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Oila, J., Kivioja, J., Ranki, V., Saarinen, K., Look, D. C., Molnar, R. J., Park, S. S., Lee, S. K., & Han, J. Y. (2003). Ga Vacancies as Dominant Intrinsic Acceptors in GaN Grown by Hydride Vapor Phase Epitaxy. *Applied Physics Letters, 82* (20), 3433-3435.
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Ga vacancies as dominant intrinsic acceptors in GaN grown by hydride vapor phase epitaxy

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(Received 18 December 2002; accepted 26 February 2003; publisher error corrected 20 May 2003)

Positron annihilation measurements show that negative Ga vacancies are the dominant acceptors in *n*-type gallium nitride grown by hydride vapor phase epitaxy. The concentration of Ga vacancies decreases, from more than 10^{19} to below 10^{16} cm^{-3}, as the distance from the interface region increases from 1 to 300 μm. These concentrations are the same as the total acceptor densities determined in Hall experiments. The depth profile of O is similar to that of V_{Ga}, suggesting that the Ga vacancies are complexed with the oxygen impurities. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1569414]

Hydride vapor phase epitaxy (HVPE) is a method for the fast growth of GaN layers on sapphire substrates. The quality of these layers improves drastically with thickness, making them interesting candidates for substrates of GaN homoepitaxy. For example, the dislocation densities decrease from the very high values of $>10^{11}$ cm^{-2} close to GaN/sapphire interface to less than 10^{8} cm^{-2} in films which are thicker than 50 μm.[1–4] The impurity concentrations,[5,6] electrical and optical properties,[1,5–8] and deep level defects[2,9] have also qualitatively similar depth profiles. The atomic structures of the dominating point defects, however, have not been identified and their role as electrically active centers has not been quantitatively estimated.

Earlier positron annihilation experiments in GaN have identified the Ga vacancy,[10] which most likely forms defect complexes with O_N impurities.[11,12] These previous works have been performed either in bulk crystals where the impurity concentrations are high or in epitaxial samples with dislocation densities above 10^{9} cm^{-2}. As both negative impurities[13] and dislocations[14] are positron traps in GaN, it has not been possible to determine experimentally the charge of V_{Ga} complexes or the quantitative role of them in the electrical properties of the material. In this work, we show that negatively charged Ga vacancies are the dominant acceptor defects in *n*-type HVPE GaN.

The GaN samples were grown by hydride vapor phase epitaxy on sapphire substrates. The layers with thicknesses of 1, 5, 10–14, 36–39, and 49–68 μm were fabricated at MIT Lincoln Laboratory. A free-standing 300-μm-thick sample was grown at Samsung Advanced Institute of Technology. It was separated from the sapphire by laser-induced lift-off. The electron concentrations of the *n*-type GaN layers decrease with thickness from mid 10^{19} cm^{-3} (1 μm sample) to 10^{6} cm^{-3} (60 μm sample). In the free-standing GaN sample the electron concentration is only 5×10^{15} cm^{-3}.

Conventional positron lifetime spectroscopy[15] was performed in samples thicker than 30 μm. The positron annihilations in the sapphire substrate were subtracted from the spectra by estimating their fraction (20%–40%) from the exponential stopping profile of fast positrons from ^{22}Na source. In order to measure depth profiles, all GaN layers were investigated by implanting 0–25 keV positrons from a monoenergetic beam at the depths of 0–1 μm from the surface. The measured Doppler broadening of the 511 keV annihilation radiation was characterized by the low and high electron-momentum parameters *S* and *W*.[15]

The average positron lifetime τ_{av} in the free-standing HVPE GaN sample is indistinguishable from that in the GaN lattice ($\tau_B = 160$ ps) at 300–500 K but increases to 162 ps at 30 K (Fig. 1). The average positron lifetime in the 40–60 μm GaN layers is larger than in the free-standing GaN. The positron lifetime spectra can be decomposed into two components, corresponding to annihilations in the bulk lattice (lifetime τ_1) and at vacancy defects (lifetime τ_2). The lifetime $\tau_2 = 235\pm5$ ps is the same as identified previously for the positrons annihilating as trapped at Ga vacancies,[10–13] indicating that defects involving V_{Ga} are present.

