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Direct evidence of impurity decoration of Ga vacancies in GaN from positron annihilation spectroscopy

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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 $V_{\text{Ga}}\text{-O}_{\text{N}}$ complexes in highly O-doped high-purity GaN. Evidence of H decoration of Ga vacancies is obtained in epitaxial GaN grown by metalorganic chemical-vapor deposition.

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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 has been often suggested by correlative studies,^{1,2} and also directly observed, e.g., in the case of dislocations,³ pyramidal defects⁴ 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 band 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.⁷ The annealing experiment at 500–600 K shows that Ga vacancy formed in electron irradiation starts to migrate, whereas V_{Ga} formed in growth is much more stable in annealings up to 1300–1500 K.⁸ This suggests 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 residual impurity (10^{16} cm⁻³) and dislocation ($<10^8$ cm⁻²) densities. 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 neutral 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 nar-

rows the positron-electron momentum distribution. The latter can be observed by recording the Doppler broadening of the energy spectrum of the annihilation radiation. Especially the momentum distribution of the core electrons is sensitive to the chemical environment of an annihilation site. However, in the case of light elements such as O or N the annihilation probability with the core electrons is negligible.

In this work we show that the isolated Ga vacancy formed by electron irradiation is indeed distinguishable from $V_{\text{Ga}}\text{-O}_{\text{N}}$ and $V_{\text{Ga}}\text{-H}$ complexes formed during growth. The identification is reached purely by recording the different valence electron momenta of O and N atoms and confirmed by *ab initio* theory. The results provide direct experimental evidence of impurity decoration of native Ga vacancies in GaN. We further show that the $V_{\text{Ga}}\text{-O}_{\text{N}}$ complexes are the dominant acceptor defects in *n*-type GaN over a range of four orders of magnitude of intentional oxygen doping.

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 $\tau_{\text{ave}} = \sum_i I_i \tau_i$ 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) method¹⁰ and a plane-wave code VASP.^{11,12} The ionic structures found for V_{Ga}^{3-} and $(V_{\text{Ga}}\text{-O}_{\text{N}})^{2-}$ are in a good agreement with Ref. 13. The ensuing positron states and annihilation characteristics were calculated using the LDA¹⁴ and the state-dependent scheme for electron-positron correlation.¹⁵ Momentum distributions were calculated using

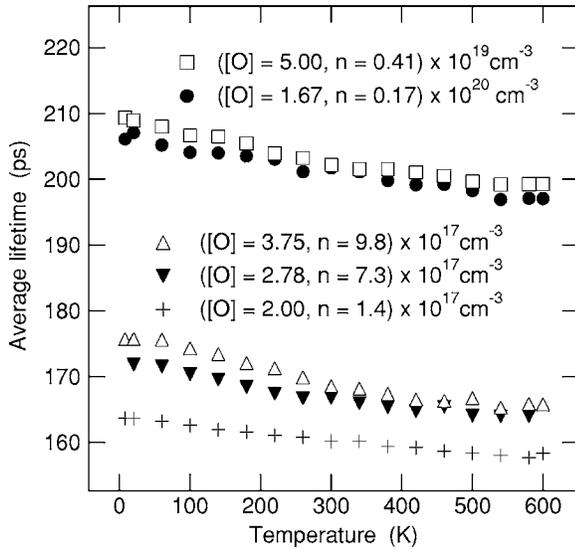


FIG. 1. The average positron lifetime as a function of measuring temperature. The first number in the parentheses stands for O concentration and the second one indicates the free carrier concentration.

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 asymmetric 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 levels of intentional oxygen doping were grown by HVPE. The free electron and oxygen concentrations were measured with Hall experiments and secondary ion mass spectrometry, respectively (see Fig. 1). The thicknesses of samples varied between 350 and 810 μm . To create a reference sample with isolated Ga vacancies, we irradiated a nominally undoped HVPE GaN sample¹⁸ with 2 MeV electrons at 300 K to a dose of $5 \times 10^{17} \text{ e}^- \text{ cm}^{-2}$.

