10^{17}\mathrm{e}^{-}\mathrm{cm}^{-2}$.

Fig. 1 shows the positron average lifetime as a function of measuring temperature. The positron lifetime in undoped GaN is 160-163 ps. This is the same as the lifetime in the GaN lattice [5, 6, 18] indicating low native vacancy concentrations. As can be seen in Fig. 1 the measured average lifetimes in O-doped HVPE GaN are clearly higher than the lattice lifetime τ_b for all the samples over the whole temperature range. In decomposition two different lifetimes are found, where the longer one is $\tau_2 = 235 \pm 5$ ps. This is the same as measured before for the gallium vacancy [1, 6]. The other lifetime component is $\tau_1 \approx 130$ ps. This is shorter than the lattice lifetime reflecting both annihilation and trapping from the delocalized state.

The average positron lifetime increases when the measuring temperature is decreased (Fig. 1). This kind of behavior of the average lifetime is the fingerprint of negatively charged vacancies. Because of the Coulombic nature of the free positron wave function the trapping at vacancies enhances as the thermal velocity of the positron decreases [9, 20]. No other negative centers compete with the Ga vacancy in positron trapping. Negative ions, for example, would localize positrons in a hydrogenic state at a low temperatures, strongly decreasing the fraction of annihilations at vacancies and the average lifetime at low temperatures [18]. The positron data thus show that the Ga vacancy related defects are dominating negatively charged acceptors. This has been demonstrated before in nominally undoped GaN [19], but the present data show the dominant role of $\mathrm{V_{Ga}}$-related defects over four orders of magnitude of O doping.

The vacancy concentration can be estimated from the measured lifetimes. Since a single vacancy type is present, the vacancy concentration is obtained as [9]

$$c_V = \frac{N_{at}}{\mu_V \tau_b} \frac{\tau_{ave} - \tau_b}{\tau_D - \tau_{ave}}, \qquad (1)$$

where N_{at} is the atomic density, τ_b=160 ps is the positron lifetime in the GaN lattice, μ_V=7×10^{15} at. s^{-1} is positron trapping coefficient at the vacancy at 20 K, and $\tau_D = 235$ ps is the positron lifetime at the Ga vacancy. As can be seen in Fig. 2 the increase of the O doping of the samples increases the $\mathrm{V_{Ga}}$ concentration. This trend is theoretically predicted for acceptor defects like $\mathrm{V_{Ga}}$ [13], and suggests that the gallium vacancy is complexed with an oxygen atom. However, the positron lifetime is too insensitive to tell if the $\mathrm{V_{Ga}}$ is isolated or complexed.

In order to identify an intrinsic Ga vacancy we studied an electron irradiated undoped GaN sample (2 MeV,

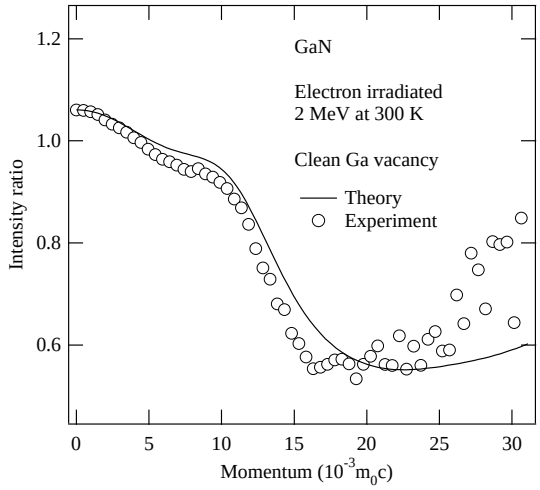

FIG. 3: The measured and calculated momentum distribution for an isolated Ga vacancy. Both of these curves are shown as ratios to the data obtained in the GaN lattice.

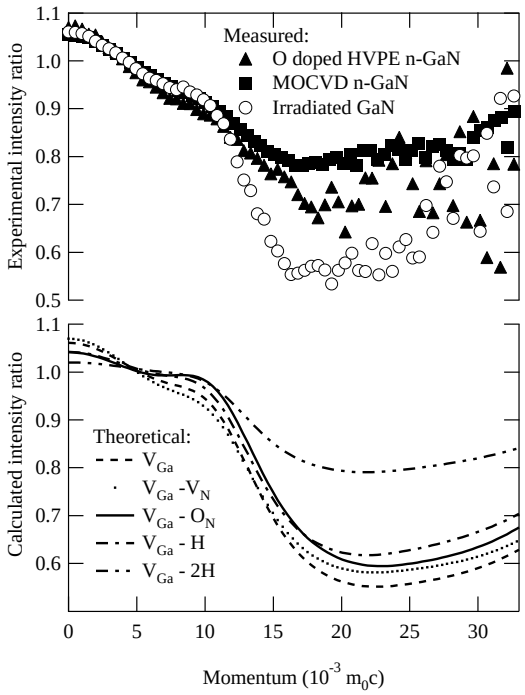

FIG. 4: Measured and calculated momentum distribution curves for different types of samples and defects, respectively. All these curves are shown as ratios to the data obtained in the GaN lattice.

