Vacancy Defects as Compensating Centers in Mg-Doped GaN

S. Hautakangas,[1] J. Oila,[1] M. Alatalo,[1,2] and K. Saarinen[1]

[1]*Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02150 Espoo, Finland*
[2]*Department of Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 Oulu, Finland*

L. Liszkay*

Institut für Nukleare Festkörperphysik, Universität der Bundeswehr München, 85577 Neubiberg, Germany

D. Seghier and H. P. Gislason

Science Institute, University of Iceland, Dunhagi 3, IS-107 Reykjavik, Iceland

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We apply positron annihilation spectroscopy to identify V_N-Mg_{Ga} complexes as native defects in Mg-doped GaN. These defects dissociate in postgrowth annealings at 500–800 °C. We conclude that V_N-Mg_{Ga} complexes contribute to the electrical compensation of Mg as well as the activation of *p*-type conductivity in the annealing. The observation of V_N-Mg_{Ga} complexes confirms that vacancy defects in either the N or Ga sublattice are abundant in GaN at any position of the Fermi level during growth, as predicted previously by theoretical calculations.

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Gallium nitride has become one of the most investigated materials for optoelectronic devices. The large direct band gap and strong interatomic bonds enable the material to be exploited in short-wavelength devices, such as blue light emitting diodes and lasers. The control of the electrical properties of GaN remains one of the foremost obstacles in the progress of device development.

While *n*-type conductivity of GaN is easily achieved with Si or O doping, the *p*-type material is generally much more difficult to fabricate. Mg-doped GaN grown by metal organic chemical vapor deposition (MOCVD) is semi-insulating after the growth and has to be annealed at high temperature in order to achieve significant hole concentrations [1]. This behavior is generally attributed to hydrogen atoms [2–4] that bond to the Mg acceptors passivating them electrically. The heat treatment (at 500–800 °C) dissociates the Mg-H complexes leading to the *p*-type conductivity due to the hole emission from the isolated Mg. There is strong evidence that *p*-type doping of GaN is a more complex process and Mg-H complexes may not be the only passivating centers [5]. The transmission electron microscope (TEM) measurements of Liliental-Weber *et al.* have shown the presence of either planar or pyramidal extended defects in MOCVD grown GaN, depending on the growth polarity [6,7]. Segregation of electrically inactive Mg is observed on the internal surfaces of both these defects.

Theoretical calculations predict that vacancies are the dominant point defects in GaN at any position of the Fermi level [8]. In *n*-type GaN, V_{Ga} and associated complexes have been observed and studied extensively by positron annihilation spectroscopy [9]. In *p*-type and resistive GaN, N vacancies are expected [8], but they have escaped the experimental detection. In this Letter, we identify the V_N-Mg_{Ga} complexes with positron annihilation spectroscopy. These defects are important compensating centers in Mg-doped GaN and contribute to the activation of *p*-type conductivity by dissociating during annealing. We show that positron lifetime spectroscopy in GaN layers is able to distinguish between N vacancies and larger open volume defects, yielding quantitative information on the concentrations of both of them.

We apply a monoenergetic positron beam to probe native vacancy defects in epitaxial GaN samples. Positrons get trapped at neutral and negative vacancies because of the missing positive charge of the ion cores. In the vacancy, the reduced electron density increases the lifetime of the positron and narrows the positron-electron momentum distribution. Both these quantities can be measured and calculated from the first principles.

The momentum density is measured by detecting the Doppler broadening spectrum of the annihilation photons. These spectra are characterized by conventional parameters *S* and *W* [10], which quantify the annihilations in the low and high momentum parts of the distribution, respectively. The identification of atoms neighboring vacancies is reached by detecting annihilations with core electrons. This is accomplished by the coincidence detection of both annihilation photons using a double Ge-detector system with an energy resolution of 1.1 keV and a peak-to-background ratio of better than 10^6.