Figure 1 shows the positron average lifetime as a function of measuring temperature. The positron lifetime in the GaN lattice is $\tau_b = 160 \text{ ps}$.^{5,6,19} The measured average lifetimes in O-doped HVPE GaN are clearly higher than the lattice lifetime for all the samples at low temperature. In decomposition two different lifetimes are found, where the longer one is $\tau_2 = 235 \pm 5 \text{ ps}$. This is the same as measured before for the gallium vacancy.^{1,6}

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 temperature, strongly decreasing the fraction of annihilations at vacancies and the

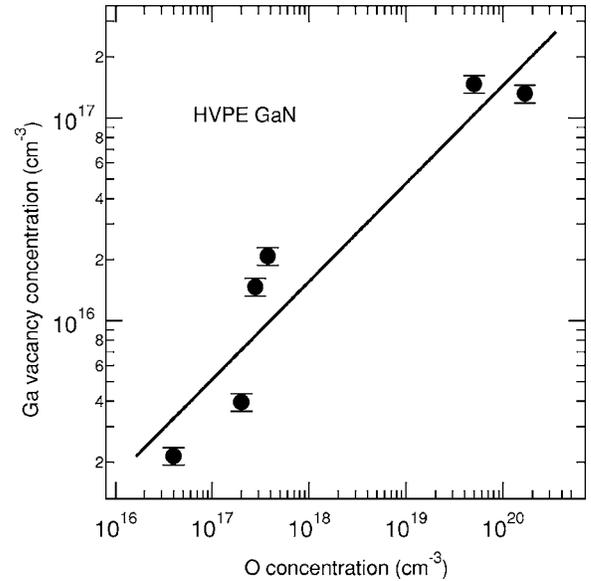


FIG. 2. Gallium vacancy concentration as a function of doping. The solid line is a guide to the eye. The results in the sample with the lowest O concentration have been taken from Ref. 18.

average lifetime at low temperatures.¹⁹ 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,¹⁸ but the present data show the universal role of V_{Ga} -related defects over almost 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 as⁹

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

where N_{at} is the atomic density, $\tau_b = 160 \text{ ps}$ is the positron lifetime in the GaN lattice, $\mu_V = 7 \times 10^{15} \text{ at. s}^{-1}$ is positron trapping coefficient at the vacancy at 20 K,¹⁸ and $\tau_D = 235 \text{ ps}$ 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 V_{Ga} concentration. This trend is theoretically predicted for acceptor defects like V_{Ga} and $V_{\text{Ga}}\text{-O}_N$.¹³ However, the positron lifetime is too insensitive to tell if the V_{Ga} is isolated or complexed.

In order to identify an intrinsic Ga vacancy, we studied undoped HVPE GaN¹⁸ after electron irradiation (2 MeV, $5 \times 10^{17} \text{ e}^- \text{ cm}^{-2}$). The average positron lifetime is $205 \pm 3 \text{ ps}$ 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 $230 \pm 5 \text{ ps}$, i.e., the same as in O-doped HVPE GaN. The concentration of Ga vacancies is about $5 \times 10^{17} \text{ cm}^{-3}$ [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

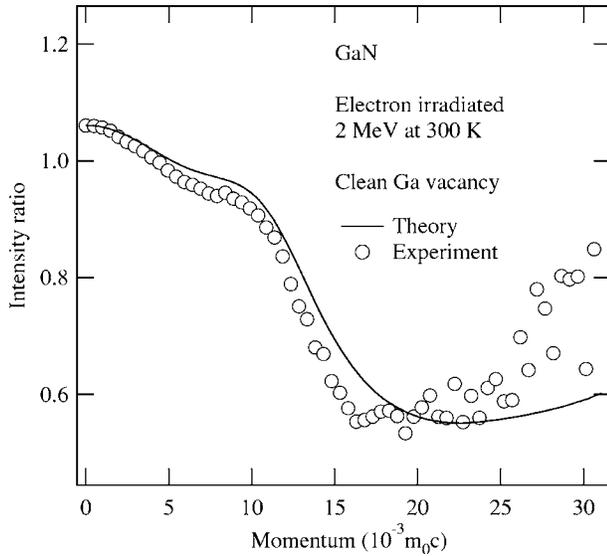


FIG. 3. The measured and calculated momentum distribution for an isolated Ga vacancy. Both of these curves are shown as ratios to the data obtained in the GaN lattice.

of 1 cm^{-1} is typical for primary defects formed in electron irradiation.⁸ The oxygen concentration¹⁸ of irradiated GaN is more than one order of magnitude lower than the gallium vacancy concentration. We conclude that positrons are trapped at isolated Ga vacancies in the irradiated GaN sample.