5×10^{17}e$^-$cm^{-2}). The average positron lifetime is 205 $\pm$ 3 ps at 380 K. The slightly higher measuring temperature was chosen to introduce maximal trapping at vacancies and minimize the effect of negative ions. The decomposition of the lifetime spectrum of electron irradiated GaN reveals a Ga vacancy related lifetime 230 $\pm$ 5 ps, i.e. the same as in O-doped HVPE GaN. The concentration of Ga vacancies is about 5×10^{17}cm^{-3} (Eq. 1). Electron irradiation (2-MeV) of GaN samples thus generates intrinsic Ga vacancies with an introduction rate of 1 cm^{-1} by removing the Ga atom from lattice site to the interstitial site [8]. The introduction rate of 1 cm^{-1} is typical for primary defects formed in electron irradiation. The oxygen concentration of irradiated GaN is two orders of magnitude lower than the gallium vacancy concentration. We conclude that positrons are trapped at isolated Ga vacancies in the irradiated GaN sample.

Fig. 3 shows the electron momentum distribution of the Ga vacancy in electron-irradiated GaN. The signal of a clean Ga vacancy is obtained by decomposing the original Doppler broadening spectrum by determining the fraction of annihilations of delocalized positrons $\eta_b \approx 40$ % from the lifetime measurement. The calculated curve for the isolated Ga vacancy is also shown. Both of these curves are shown as ratios to the spectrum of the perfect bulk GaN lattice.

The behavior of the calculated annihilation curve correlates well with the experimental one through the whole momentum range (Fig. 3), supporting the identification of the isolated Ga vacancy. The main contribution in the range between 15-30$\times10^{-3}$m$_0$c arises from annihilations with Ga 3*d* electrons. The decrease in intensity at this momentum region is due to the reduced intensity of Ga 3*d* electrons in a Ga vacancy. The good agreement at both valence and core electron regions manifests the accuracy and predictive power of the theoretical calculations.

Fig. 4 shows the electron momentum distributions in various GaN samples having Ga vacancy related defects. The curves are not similar, which indicates that different complexes can be distinguished. In the momentum range between 15-30$\times10^{-3}$m$_0$c the data have clear order. The intensity of irradiated GaN is the lowest while the oxygen doped GaN has higher intensity. The difference between irradiated and O-doped GaN is interesting. While electron irradiation generates isolated Ga vacancies, the O-doping increases the native Ga vacancy concentration (Fig. 2) which suggests a formation of V_{Ga}-O_N-pairs in growth. In Fig. 4 the O doped HVPE GaN has higher relative intensity in high momentum region when compared to electron irradiated GaN. This effect could be attributed to oxygen surrounding the Ga vacancy: O ion is smaller than N and thus contributes more at high electron momentum. The same behavior can be seen in the calculated momentum ratio curves. The difference between V_{Ga}-O_N and isolated V_{Ga} is arising from the valence electron states derived from the atomic 2*p* orbitals. Although the electron densities around O and N nuclei are almost the same the difference between the curves is clear.

Table I shows the positron annihilation parameters for studied samples and defects. The relative $S_{rel}=S_V/S_b$

TABLE I: The positron annihilation parameters and defect related lifetimes for studied samples and defects.

	τ_V [ps]	S_V/S_b	W_V/W_b
Experimental:			
Irr. V_{Ga}	230(5)	1.042(3)	0.58(3)
HVPE V_{Ga}	235(5)	1.050(3)	0.73(3)
MOCVD V_{Ga}	-	1.039(3)	0.80(3)
GaN lattice	160(3)	1	1
Theoretical:			
V_{Ga}	200	1.048	0.583
V_{Ga}-V_N	203	1.055	0.608
V_{Ga}-O_N	200	1.032	0.630
V_{Ga}-H	180	1.034	0.642
V_{Ga}-2H	155	1.017	0.803
GaN lattice	131	1	1