The positron lifetime measurement enables one to distinguish different open volumes of vacancy defects. In thin layers, the lifetimes can be measured by a pulsed low-energy beam by recording the time difference of the pulse and the detected annihilation photon (time resolution was 250 ps). The lifetime spectra consist of exponential decay components τ_i with an intensity I_i. By decomposing the spectra, positron lifetimes and annihilation fractions at free and trapped positron states can be

resolved. The combination of positron lifetime and Doppler broadening measurements thus enables one to identify both the open volume of the vacancy defect and the atoms surrounding it.

We studied three Mg-doped GaN layers with a thickness of 2 μm grown on a sapphire substrate by MOCVD. The as-grown sample was electrically resistive. The second sample was annealed at 500 °C under N_2 for 5 min, and had a net space charge concentration N_a-$N_d = 3 \times 10^{16}$ cm^{-3} as determined by capacitance-voltage measurements. This concentration is generally equal to the net hole concentration p in the valence band. The third sample was annealed at 800 °C under N_2 for 30 min and had N_a-$N_d = 1 \times 10^{17}$ cm^{-3}. A Mg-doped sample ($p \sim 10^{18}$ cm^{-3}) grown by molecular-beam epitaxy (MBE) at 800 °C was measured as a reference.

In the high temperature region ($T > 400$ K), the valence annihilation parameters have a clear order depending on the annealing temperature (Fig. 1). The sample annealed at 800 °C has almost the same S-parameter level as that in the bulk GaN lattice, and the S parameter in other samples is much higher. The average momentum of electrons at vacancies is less than in the bulk lattice, leading to a narrower positron-electron momentum distribution and increased S parameter. The results in Fig. 1 are a clear indication of vacancies in the as-grown sample. The decrease of the S parameter shows that the vacancy concentration decreases in the annealings at 500–800 °C.

The S parameter decreases toward the GaN bulk value in the low temperature region. This behavior is typically observed when positron trapping at vacancies is prevented by other defects, which do not have open volume [10]. Both negative Mg ions [11] and dislocations [12] trap positrons in GaN at low temperatures. Above 400 K, the S parameter saturates, indicating that positrons have enough thermal energy to totally escape from these shallow traps. We concentrate here on the data recorded at this temperature region, because it is dominated by a clean signal of positron annihilation at vacancy defects.

In the positron lifetime experiments performed with the pulsed beam, we used a p-type Mg-doped GaN layer grown by MBE as a reference (Fig. 2). The lifetime spectrum of this sample shows a single exponential component of 154 ps. Within experimental accuracy, this is the same as reported for annihilations in the lattice in conventional lifetime experiments in thick bulk crystals [13]. No vacancies are thus observed in the MBE grown GaN:Mg layers.

The positron lifetime spectra recorded in the MOCVD grown Mg-doped samples indicate strong evidence of vacancy defects (Fig. 2). Three positron lifetime components can be distinguished. The longest one, $\tau_3 = 500$ ps ($I_3 = 6\%$), is a typical lifetime for large open volume defects where at least ten atoms are missing from their lattice sites [10]. The second lifetime component $\tau_2 = 180$ ps ($I_2 = 74\%$) is also larger than the lifetime in the lattice $\tau_B = 154$ ps indicating the presence of monovacancy defects. The shortest lifetime component is typically $\tau_1 = 90$–140 ps and corresponds to delocalized positrons annihilating in the GaN lattice. Its value is less than τ_B because it reflects both the annihilation and trapping of positrons. The annealings have a strong