Figure 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 correlates well with the experimental one through the whole momentum range, supporting the identification of the isolated Ga vacancy. The main contribution in the range between 15 and $30 \times 10^{-3} m_0c$ arises from annihilations with Ga $3d$ electrons. The decrease in intensity at this momentum region is due to the reduced intensity of Ga $3d$ 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.

Figure 4 shows the decomposed electron momentum distributions for the vacancy related defects in various GaN samples. The curves are not similar, which indicates that different complexes can be distinguished. In the momentum range between 15 and $30 \times 10^{-3} m_0c$ the data have clear order. The intensity of irradiated GaN is the lowest while the oxygen doped GaN has higher intensity. This effect can be attributed to oxygen surrounding the Ga vacancy in the defect complex: 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 $V_{\text{Ga}}\text{-O}_N$ and isolated V_{Ga} is arising from the valence electron states derived from the atomic $2p$ orbitals.

Table I shows the positron annihilation parameters for studied samples and defects. The relative $S_{\text{rel}} = S_V/S_b$ and $W_{\text{rel}} = W_V/W_b$ parameters are determined from the annihila-

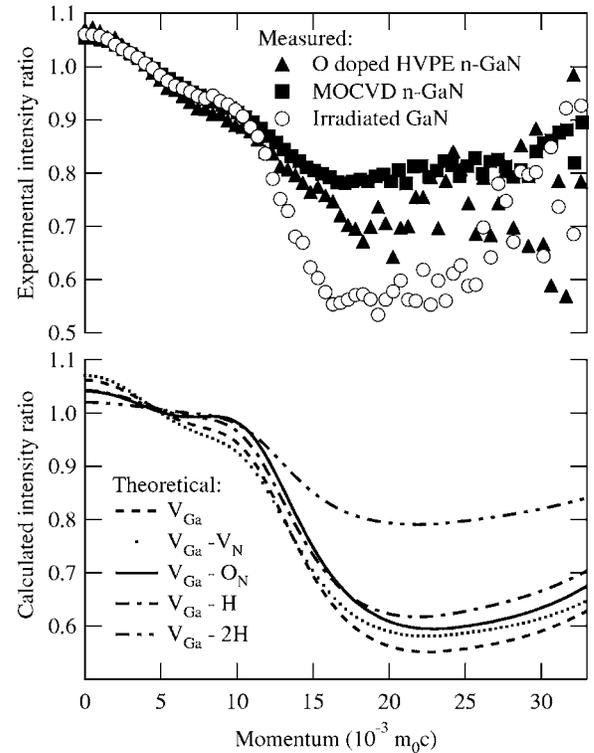


FIG. 4. Measured and calculated momentum distribution curves for different types of samples and defects, respectively. All these curves are shown as ratios to the data obtained in the GaN lattice.

tion momentum distribution as integrals at $p_L \leq |3.7| \times 10^{-3} m_0c$ and $10 \times 10^{-3} m_0c \leq p_L \leq 25 \times 10^{-3} m_0c$, 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 increase of W parameter due to O decoration is clear in the experiment and theory, which provides direct evidence that $V_{\text{Ga}}\text{-O}_N$ complexes are formed in the oxygen doping of HVPE GaN. The S parameter in O-doped GaN is higher than the calculated value for $V_{\text{Ga}}\text{-O}_N$. This suggests that the simple $V_{\text{Ga}}\text{-O}_N$ pair may not be the only form of the complex, but other V_{Ga} related defects such as divacancies also exist. However, divacancies alone cannot explain the data since (i) their calculated W parameter is very close to the that of V_{Ga} , (ii) the formation of V_{Ga} defects in GaN strongly favors the N rich stoichiometry,²¹ which is not expected for $V_{\text{Ga}}\text{-V}_N$, and (iii) divacancies have larger formation energies than V_{Ga} or $V_{\text{Ga}}\text{-O}_N$.^{13,22} Thus, the high intensity of the momentum distribution above $10 \times 10^{-3} m_0c$ together with the positron lifetime of 235 ps indicates the oxygen decoration of the dominant Ga vacancy complex.