and $W_{rel}=W_V/W_b$ parameters are determined from the annihilation momentum distribution as integrals at $p_L \leq |3.7|\times10^{-3} m_0c$ and 15×10^{-3} $m_0c \leq p_L \leq 25\times10^{-3}$ m_0c, respectively. Calculated positron lifetimes are shorter than the experimental ones, but the lifetime differences between the Ga vacancy and bulk lattice are the same, $\tau_V - \tau_b \approx 70$ ps. The experimental and theoretical annihilation parameters (Table I) are in good agreement in the case of the isolated Ga vacancy. The remaining discrepancies are in the limits of the accuracies of both experimental and theoretical methods. The increase of W parameter due to O decoration is clear in the experiment and theory, which provides direct evidence that V_{Ga}-O_N complexes are formed in the oxygen doping of HVPE GaN. However, the S parameter in O-doped GaN is higher than the calculated value for V_{Ga}-O_N. This could indicate that V_{Ga}-V_N divacancies are present, as predicted by the low calculated formation energy of such defects [13, 21]. The presence of divacancies is also supported by the slightly higher positron lifetime at vacancies in O-doped than in irradiated GaN. The high value of W_{rel} (Table I) shows that the divacancies are likely to be decorated with oxygen.

The GaN grown by metal-organic chemical vapor deposition (MOCVD) is the most important for optoelectronic applications. In this material the concentrations of residual impurities, especially of hydrogen, are high due to organic precursors applied in the growth. The electron momentum distribution at V_{Ga} related defect (Fig. 4 and Refs. 6 and 22) is different from both V_{Ga} and V_{Ga}-O_N. To explain the data in MOCVD GaN at high momentum region, we performed a calculation in Ga vacancy related defects containing 1-2 hydrogen atoms (Fig. 4). H pushes the positron density out from the vacancy leading to a shorter lifetime and a higher intensity ratio at the high momentum region (Table I). The experimental curve measured in MOCVD GaN is close to the calculated one at V_{Ga}-H or V_{Ga}-2H complexes, suggesting that the Ga vacancy in MOCVD GaN is decorated by hydrogen or possible also by oxygen. Such complexes have low formation energies according to calculations [17, 23].

In conclusion we have studied Ga-vacancy-related defects with positron annihilation spectroscopy in high-purity GaN. By combining experiment and theory we show that the measurement of momentum density is sensitive enough to distinguish between O and N atoms neighboring the Ga vacancy. We identify the isolated V_{Ga} in undoped electron irradiated GaN, and show that in O-doped HVPE GaN the Ga vacancy is complexed with the O atom forming V_{Ga}-O_N-pairs. In MOCVD material our data show that the Ga vacancy is likely to be decorated by both oxygen and hydrogen.

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[1] J. Oila *et al.*, Phys. Rev. B **63**, 045205 (2001).
[2] D. C. Look *et al.*, Solid State Communications **117**, 571 (2001).
[3] I. Arslan and N. B. Browning, Phys Rev. Lett. **91**, 165501 (2003).
[4] Z. Liliental-Weber *et al.*, Phys. Rev. Lett. **93**, 206102 (2004).
[5] S. Hautakangas *et al.*, Phys. Rev. Lett. **90**, 137402 (2003).
[6] K. Saarinen *et al.*, Phys. Rev. Lett. **79**, 3030 (1997).
[7] K. H. Chow, G. D. Watkins, A. Usui, and M. Mitzuta, Phys. Rev. Lett. **85**, 2761 (2000).
[8] K. Saarinen, T. Suski, I. Grzegory and D. C. Look, Phys. Rev. B **64**, 233201 (2001).
[9] K. Saarinen, P. Hautojärvi, and C. Corbel, in *Identification of Defects in Semiconductor*, edited by M. Stavola (Academic, New York, 1998).
[10] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[12] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[13] J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
[14] We use the parametrization by E. Boroński and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).
[15] M. Alatalo *et al.*, Phys. Rev. B **54**, 2397 (1996).
[16] I. Makkonen, M. Hakala, and M. J. Puska, J. Phys. Chem. Solids (accepted for publication, cond-mat/0409451).
[17] A. F. Wright, J. Appl. Phys. **90**, 1164 (2001).
[18] K. Saarinen *et al.*, Appl. Phys. Lett. **75**, 2441 (1999).
[19] J. Oila *et al.*, Appl. Phys. Lett. **82**, 3433 (2003).
[20] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
[21] T. Mattila and R. M. Nieminen, Phys. Rev. B **55**, 9571 (1997).
[22] K. Saarinen *et al.*, Appl. Phys. Lett. **73**, 3253 (1998).
[23] C. G. Van de Walle, Phys. Rev. B **56**, R10020 (1997).