The increase of the average positron lifetime at low temperatures shows that the positron trapping rate[15]

$$\kappa = \mu_V[V_{Ga}] = \frac{1}{\tau_B}\frac{\tau_{av}-\tau_B}{\tau_2-\tau_{av}} = \frac{1}{\tau_B}\frac{S_L-S_B}{S_V-S_L} \tag{1}$$

increases roughly as $\kappa \propto T^{-1/2}$ (μ_V is the positron trapping coefficient, see later for the definitions of the *S* parameters). The temperature dependence of the average positron lifetime is totally reversible and reproducible, indicating that the concentration of Ga vacancies remains constant. Because the Fermi level is close to the conduction band, the charge states

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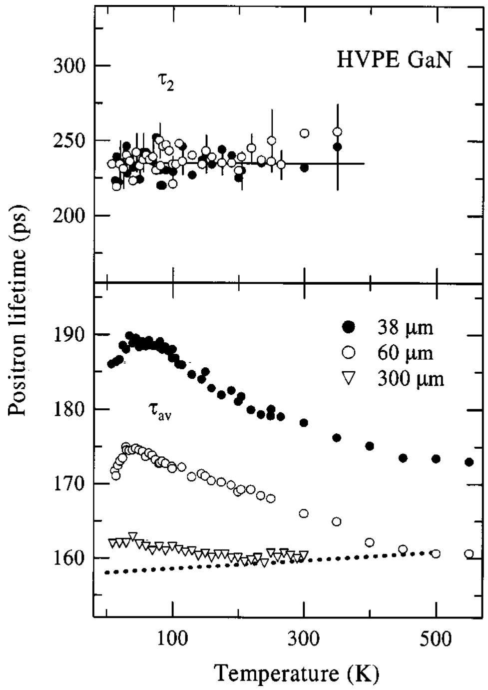

FIG. 1. Average positron lifetime (τ_{av}) and the lifetime of positrons trapped at vacancies (τ_2) vs measurement temperature in GaN samples with three different thicknesses. The dashed line shows the temperature dependence the positron lifetime in bulk GaN lattice (see Ref. 13).

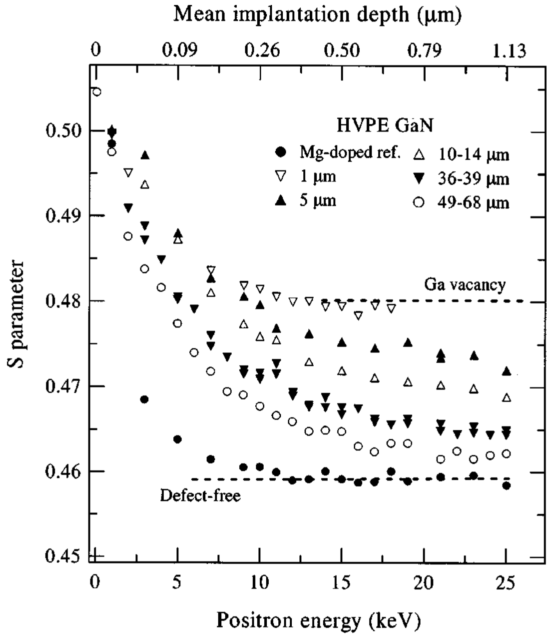

FIG. 2. The low electron-momentum parameter S as a function of the positron implantation energy. The dashed lines show the values of S parameter in defect-free GaN and at the Ga vacancy. The top axis indicates the mean stopping depth corresponding to the positron implantation energy.

of acceptor-like defects like V_{Ga} do not change with the measurement temperature. The temperature dependence of the positron trapping rate $\kappa \propto T^{-1/2}$ thus reflects the increase of the positron trapping coefficient μ_V at low temperatures. This behavior is expected for negative vacancies.[15,16] When the thermal velocity of positrons decreases, the overlap of the positron wave function with the attractive Coulomb potential becomes more efficient, thus facilitating faster transition into the vacancy.[16]

Thus, the increase of positron trapping at low temperatures gives direct experimental evidence that the charge of Ga vacancies is negative. This is in good agreement with the results of theoretical calculations,[17] which predict a charge state of 3- for isolated Ga vacancies and 2-for V_{Ga}–Si_{Ga} and V_{Ga}–O_N complexes in n-type GaN.

