Observation of Native Ga Vacancies in GaN by Positron Annihilation

K. Saarinen,[1] T. Laine,[1] S. Kuisma,[1] J. Nissilä,[1] P. Hautojärvi,[1] L. Dobrzynski,[2] J. M. Baranowski,[3] K. Pakula,[3] R. Stepniewski,[3] M. Wojdak,[3] A. Wysmolek,[3] T. Suski,[4] M. Leszczynski,[4] I. Grzegory,[4] and S. Porowski[4]

[1]*Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland*

[2]*Institute of Physics, Warsaw University Branch, Lipowa 41, 15-424 Bialystok, Poland and Soltan Institute of Nuclear Studies, 05-400 Otwock-Swierk, Poland*

[3]*Institute of Experimental Physics, University of Warsaw, 00-681 Warsaw, Poland*

[4]*UNIPRESS, High Pressure Research Center, Polish Academy of Sciences, 01-142 Warsaw, Poland*

(Received 3 February 1997)

Positron annihilation experiments were performed to identify native point defects in *n*-type GaN bulk crystals as well as in epitaxial layers. The results show that Ga vacancies are present at concentrations $10^{17}-10^{18}$ cm^{-3} in both GaN bulk crystals and layers. The Ga vacancies are negatively charged, and their concentration correlates with the intensity of the yellow luminescence. We conclude that the Ga vacancies contribute to the electrical compensation of *n*-type GaN and that their acceptor levels are involved in the yellow luminescence transition. [S0031-9007(97)04289-0]

PACS numbers: 71.55.Eq, 61.72.Ji, 78.55.Cr, 78.70.Bj

Gallium nitride exhibits electronic, optical, and thermal properties, which make it a promising material for optoelectronic and high-power devices. Especially, its large direct band gap (3.4 eV) and strong interatomic bonds enable the construction of very efficient blue light-emitting diodes and promise the development of long-lifetime blue lasers. However, the role of various defects in the properties of this material still awaits a detailed description. For example, the origin of the *n*-type conductivity of undoped GaN has been associated to N vacancies [1,2], but recently it has also been attributed to residual impurities such as O and Si [3–6]. The parasitic optical transition leading to the yellow luminescence is observed in both GaN bulk crystals and layers, but even the positions of the electronic levels participating in this optical process are under discussion [2,4,5,7].

In this Letter, we use positron annihilation spectroscopy to obtain structural information on native point defects in GaN bulk crystals as well as in epitaxial layers. Positrons get trapped at neutral and negative vacancies because of the missing positive charge of the ion cores. The reduced valence and core electron density at a vacancy increases the positron lifetime and narrows the positron-electron-momentum distribution. Very few positron results have been published in GaN [8]. In this Letter, we show that negative Ga vacancies exist at concentrations $10^{17}-10^{18}$ cm^{-3} in both *n*-type GaN bulk crystals and layers. The Ga vacancies compensate *n*-type conductivity and participate in the yellow luminescence transition.

The bulk crystals were grown at a nitrogen pressure of about 1.5 GPa and a temperature of 1500 °C [9]. Their free electron concentration is about 5×10^{19} cm^{-3} at 300 K. The epitaxial layers were grown on a sapphire substrate in atmospheric-pressure MOCVD (metal-organic-chemical-vapor deposition) equipment with the gas system and the quartz reactor especially designed for the growth of nitride compounds. Ammonia and trimethylgallium were used as source gases, and hydrogen was used as a carrier gas. After thermal annealing at 1000 °C in H_2 and nitridization of the surface in NH_3, a low temperature GaN buffer layer was deposited. Then, a GaN layer with a thickness of 2 μm was grown at a temperature in the range of 1000–1050 °C.

The GaN layers were characterized by the Hall effect and photoluminescence measurements at 300 K. The carrier concentration varied from 3.7×10^{17} to 2.0×10^{18} cm^{-3} in the four studied layers. The intensity of the yellow luminescence was determined by exciting with the 325 nm line of a He-Cd laser. In order to probe approximately the same region below the surface of the epilayer as in the positron experiments, the luminescence was excited from the substrate side of the sample. The emitted radiation was analyzed by a 0.5-m monochromator equipped with a photomultiplier. In order to compare the yellow luminescence of different samples, its intensity was averaged over the surface of a particular sample, and the same optical alignment was used to collect the light emitted by each sample.