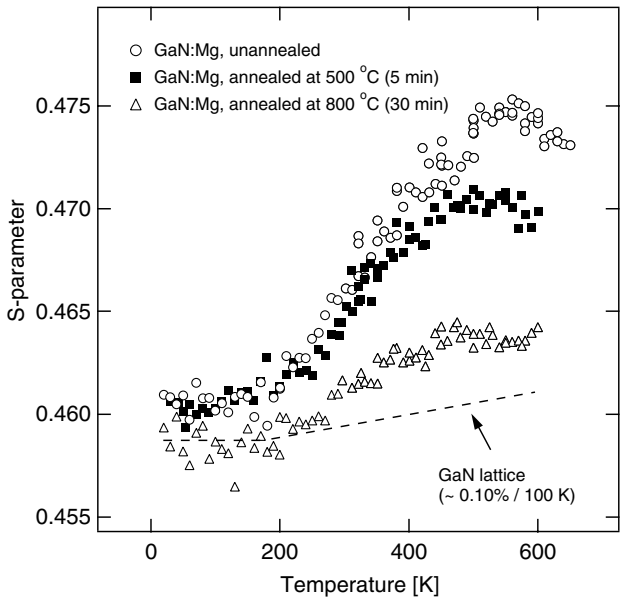

FIG. 1. The low electron-momentum parameter S as a function of temperature in MOCVD GaN samples. The dashed line represents the temperature behavior of the S parameter in the GaN lattice. Incident positron energy was 15 keV, which corresponds to a mean penetration depth of ≈ 0.5 μm.

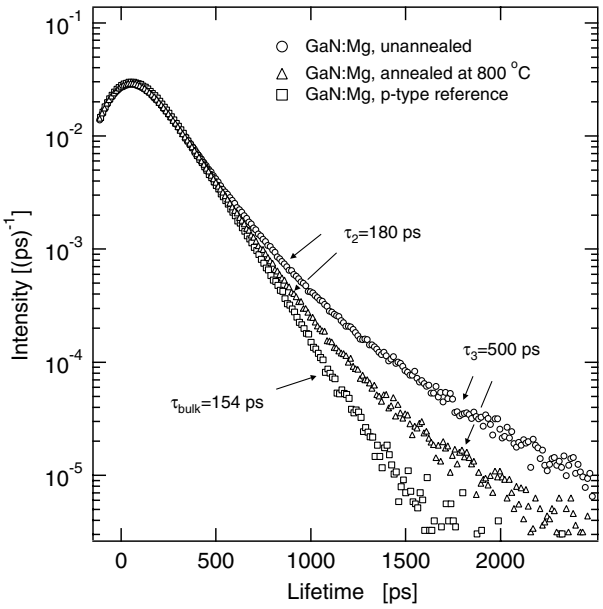

FIG. 2. The measured positron lifetime spectra in Mg doped GaN layers, grown by MBE (reference) or by MOCVD (others). The pulsed positron beam energy was 16 keV and measuring temperature 540 K.

effect on the lifetime spectra by decreasing the intensities I_2 and I_3.

The lifetime $\tau_2 = 180$ ps is clearly smaller than obtained previously for Ga vacancies (235 ps), indicating larger electron density and smaller open volume. The only possible candidates for such defects are N vacancies or complexes involving V_N. The lifetime of 180 ps is close to those expected for V_N according to theoretical calculations [9]. On the other hand, isolated N vacancy is not expected to be a positron trap because of its positive charge. This suggests that neutral or negative complexes involving V_N are present in Mg-doped GaN.

The atoms neighboring the N vacancy can be experimentally identified by recording the momentum distribution of the annihilating core electrons, using the coincidence technique to measure the Doppler broadening spectrum [14]. The measurement was done at 550 K in order to maximize the positron trapping at the vacancy. The lifetime experiments show that the measured Doppler spectrum $\rho(p)$,

$$\rho(p) = \eta_B \rho_B + \eta_V \rho_V + \eta_{Cl} \rho_{Cl}, \quad (1)$$

is a superposition of the momentum distributions in the lattice ρ_B, at V_N related defects ρ_V, and at larger vacancy clusters ρ_{Cl}. To decompose the Doppler spectrum, we calculate the positron trapping rates κ_V and κ_{Cl} from the measured intensities of the lifetime components τ_2 and τ_3, using the standard positron trapping model with two defects [10]. With the help of trapping rates, the fractions of positron annihilations at the V_N complexes $\eta_V = 0.372$ and at vacancy clusters $\eta_{Cl} = 0.048$ can be estimated in the as-grown sample at 550 K. The momentum distribution of the V_N complexes can be decomposed from Eq. (1) by recording ρ_B in MBE grown reference sample and ρ_{Cl} in MBE grown GaN:Si, where clusters have been observed [15]. Since the fraction of annihilations in the clusters is small, the possible error due to the inaccuracy of the cluster data is small.