The GaN grown by metalorganic chemical vapor deposition (MOCVD) is the most important for optoelectronic applications. In this material the concentrations of residual oxygen (10^{18} cm^{-3}) and hydrogen (10^{19} cm^{-3}) are high. The electron momentum distribution at V_{Ga} related defect (Fig. 4 and Refs. 6 and 21) is different from both V_{Ga} and $V_{\text{Ga}}\text{-O}_N$. To explain the data in MOCVD GaN at high momentum

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) | 0.64(1) |
| HVPE V_{Ga} | 235(5) | 1.050(3) | 0.77(1) |
| MOCVD V_{Ga} | ... | 1.039(3) | 0.82(1) |
| GaN lattice | 160(3) | 1 | 1 |
| Theoretical: | | | |
| V_{Ga} | 200 | 1.048 | 0.67 |
| $V_{Ga}-V_N$ | 203 | 1.055 | 0.68 |
| $V_{Ga}-O_N$ | 200 | 1.032 | 0.71 |
| $V_{Ga}-H$ | 180 | 1.034 | 0.71 |
| $V_{Ga}-2H$ | 155 | 1.017 | 0.81 |
| GaN lattice | 131 | 1 | 1 |

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 possibly 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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- ¹J. Oila, V. Ranki, J. Kivioja, K. Saarinen, P. Hautojärvi, J. Likonen, J. M. Baranowski, K. Pakula, T. Suski, M. Leszczynski, and I. Grzegory, Phys. Rev. B **63**, 045205 (2001).
- ²D. C. Look, C. E. Stutz, R. J. Molnar, K. Saarinen, and Z. Liliental-Weber, Solid State Commun. **117**, 571 (2001).
- ³I. Arslan and N. D. Browning, Phys. Rev. Lett. **91**, 165501 (2003).
- ⁴Z. Liliental-Weber, T. Tomaszewicz, D. Zakharov, J. Jasinski, and M. A. O'Keefe, Phys. Rev. Lett. **93**, 206102 (2004).
- ⁵S. Hautakangas, J. Oila, M. Alatalo, K. Saarinen, L. Liskay, D. Seghier, and H. P. Gislason, Phys. Rev. Lett. **90**, 137402 (2003).
- ⁶K. Saarinen, T. Laine, S. Kuisma, J. Nissilä, P. Hautojärvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, and M. Wojdak *et al.*, Phys. Rev. Lett. **79**, 3030 (1997).
- ⁷K. H. Chow, G. D. Watkins, A. Usui, and M. Mizuta, Phys. Rev. Lett. **85**, 2761 (2000).
- ⁸K. Saarinen, T. Suski, I. Grzegory, and D. C. Look, Phys. Rev. B **64**, 233201 (2001).
- ⁹K. Saarinen, P. Hautojärvi, and C. Corbel, in *Identification of Defects in Semiconductor*, edited by M. Stavola (Academic, New York, 1998).
- ¹⁰P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

- ¹¹G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- ¹²G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- ¹³J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
- ¹⁴E. Boroński and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).
- ¹⁵M. Alatalo, B. Barbiellini, M. Hakala, H. Kauppinen, T. Korhonen, M. J. Puska, K. Saarinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **54**, 2397 (1996).
- ¹⁶I. Makkonen, M. Hakala, and M. J. Puska, Phys. Rev. B **73**, 035103 (2006).
- ¹⁷A. F. Wright, J. Appl. Phys. **90**, 1164 (2001).
- ¹⁸J. Oila, J. Kivioja, V. Ranki, K. Saarinen, D. C. Look, R. J. Molnar, S. S. Park, S. K. Lee, and J. Y. Han, Appl. Phys. Lett. **82**, 3433 (2003).
- ¹⁹K. Saarinen, J. Nissilä, P. Hautojärvi, J. Likonen, T. Suski, B. L. I. Grzegory, and S. Porowski, Appl. Phys. Lett. **75**, 2441 (1999).
- ²⁰M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
- ²¹K. Saarinen, P. Seppälä, J. Oila, P. Hautojärvi, C. Corbel, O. Briot, and R. L. Aulombard, Appl. Phys. Lett. **73**, 3253 (1998).
- ²²T. Mattila and R. M. Nieminen, Phys. Rev. B **55**, 9571 (1997).
- ²³C. G. Van de Walle, Phys. Rev. B **56**, R10020 (1997).