The GaN bulk crystal was studied by sandwiching two identical sample pieces with a 30 μCi ^{22}Na positron source. Both the positron lifetime and the Doppler broadened shape of the 511 keV annihilation radiation were recorded using conventional instrumentation [10]. The GaN layers were investigated with Doppler broadening experiments using a variable energy positron beam, the energy of which was chosen so that all positron annihilate in the GaN epilayer. The shape of the 511 keV line was described using the conventional low and high electron-momentum parameters *S* and *W* [10]. When positrons annihilate at vacancies, the *S* parameter increases and the *W* parameter decreases, since a larger fraction of annihilations takes place with the low-momentum valence

 0031-9007/97/79(16)/3030(4)$10.00

electrons. The details of the core electron-momentum distribution was studied by the coincidence measurement of Doppler broadening, where the experimental background is reduced by detecting simultaneously the two annihilation photons [11].

The average positron lifetime in the GaN bulk crystal is constant $\tau_{av} = 167$ ps at temperatures $T = 10-150$ K but increases up to $\tau_{av} = 191$ ps at 500 K (Fig. 1). The lifetime spectra recorded at 200–500 K can be decomposed into two components. The longer lifetime component is constant $\tau_2 = 235 \pm 5$ ps (Fig. 1) as a function of temperature. By also fixing this lifetime, the spectra measured at 10–200 K could be decomposed. The lifetime component τ_1 is a constant $\tau_1 = 164 \pm 1$ ps at 10–150 K and then decreases to about $\tau_1 = 140$ ps at 500 K.

The two-componential lifetime spectrum implies that positrons in GaN bulk crystal annihilate either from a delocalized state in the lattice or as localized at vacancy defects. The positrons trapped at vacancies annihilate with the longer lifetime $\tau_V = \tau_2 = 235 \pm 5$ ps. The decrease of the average lifetime at low temperatures indicates that the fraction η_V of positron annihilations at vacancies decreases. When $\eta_V \rightarrow 0$, the component τ_1 approaches the lifetime value τ_B of delocalized positrons in the lattice. At 10 K, we have $\tau_1 = 164 \pm 1$ ps and $\tau_{av} = 167$ ps. The positron lifetime in the GaN lattice is between these values, i.e., $\tau_B = 166 \pm 1$ ps.

The low-momentum annihilation parameter S in the GaN ($n = 2.0 \times 10^{18}$ cm^{-3}) layer increases only slightly as a function of temperature (Fig. 2). This increase is similar to that observed generally in defect-free Si, GaAs, and InP, and it can be attributed to the thermal expansion of the lattice. The S parameter in all other GaN layers is clearly larger (Fig. 2), indicating that vacancies are present. The temperature dependence of the S parameter in GaN ($n = 3.7 \times 10^{17}$ cm^{-3}) and GaN ($n = 1.2 \times 10^{18}$ cm^{-3}) samples is similar to that of the average positron lifetime in the GaN bulk crystal (Fig. 1): S decreases at low temperatures because less positrons annihilate at vacancies (Fig. 2).

The number of different vacancy-type positron traps in the material can be studied by investigating the linearity between the annihilation parameters τ_{av}, S, and W [10,12]. If only a single type of vacancy is present, these parameters depend linearly on each other, when the fraction η_V of positron annihilations at vacancies varies: $A = (1 - \eta_V)A_B + \eta_V A_V$, where A is τ_{av}, S, or W. The data in all GaN samples at various temperatures form a straight line in the (S, W) plane (Fig. 3). The same type of vacancy is thus present in the bulk crystal as well as in all GaN layers. In the GaN bulk crystal the (S, τ_{av}) and (W, τ_{av}) plots can be used to determine the S and W parameters corresponding to the lifetimes $\tau_B = 166$ ps in the lattice and $\tau_V = 235$ ps at the vacancy. The relative changes of S and W due to positron trapping at the vacancy with $\tau_V = 235$ ps are $S_V/S_B = 1.038(2)$ and $W_V/W_B = 0.86(2)$.

The high-momentum part of the Doppler broadening spectrum was recorded in GaN ($n = 3.7 \times 10^{17}$ cm^{-3})

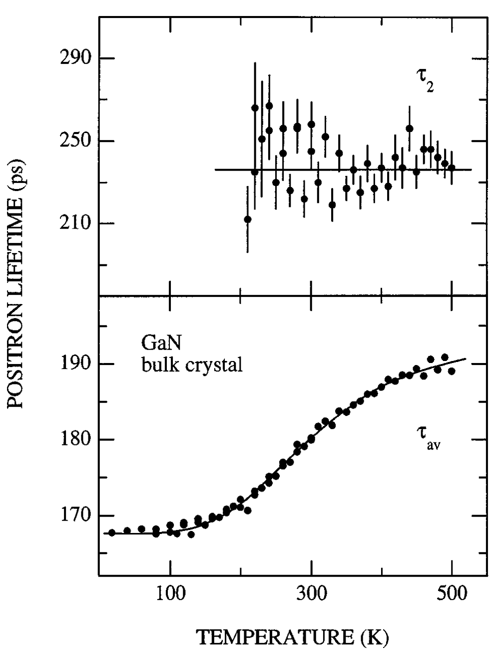

FIG. 1. The average positron lifetime τ_{av} and the lifetime component τ_2 vs measurement temperature GaN bulk crystal. The lifetime component τ_2 could be decomposed only at $T > 200$ K. The solid lines are drawn to guide the eye.