The experimental core electron momentum distributions in the GaN lattice and in the N vacancy complexes are shown in Fig. 3. The curves have equal slopes, indicating that the dominant core electron shell is the same. The intensity of the distribution is smaller in the case of the N vacancy complex, which is typical for an open volume defect. However, the intensity is larger than previously recorded for the Ga vacancy in GaN, supporting the identification of the V_N related defect.

A more detailed identification can be reached by comparison with theoretical calculations (Fig. 3). As shown earlier [14,16], atomic wave functions can be used to obtain good quantitative agreement with the experimental core electron momentum distributions at momenta above $15 \times 10^{-3} m_0 c$. To mimic the experimental lattice distortions, the calculations were performed in a model structure where the atoms neighboring the vacancy were symmetrically relaxed in order to reproduce the experimental positron lifetime (180 ps). The results show that Ga $3d$ core electrons are dominant both for annihilation in the bulk lattice and at N vacancy related defects, explaining the similar slopes of the experimental curves in Fig. 3. The intensity of the momentum distribution for isolated V_N is much too high. The conventional W parameter, calculated as the integral from Fig. 3 at $(15–20) \times 10^{-3} m_0 c$ and scaled to the lattice value W_B, is $W_{V_N}/W_B = 0.948$, which is much larger than the experimental result of $W_{\text{rel}} = 0.86(2)$. As expected from its repulsive positive charge, the isolated N vacancy is thus not the defect trapping positrons in Mg-doped GaN.

The low intensity of the experimental ρ_V suggests that one of the Ga atoms neighboring the N vacancy is replaced by an atom which does not have the Ga $3d$ core electrons. An obvious candidate is the Mg dopant atom, which has an opposite charge to V_N and thus may form a neutral V_N-Mg_{Ga} complex. The calculated momentum distribution for the V_N-Mg_{Ga} complex is in good agreement with the experimental one (Fig. 3). The relative W parameter is $W_{V_N\text{-}Mg_{Ga}}/W_B = 0.851$, which is the same as the measured $W_{\text{rel}} = 0.86(2)$ within the experimental accuracy. We can thus positively identify the native vacancy in the Mg-doped GaN as a V_N-Mg_{Ga} pair.

The observation of V_N-Mg_{Ga} complexes is in good agreement with theoretical calculations, which predict a low formation energy (~ 1.4 eV) for such pairs [5,8,17]. According to theory, the vacancy complexes involving

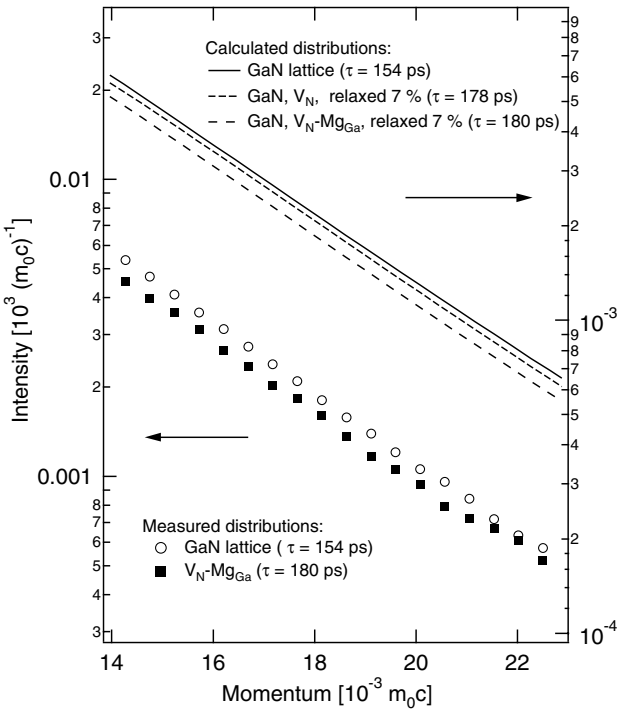

FIG. 3. The experimental and calculated core electron momentum distributions. The calculated structures were relaxed outwards to obtain the experimental positron lifetime. The measurements were done at 550 K using an incident positron energy of 15 keV.

either V_N or V_{Ga} should be the dominant defects at any position of the Fermi level during growth. The presence of V_{Ga} complexes [9] is well established earlier in *n*-type GaN. Confirming the theoretical prediction, these results show that V_N-Mg_{Ga} pairs exist in semi-insulating and *p*-type GaN.

