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Effect of growth polarity on vacancy defect and impurity incorporation in dislocation-free GaN

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Effect of growth polarity on vacancy defect and impurity incorporation in dislocation-free GaN

F. Tuomisto[a] and K. Saarinen
Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland

B. Lucznik, I. Grzegory, H. Teisseyre, T. Suski, and S. Porowski
High Pressure Research Center, Unipress, Polish Academy of Sciences, 01-142 Warsaw, Poland

P. R. Hageman
NSRIM, Radboud University Nijmegen, Toernooiveld 1, 6525 ED, Nijmegen, The Netherlands

J. Likonen
VTT Processes, P. O. Box 1608, 02044 VTT, Finland

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We have used positron annihilation, secondary ion mass spectrometry, and photoluminescence to study the point defects in GaN grown by hydride vapor phase epitaxy (HVPE) on GaN bulk crystals. The results show that N polar growth incorporates many more donor and acceptor type impurities and also Ga vacancies. Vacancy clusters with a positron lifetime $\tau_D = 470 \pm 50$ ps were found near the N polar surfaces of both the HVPE GaN layers and bulk crystals. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854745]

The properties of gallium nitride (GaN) depend strongly on the crystal orientation along the polar *c*-axis of the wurtzite structure. Studies on thin heteroepitaxial GaN overlayers grown on sapphire (Al_2O_3) by molecular beam epitaxy (MBE)[1,2] and metalorganic vapor phase epitaxy (MOVPE)[3] have shown that the layer polarity [Ga(0001) or N(000$\bar{1}$)] has a significant impact on the incorporation of oxygen. However, the heteroepitaxial layers have a high dislocation density due to the substantial lattice mismatch between the layer and the substrate, which has been shown to affect the impurity incorporation, diffusion, and point defect formation in the material.[4] Homoepitaxial growth of overlayers minimizes the impurity levels in the growth environment, since only native materials are present. No buffer layers are needed to produce different growth polarities, since the layers can be grown on different polarity surfaces of the substrate GaN crystal. Thus, layers with both polarities can be grown simultaneously.

The high pressure (HP) method[5,6] can be used to grow dislocation-free bulk GaN single crystals. Thick overlayers can be grown with hydride vapor phase epitaxy (HVPE) within reasonably short times. This provides an ideal system for investigating the effect of the growth polarity on the impurity incorporation and point defect formation. In addition to the low oxygen content of the substrate bulk GaN (compared to Al_2O_3), the lack of dislocations minimizes the diffusion of impurities from the substrate. Thus the properties of the HVPE layers should be independent of the layer thickness, in contrast to heteroepitaxial HVPE GaN, where the physical properties of the layers vary along the *c*-axis due to the dislocations.[7] The incorporation of impurities and formation of point defects during growth should then be limited by the (polarity dependent) surface kinetics and thermodynamics (independent of the polarity).

In this work we utilize positron annihilation spectroscopy (PAS), secondary ion mass spectrometry (SIMS), and photoluminescence (PL) to investigate HVPE GaN overlayers grown on facets of both Ga and N polarities of bulk HP GaN substrates. We show that the concentrations of Ga vacancy related defects and impurities are significantly higher in the N polar layer than in the Ga polar layer. In addition vacancy clusters are observed in the N polar layer. Similar trends are observed near the N and Ga polar surfaces of HP GaN.

The GaN layers were grown by hydride vapor phase epitaxy to thicknesses 30–160 μm. Four layers were grown on the Ga face and one layer on the N face of the HP GaN substrate. One of the Ga polar layers (30 μm) was grown in the same run with the N polar layer. Apart from the thickness, the properties of the Ga polar layers were similar to each other.[10] The impurity concentrations obtained by SIMS in the Ga and N polar HVPE GaN layers are presented in Table I.

The difference in the optical properties between the N and Ga polar HVPE GaN layers is seen in Fig. 1. The PL spectrum of the N polar layer is qualitatively very similar to the typical spectrum of HP GaN, exhibiting a yellow luminescence (YL) band. The Ga polar layer on the other hand shows excellent optical quality: the spectrum is dominated by exciton (X) and donor-acceptor pair (DAP) transition peaks and their satellites, with an intensity ratio (X/DAP)

TABLE I. Defect concentrations in the GaN samples.

Defect (cm^{-3})	HVPE GaN		Bulk GaN	
	Ga polar	N polar	Ga polar	N polar
[O]	4×10^{17}	2×10^{19}	4×10^{19}[a]	8×10^{19}[b]
[Mg]	4×10^{16}	2×10^{17}	1×10^{18}[a]	
[C]	5×10^{16}	2×10^{17}		
[V_{Ga}]	$\leqslant10^{15}$	7×10^{17}	2×10^{17}	7×10^{17}
c_{ion}	$\leqslant10^{15}$	5×10^{18}	3×10^{18}	3×10^{18}
c_{cl}	$\leqslant10^{15}$	$0.5–15\times10^{16}$	$\leqslant10^{15}$	$0.5–15\times10^{16}$

[a]Taken from Ref. 8.
[b]Estimated from Ref. 9.