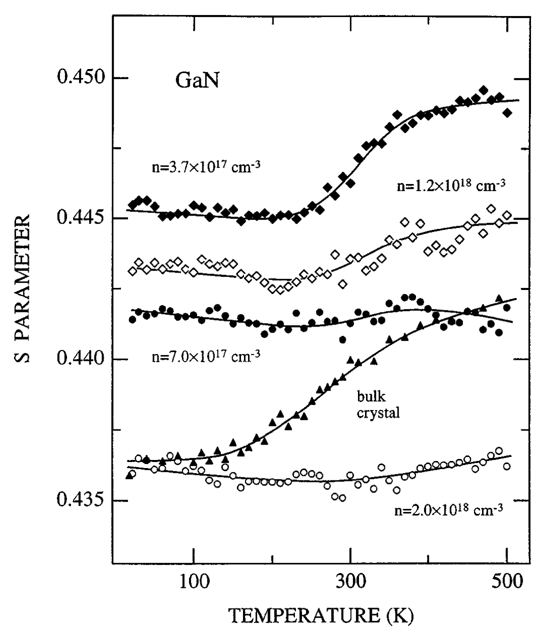

FIG. 2. The low electron-momentum parameter S vs measurement temperature in various GaN samples. The carrier concentrations of the GaN layers at 300 K are indicated in the figure. The solid lines are fits to the temperature dependent positron trapping model (Ref. [14]).

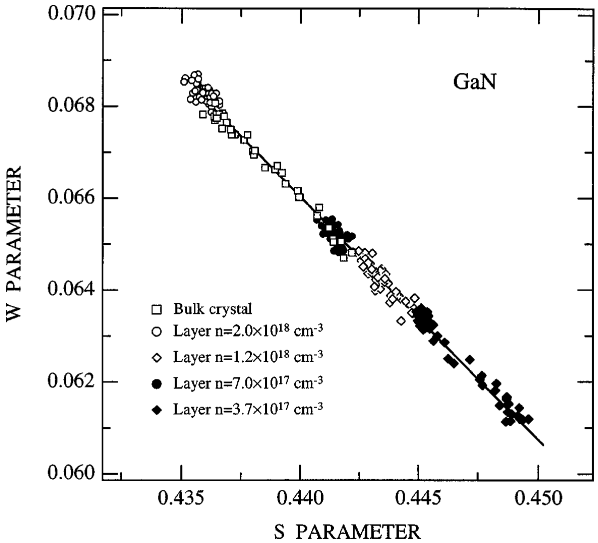

FIG. 3. The electron-momentum parameters S and W in the GaN samples at various temperatures. The straight line indicates that the same defect (Ga vacancy) is found in all samples.

and GaN ($n = 2.0 \times 10^{18}$ cm^{-3}) layers using the coincidence technique [11]. As explained above, no signs of vacancy defects were observed in the GaN ($n = 2.0 \times 10^{18}$ cm^{-3}) layer at 300 K, and the experiment thus yields the core electron-momentum distribution encountered by the free positrons in the GaN lattice (Fig. 4). Using the ratio $S_V/S_b = 1.038$ determined above, we can estimate that in the GaN ($n = 3.7 \times 10^{17}$ cm^{-3}) layer the fraction of positrons annihilating at the vacancies is $\eta_V = (S - S_B)/(S_V - S_B) = 79\%$ at 450 K. With this information, the data recorded in this layer at 450 K can