The thermal annealing at 500–800 °C decreases the *S* parameter (Fig. 1) and makes the vacancies disappear. The obvious explanation is that the V_N-Mg_{Ga} pairs dissociate and V_N migrates to the surface. By applying simple first-order kinetics (as in Ref. [13]), we can estimate an activation energy of 3.0(3) eV for the dissociation. This energy corresponds to the sum $E_M + E_B$ of the migration energy of V_N and the binding energy of the V_N-Mg_{Ga} pair. Taking $E_B \sim 0.5$ eV from a theoretical calculation [17,18], we obtain the migration energy of $E_M \sim 2.5(3)$ eV. This is slightly larger as estimated previously for the Ga vacancy [13] and close to the very recent theoretical result (2.6 eV for V_N in *p*-type GaN [19]).

It is interesting that the V_N-Mg_{Ga} pairs are observed in as-grown MOCVD GaN, but not in the material grown by MBE (Fig. 2). The relevant difference is related to the presence of hydrogen in the growth environment. The as-grown MOCVD GaN is semi-insulating because Mg atoms are passivated by H. A postgrowth heat treatment is required to activate the Mg dopants and the *p*-type conductivity. Hydrogen is absent in the MBE growth and already the as-grown material possesses *p*-type conductivity. The results suggest that the V_N-Mg_{Ga} complexes are stable at the growth temperatures of 800–1000 °C only if the Fermi level is close to the midgap; otherwise the pairs dissociate. This is supported by theoretical calculations, which show that the migration energy of V_N is strongly reduced in *p*-type GaN due to the change of the charge state of the N vacancy from V_N^{1+} to V_N^{3+} [19].

The long positron lifetime component of $\tau_3 = 500$ ps indicates that vacancy clusters or microvoids exist in Mg-doped GaN [20]. These defects are likely to be the hollow pyramidal defects observed previously by TEM [6,7]. The positron experiments show that two defects prevent Mg atoms from activating as acceptors: (i) the V_N-Mg_{Ga} pairs and (ii) the microvoids, which have been attributed as gettering centers of electrically inactive Mg by TEM. The positron trapping rates allow us to estimate the concentrations c_V and c_{Cl} of both these defects quantitatively. For neutral V_N-Mg_{Ga} pairs, we obtain an estimate of $c_V = 10^{17}$–10^{18} cm^{-3} (positron trapping coefficient of 10^{15} s^{-1} was used). The dissociation of these pairs during annealing thus leads to 10^{17}–10^{18} cm^{-3} electrically active Mg. By assuming that the positron trapping at the microvoids is limited by diffusion (diffusion coefficient 1 cm^2/s and capture radius of 1 nm), we get an order of magnitude estimate of $c_{Cl} = 10^{15}$ cm^{-3}, which is in agreement with the TEM results for pyramidal defects [7]. Since the Mg concentration is in the 10^{19} cm^{-3} range, we conclude that both the V_N-Mg_{Ga} pairs and the Mg decorated microvoids may contribute significantly to the compensation. However, the hydrogen passivation seems to be the dominant effect according to these estimates.

In summary, we identify N vacancies in Mg-doped GaN layers by positron measurements. The core electron momentum spectroscopy shows that the N vacancies are complexed with a magnesium atom. After thermal annealing at 500–800 °C the V_N-Mg_{Ga} pairs dissociate. We conclude that these defects contribute to both activation and compensation of Mg doping. Their existence, stability, and dissociation temperature are in good agreement with theoretical predictions.

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*On leave from KFKI Central Research Institute for Nuclear and Particle Physics, H-1525 Budapest, P.O.B. 49, Hungary.

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