[a]Electronic mail: filip.tuomisto@hut.fi

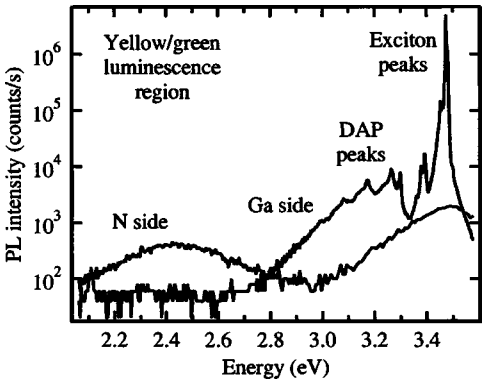

FIG. 1. Photoluminescence spectra of the Ga and N polar HVPE GaN layers.

$\sim 10^3$. No YL is observed in the Ga polar layer.

Positron lifetime spectroscopy[11] was performed on the HVPE GaN layers and the HP GaN substrates. The fast positrons enter the GaN lattice to an average depth of 30 μm. The electron density in the vacancies is lower than in the bulk lattice, and the trapping of positrons at these defects is observed as an increase in the average positron lifetime τ_{ave}. The vacancy defects can be identified by the lifetime component they introduce to the exponential annihilation spectrum.

The positron lifetime measured in the HVPE layers grown on the Ga side of the substrate crystal is constant over the whole temperature range and the same in all samples, $\tau_{\text{ave}}=160$ ps (Fig. 2). The lifetime spectrum has only a single component and τ_{ave} coincides with the lifetime of positrons in defect-free GaN,[8] $\tau_B=160$ ps. Thus, in the Ga polar HVPE layers, the concentration of vacancy-type defects is below the sensitivity range of the method, 1×10^{15} cm^{-3}.

The average positron lifetime measured in the Ga side of HP GaN is identical to that determined in earlier studies[8,12] and similar in shape to those measured in the N polar samples [Fig. 2(a)]. In these three samples, τ_{ave} is longer than τ_B, which indicates the presence of vacancy defects. A second (higher) lifetime component $\tau_2=235\pm10$ ps [Fig. 2(b)] could be fitted to the experimental lifetime spectra measured in the Ga and N sides of HP GaN and in the N polar HVPE layer. This component can be attributed to the Ga vacancy, which is in the negative charge state and most likely complexed with oxygen.[12,13] A third (higher) lifetime component $\tau_3=470\pm50$ ps [Fig. 2(c)] could be fitted to the lifetime spectra measured in the two N polar samples. This component can be attributed to vacancy clusters which involve at least 20 vacancies. The decrease of the average positron lifetime with decreasing temperature in the samples where τ_{ave} is longer than τ_B is a clear indication of the presence of negative ion defects trapping positrons at low temperature to hydrogenic states where the positron lifetime is equal to τ_B.[8,11]

The difference in the Ga vacancy concentrations between the Ga and N faces of HP GaN is significant. It correlates with the observation of a free carrier and oxygen concentration gradient along the *c*-axis.[9] As a compensating acceptor, the V_{Ga} concentration generally follows the increase of *n*-type doping.[14] The model in Ref. 9 proposes that the oxygen incorporation is much stronger during growth in the nonpolar (1010) directions, in which the N polar growth

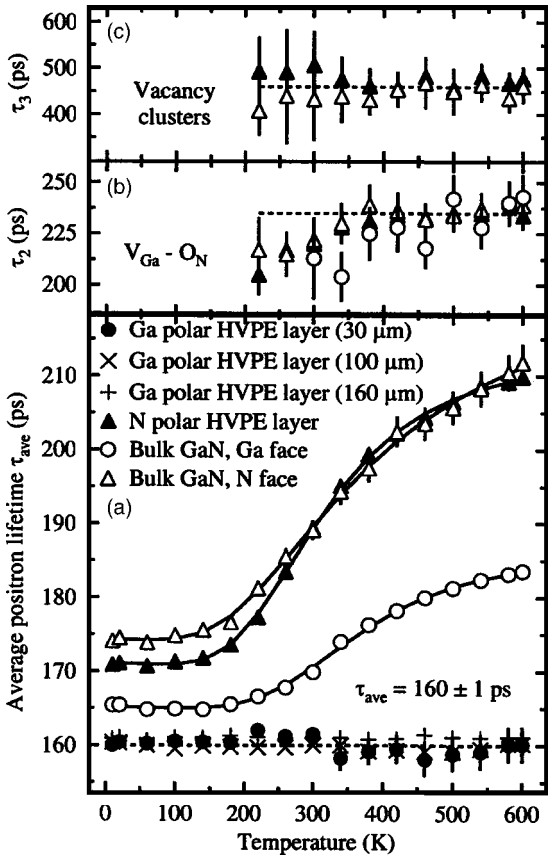

FIG. 2. Average positron lifetimes (a) and the second and third lifetime components extracted from the lifetime spectra (b), (c) measured in the GaN samples. The solid lines represent the fits of the temperature dependent trapping model to the data.

mainly proceeds. The Ga-polar growth on the other hand proceeds in the Ga polar (0001) direction. Recent experiments performed on nonpolar HVPE GaN grown on *R*-plane sapphire[15] also support this model. The model provides an explanation also for the difference in the Ga vacancy and oxygen concentrations between the Ga and N polar homoepitaxial HVPE GaN layers. The difference between the polarities is larger than in the bulk GaN crystals. This can be explained by the lower temperature and pressure at growth, which reduce the oxygen diffusion, and by the presence of more oxygen in the high-pressure growth.