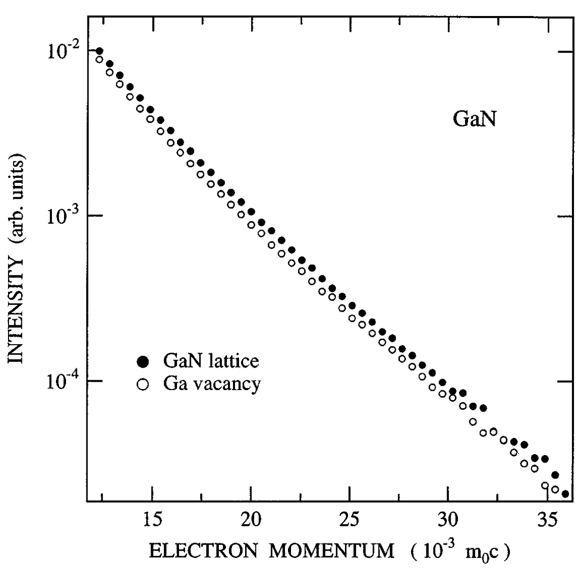

FIG. 4. The core electron momentum distribution at the GaN lattice and at the Ga vacancy, obtained after decomposition of the original Doppler broadening data.

be decomposed, and the core electron-momentum distribution at the vacancy defect in GaN can be extracted (Fig. 4). The intensity of the core electron-momentum distribution is clearly smaller in the vacancy than in the GaN lattice. However, the momentum distributions at vacancies and in the bulk have clearly similar shapes over a wide-momentum range.

The positron lifetime $\tau_V = 235$ ps and the relative S parameter $S_V/S_B = 1.038$ are typical values for monovacancies in materials which have the same atomic density as GaN. The recent theoretical calculations predict the lifetimes $\tau_B = 156$ ps for the GaN lattice and $\tau_V = 213$ ps and $\tau_V = 169$ ps for unrelaxed Ga and N vacancies, respectively [13]. We can conclude that the observed vacancies have the open volume of the monovacancy, but only the Ga vacancy is compatible with the experimental annihilation characteristics. The open volume of the N vacancy is much too small to account for the long lifetime of 235 ps, and the Ga atoms surrounding V_{N} yield a much stronger core annihilation component than that observed for the vacancy in the data of Fig. 4 [13]. Both the long lifetime and the low intensity of the core annihilation, however, can be expected for V_{Ga}, since the neighboring N atoms are small and the d electrons forming the outermost core shell of Ga are missing. We thus conclude that Ga vacancies are observed in the positron experiments in both GaN bulk crystals and layers.

The temperature dependence of the average positron lifetime (Fig. 1) and S parameter (Fig. 2) is typically observed when negative ions compete with vacancies as positron traps [14]. The negative ions possess no open volume, but they are able to bind positrons at shallow (<0.1 eV) Rydberg states in their attractive Coulomb field. The average lifetime and S parameter increase above 150 K, when positrons start to escape from the ions and a larger fraction of them annihilates at vacancies. At $T < 150$ K the positron trapping coefficient at negative ions depends on a temperature roughly as T^{-n} ($n \approx 0.5$), implying that their contribution to the measured τ_{av} and S should magnify [15]. However, both τ_{av} and S remain constant or even decrease over this temperature range (Figs. 1 and 2). The T dependence of the positron trapping at vacancies must thus cancel that at the negative ions, i.e., trapping coefficient at vacancies μ_V varies also as $\mu_V \propto T^{-n}$. Since positron trapping at neutral vacancies is independent on temperature [15], we conclude that the observed Ga vacancies are negatively charged in n-type GaN.

The temperature dependence of the S parameter can be modeled with kinetic trapping equations including positron detrapping from the negative ions [14]. As shown by the solid lines in Fig. 2, the fits are in excellent agreement with the data assuming that the trapping rates at both negative ions and vacancies depend on temperature as T^{-n} ($n \approx 0.5$). This analysis confirms that the observed Ga vacancies are negatively charged.

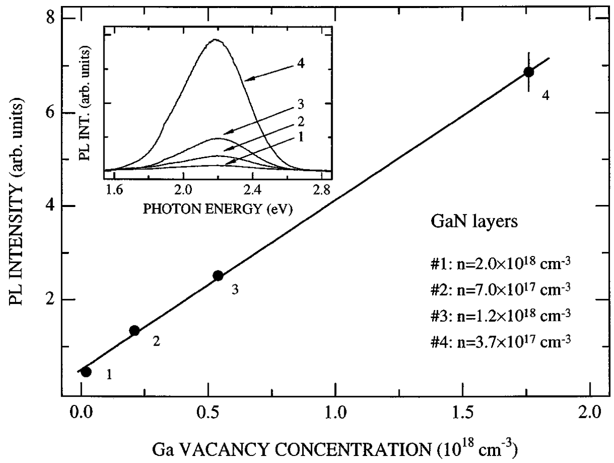

FIG. 5. The intensity of the yellow luminescence vs the Ga vacancy concentration in GaN epitaxial layers. The inset shows the luminescence spectrum in the four studied layers, indexed according to the increasing Ga vacancy concentration.