The concentrations of Ga vacancies can be estimated from the positron results by applying Eq. (1). We assume a positron trapping coefficient of $\mu_V = 3\times10^{15}\ \mathrm{s}^{-1}/N_{at}$ ($N_{at} = 8.775\times10^{22}\ \mathrm{cm}^{-3}$ is the atomic density of GaN).[13,15] The Ga vacancy concentrations are $6\times10^{16}\ \mathrm{cm}^{-3}$ and $2\times10^{16}\ \mathrm{cm}^{-3}$ in the 40- and 60-μm-thick layers, respectively. By scaling the positron trapping coefficient as $\mu_V \propto \kappa_V \propto T^{-1/2}$, we can estimate the V_{Ga} concentration of $2\times10^{15}\ \mathrm{cm}^{-3}$ in the free-standing GaN sample.

The positron data show further that the defects involving Ga vacancies are the dominant negatively charged acceptors in the samples. The enhancement of positron trapping at low temperatures would not be observed, if other negative centers competed with V_{Ga} as positron traps. For example, negative ions such as Mg_{Ga}^- localize positrons at hydrogenic states at low temperatures, strongly decreasing the fraction of positron annihilations at vacancy defects and consequently the average positron lifetime.[13] In the present HVPE GaN samples, only a small decrease of τ_{av} is detected at $T < 30$ K. In fact, the secondary ion-mass spectrometry in the bulk of the 60-μm-thick layer has shown that the concentrations of typical acceptor impurities are $[\mathrm{Mg}] < 10^{16}\ \mathrm{cm}^{-3}$ and $[\mathrm{C}] < 10^{15}\ \mathrm{cm}^{-3}$,[5] i.e., clearly less than $[V_{Ga}]$.

The temperature-dependent Hall experiments yield the total donor and acceptor concentrations of $N_D = 8\times10^{16}\ \mathrm{cm}^{-3}$ and $N_A = 3\times10^{16}\ \mathrm{cm}^{-3}$ in the 60-μm-thick GaN on sapphire and $N_D = 8\times10^{15}\ \mathrm{cm}^{-3}$ and $N_A = 3\times10^{15}\ \mathrm{cm}^{-3}$ in the free-standing GaN sample. The total acceptor concentrations are in very good agreement with the concentrations of Ga vacancies determined in positron experiments, confirming that Ga vacancies are the dominant acceptors in HVPE GaN.

To detect positron trapping at Ga vacancies in thinner ($<30\ \mu$m) films we implant positrons from a monoenergetic beam and probe the Doppler broadening of the annihilation radiation (Fig. 2). At low positron implantation energies surface effects with a high characteristic S parameter of $S > 0.5$ are observed. With increasing E the positron diffusion to the surface decreases and the $S(E)$ curve saturates to a constant level $S = S_L$, characterizing the interior of the layer at about 0.5–1 μm below the surface. The S_L values are systematically larger than S_B recorded in defect free GaN, demonstrating the presence of vacancy defects. The linearity of valence and core electron momentum distributions (i.e., the so-called S vs W plot)[15] indicates that (i) the samples have a single dominant vacancy-type positron trap and (ii) the momentum distribution of annihilating electrons in this vacancy is similar to that of Ga vacancy detected in thicker ($>30\ \mu$m) films where both positron lifetime and Doppler broadening experiments could be performed. Hence, the Ga vacancy is the dominant positron trap in all layers.