Interestingly, the Ga vacancy and O impurity concentrations ($[V_{Ga}]\simeq7\times10^{17}$ cm^{-3}, $[O]\simeq2\times10^{19}$ cm^{-3}) are the same in the N polar HVPE layer and N polar side of the substrate bulk GaN, although their growth temperatures were very different (around 1300 K in the HVPE and 1800 K in the HP growth). The isolated Ga vacancies become unstable at temperatures 500–600 K,[16] thus the Ga vacancies observed in the HVPE and bulk GaN samples are likely complexed with oxygen. Considering the calculated formation energies[14] of V_{Ga} and V_{Ga}–O_N ($E_V^f\simeq1.3$ eV and $E_{VO}^f\simeq1.0$ eV in *n*-type GaN) as well as the available sites of formation (limited by the oxygen concentration for the latter), the equilibrium concentrations of isolated Ga vacancies at the growth temperatures dominate by a factor of roughly 100, in spite of the lower formation energy of the complex. Thus, the final concentration of V_{Ga}–O_N in the material is determined by the ability of the isolated vacancies to diffuse and form pairs with the oxygen impurities. However, the

$V_{Ga}-O_N$ complexes have been observed to be unstable above 1300 K.[16] Thus the $V_{Ga}-O_N$ concentrations are determined by the equilibrium at about 1300 K during cooling down, resulting in $[V_{Ga}] \simeq 10^{17}-10^{18}$ cm^{-3} in both materials.

The concentrations of the Ga vacancies and negative ions can be estimated by fitting a temperature dependent trapping model[8,11] to the lifetime data in Fig. 2. They are shown in Table I. The negative ion concentration in the bulk crystals (Table I) correlates with that of Mg, similarly as earlier.[8] The negative ion concentration in the N polar HVPE layer is significantly higher than the concentrations of Mg and C, indicating that other negative ion type defects such as antisites or interstitials are also present in the layer.

The vacancy clusters, with positron lifetime $\tau_3 = 470 \pm 50$ ps, have a constant positron trapping fraction $\eta_{cl} = 2.5\% \pm 1\%$ over the whole temperature range of the measurement. Assuming that the positron trapping is limited by positron diffusion and that the positron capture radius is $R = 1-30$ nm, depending on the size of the cluster, the vacancy cluster concentration in the N polar HVPE layer and HP GaN can be estimated to be $c_{cl} = 0.5-15 \times 10^{16}$ cm^{-3}.

The vacancy clusters present in the N polar HVPE GaN and near the N face of bulk HP GaN are likely to be the hollow pyramidal defects observed in Mg-doped GaN by TEM.[17,18] Similar clusters have been observed in Mg-doped MOCVD GaN also by positron annihilation spectroscopy.[19] All of these studies indicate that the clusters are correlated with high O and Mg impurity concentrations. From Table I it can be seen that the incorporation of both acceptor and donor type impurities is enhanced in the N polar growth of HVPE GaN, and the oxygen concentration is higher on the N side of HP GaN. These clusters can thus be formed by lateral overgrowth of the impurities,[20] which would be natural due to the nonpolar growth modes on the N polar surface.

As shown in Fig. 2(a), the $V_{Ga}-O_N$ concentration is below the detection limit in the Ga polar HVPE layers of different thicknesses. The oxygen concentration in these homoepitaxial layers is higher than in the thickest heteroepitaxial layers studied in Refs. 7 and 13. In spite of the lower oxygen content, Ga vacancies are observed in the latter.[13] This can be explained by the higher concentration of acceptor-type impurities such as Mg and C in the homoepitaxial layers, due to which the material is semi-insulating.[10] On the other hand, the heteroepitaxial HVPE layers studied in Refs. 7 and 13 are *n*-type, and the formation energy of V_{Ga} is significantly lower.

In summary, we have used positron annihilation spectroscopy and secondary ion mass spectrometry to study the effect of polarity on the incorporation of impurities and formation of vacancies in growth of GaN. We have demonstrated that the growth polarity has a crucial impact on the formation of vacancies and vacancy clusters, which are more abundant at the N polar side. The concentrations of oxygen and of acceptor-type impurities are similarly correlated with the polarity. The vacancy concentrations are similar in both HVPE and high-pressure grown GaN in spite of the much higher growth temperature of the latter. This suggests that the stability of the point defect complexes is an important factor determining which defects survive the cooling down from the growth temperature.

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