The concentration of the Ga vacancies can be estimated using the simple formula $[V_{\mathrm{Ga}}] = (S - S_B)/(\mu_V \tau_B(S_V - S))$ at the high temperature plateau of Fig. 2, where the influence of negative ions can be neglected [10,14]. Taking $\mu_V \approx 10^{15}\ \mathrm{s}^{-1}/\mathrm{N}_{\mathrm{at}}$ [14,15] (N_{at} is the atomic density), we obtain the concentrations 10^{17}–$10^{18}\ \mathrm{cm}^{-3}$ in the GaN epilayers and roughly $10^{18}\ \mathrm{cm}^{-3}$ in the GaN bulk crystal.

Recent theoretical calculations suggest that the Ga vacancy is created most abundantly of all simple intrinsic point defects in *n*-type GaN [4,5]. The experimentally observed Ga vacancies may thus exist at high concentrations in *n*-type GaN simply due to their low formation energy. In good agreement with theoretical results, the Ga vacancies found here are negatively charged in *n*-type GaN and thus act as deep, compensating acceptors.

The parasitic yellow luminescence band at about 2.2–2.3 eV is commonly observed in *n*-type GaN. There is an increasing amount of evidence that this transition takes place between a shallow donor and a deep acceptor [2,4,5], and the Ga vacancy has been suggested as the defect responsible for the acceptor level [4,5,16]. Figure 5 shows the intensity of the yellow luminescence in MOCVD layers as a function of the V_{Ga} concentration obtained from positron experiments. The yellow luminescence correlates perfectly with the concentration of the negative Ga vacancies. We thus conclude that native Ga vacancies participate in the luminescence transition by acting as the deep acceptors.

In summary, we observe Ga vacancies at concentrations 10^{17}–$10^{18}\ \mathrm{cm}^{-3}$ in *n*-type GaN bulk crystals and epitaxial layers by positron annihilation. The Ga vacancy is negatively charged and plays an important role in the electrical compensation of *n*-type material. The concentration of Ga vacancies correlates with the intensity of the yellow luminescence. We conclude that the Ga vacancies form the deep acceptor levels associated with the yellow luminescence transition.

We acknowledge M. J. Puska, T. Mattila, and R. M. Nieminen for discussions and comments. This work was supported by the Academy of Finland (EPIMATTER project) and the State Committee for Scientific Research in Poland (Grants No. 2P03B03610 and No. 1T08A06110).

[1] T. L. Tansley and R. J. Egan, Phys. Rev. B **45**, 10 942 (1992).
[2] P. Perlin, T. Suski, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian, and T. D. Moustakas, Phys. Rev. Lett. **75**, 296 (1995).
[3] W. Götz *et al.,* Appl. Phys. Lett. **68**, 3144 (1996).
[4] J. Neugebauer and C. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
[5] T. Mattila and R. M. Nieminen, Phys. Rev. B **55**, 9571 (1997).
[6] T. Suski (unpublished).
[7] E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, Phys. Rev. B **51**, 13 326 (1995).
[8] S. Dannefaer, W. Puff, and D. Kerr, Phys. Rev. B **55**, 2182 (1997).
[9] G. R. Grzegory and S. Krukowski, Phys. Scr. **T39**, 242 (1991).
[10] P. Hautojärvi and C. Corbel, in *Positron Spectroscopy of Solids,* edited by A. Dupasquier and A. P. Mills, Jr. (IOS Press, Amsterdam, 1995).
[11] M. Alatalo, H. Kauppinen, K. Saarinen, M. J. Puska, J. Mäkinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **51**, 4176 (1995).
[12] K. Saarinen, T. Laine, K. Skog, J. Mäkinen, P. Hautojärvi, K. Rakennus, P. Uusimaa, A. Salokatve, and M. Pessa, Phys. Rev. Lett. **77**, 3407 (1996).
[13] M. J. Puska and M. Hakala (private communication). These calculations utilize the generalized gradient approximation for positron-electron correlation. For more details see Barbiellini *et al.,* Phys. Rev. B **51**, 7341 (1995).
[14] C. Corbel, F. Pierre, K. Saarinen, P. Hautojärvi, and P. Moser, Phys. Rev. B **45**, 3386 (1992); K. Saarinen, S. Kuisma, J. Mäkinen, P. Hautojärvi, M. Törnqvist, and C. Corbel, Phys. Rev. B **51**, 14 152 (1995).
[15] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
[16] X. Zhang, P. Kung, D. Walker, A. Saxler, and M. Razeghi, Mater. Res. Soc. Symp. Proc. **395**, 625 (1996).