The V_{Ga} concentrations can be estimated from the Doppler data by applying Eq. (1). We determine the value $S_V = 1.046 S_B$ for total positron trapping at the Ga vacancy by

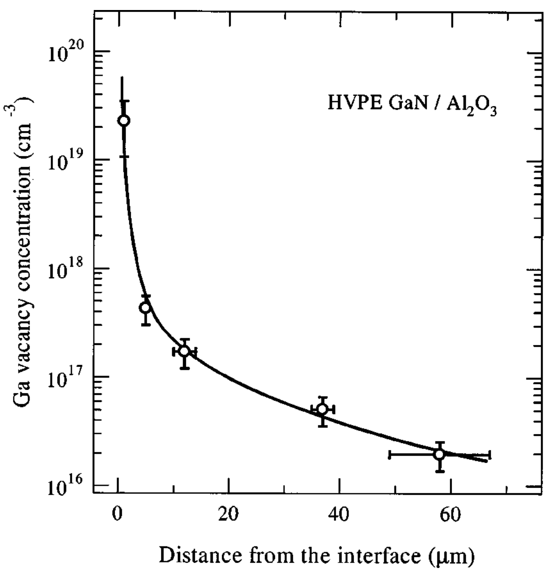

FIG. 3. The concentration of Ga vacancies as a function of the thickness of the GaN layers on sapphire.

combining positron lifetime and Doppler experiments in the thick layers, similarly as earlier.[10] Since the growth is reproducible, the estimated V_{Ga} concentrations construct a depth profile of Ga vacancies over the entire thickness of the HVPE GaN layer (Fig. 3). The concentration of Ga vacancies decreases from almost 10^{20} cm^{-3} close to the GaN/sapphire interface down to 10^{16} cm^{-3} at 60 μm. The 300-μm-thick free-standing GaN has even smaller $[V_{Ga}] \approx 10^{15}$ cm^{-3} as deduced in positron lifetime experiments.

The depth profile of Ga vacancies in Fig. 3 is very similar to those reported earlier for dislocations,[1–4] O impurities,[5,6] optical properties[1,6–8] and deep defect levels.[2,9] All these results manifest the general improvement of the quality of the HVPE GaN material with increasing thickness, but more direct correlations are not obvious. The presence of Ga vacancies in the structure of the dislocation core has been suggested by theoretical calculations.[18] Close to the interface the V_{Ga} concentration is 10^{20} cm^{-3} and the dislocation density is very high ($>10^{11}$ cm^{-2}). Obviously Ga vacancies exist close to dislocations and even in the core structure as suggested also by the consistent analysis of electrical, transmission electron microscopy, and positron data.[5]

At thicknesses of >5 μm from the interface the dislocation density is $<10^{9}$ cm^{-2}, which is less than the typical sensitivity limit of positron trapping at dislocations. Positron studies in dislocation-free bulk crystals[10] and in hetero and homoepitaxial layers[11,14] have shown that Ga vacancies are formed in *n*-type GaN independently of dislocations, and the dislocations at grain boundaries are free of V_{Ga}.[14] The Ga vacancies observed in HVPE GaN at >5 μm from the interface are thus probably not associated with dislocations, but present simply because their formation energy is low in *n*-type GaN.[17] According to electron irradiation studies the isolated V_{Ga} is mobile already at 600 K,[12] i.e., at much lower temperatures than applied in the HVPE growth. However, the Ga vacancies bound to defect complexes such as V_{Ga}–O_N have a considerably higher thermal stability.[12] In fact, SIMS experiments[5,6] show that the O concentration profile is similar to that of V_{Ga} in Fig. 3. This correlation gives further evidence to attribute the observed Ga vacancies in HVPE GaN to complexes V_{Ga}–O_N.

In summary, our positron annihilation experiments show that Ga vacancies are the dominant acceptors *n*-type GaN grown by hydride vapor phase epitaxy on sapphire. The concentration of Ga vacancies decreases from almost 10^{20} cm^{-3} to less than 10^{16} cm^{-3} when the thickness of the GaN layers increases from 1 to more than 100 μm. Furthermore, the Ga vacancy concentration is equal to the total acceptor density determined by temperature-dependent Hall experiments. The depth profile of Ga vacancies is similar to that of O, suggesting that the Ga vacancies formed during the growth are bound to defect complexes with the oxygen impurities.

This work was supported by the Academy of Finland (DENOS project). The work of D.C.L. was supported under AFOSR Grant No. F49620-00-1-0347 and the Lincoln Laboratory portion by the ONR under Air Force Contract No. F19628-00-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the authors and not necessarily endorsed by the United States Air Force.

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