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Thermal stability of in-grown vacancy defects in GaN grown by hydride vapor phase epitaxy

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We have used positron annihilation spectroscopy to study the thermal behavior of different native vacancy defects typical of freestanding GaN grown by hydride vapor phase epitaxy under high pressure annealing at different annealing temperatures. The results show that the V_{Ga}-O_N pairs dissociate and the Ga vacancies anneal out from the bulk of the material at temperatures 1500–1700 K. A binding energy of E_b=1.6(4) eV can be determined for the pair. Thermal formation of Ga vacancies is observed at the annealing temperatures above 1700 K, indicating that Ga vacancies are created thermally at the high growth temperature, but their ability to form complexes such as V_{Ga}-O_N determines the fraction of vacancy defects surviving the cooling down. The formation energy of the isolated Ga vacancy is experimentally determined. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2180450]

The thermal stability of the point defect complexes in gallium nitride (GaN) is an important factor determining which defects survive the cooling down of the crystal from growth temperature.[1] These defects define the electrical, optical, and structural qualities of the material.[2] Due to the progress in the growth of several hundred micrometer thick GaN layers by hydride vapor phase epitaxy (HVPE), the so-called freestanding HVPE GaN is considered as a good candidate for substrate material. However, the high and nonuniform distribution of impurities[3,4] and native defects[5] is a remaining problem in the heteroepitaxial freestanding layers.

The study of thermally induced native defect evolution, especially in material supposed to be used for substrate applications, is very important in order to understand the behavior and modifications of the defects at variable temperature regimes. A better understanding is highly needed to be able to reduce or compensate some of them and to control the substrate material during the different stages of device processing. In this work we use high pressure annealing as a powerful technique to influence the point defects in semiconductor materials and apply positron annihilation spectroscopy to investigate the thermally induced evolution of native in-grown vacancy defects in thick freestanding HVPE GaN. By doing this we are able to determine important thermodynamical quantities for Ga vacancy related defects, such as the binding energy of the V_{Ga}-O_N pair and the formation energy of the isolated Ga vacancy. Only theoretical estimates of these are presented in the literature.[6,7] We obtain values E_b =1.6(4) eV for the binding energy of the V_{Ga}-O_N pair and E^f=2.5–3.2 eV at Fermi level position E_C-E_F=0.5 eV for the formation energy of the isolated V_{Ga}. These values are in excellent agreement with the theoretical predictions.[6,7]

We studied 270 μm thick GaN films grown at 1350 K in a conventional horizontal HVPE reactor[8] on two-step lateral overgrown metal-organic chemical-vapor deposition (MOCVD) templates.[9] Four selected crack-free, self-separated samples from one waver were annealed at a high pressure of 10 kbars for 1 h at four different temperatures in the range of 1423–1723 K. The high pressure of nitrogen was used to prevent the dissociation of GaN at temperatures above about 1300 K. The positron lifetime experiments were performed at 10–300 K using a conventional fast-fast spectrometer in collinear geometry[10] with a time resolution of 230 ps. The fast positrons used in positron lifetime experiments enter the GaN lattice to an average depth of 30 μm with an exponential stopping profile, and thus they probe approximately one-third of the sample thickness. Hence, in order to study the distribution of the defects along the c axis, the positron lifetime in the samples was measured with both the Ga and N polar sides facing the source. The trapping of positrons at vacancy defects is observed as an increase in the average positron lifetime τ_{av}. The vacancy defects can be identified by the lifetime component they introduce to the exponential annihilation spectrum. The near-surface region of the GaN samples was studied at room temperature using a variable energy (E=0–35 keV) positron beam.[10] The trapping of positrons at vacancy defects can be observed as the narrowing of the Doppler-broadened 511 keV annihilation γ peak. The measured spectra were characterized by the conventional line shape parameters S and W.[10]

Figure 1 shows the average positron lifetime measured in the HVPE GaN samples. All the positron lifetimes measured from both faces of our samples are in the range of 160–168 ps. These values are higher compared to the room-temperature value of the bulk lifetime τ_B=160 ps found in a

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[b]Deceased.

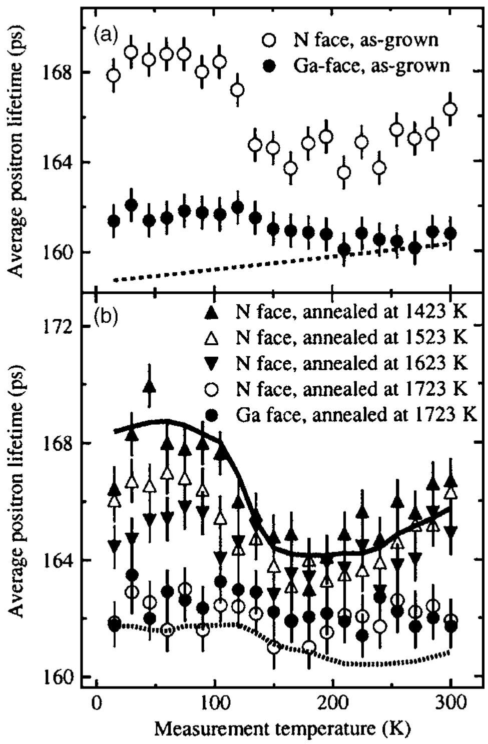

FIG. 1. The average positron lifetime measured from both the N and Ga sides of the as-grown (a) and annealed (b) HVPE GaN layers as a function of measurement temperature. The dashed line (a) shows the positron lifetime in the defect-free GaN lattice. The solid and dotted lines (b) show the lifetimes measured from the N and Ga sides of the as-grown samples, respectively.

homoepitaxial HVPE GaN sample.[1] A second lifetime component $\tau_2=240\pm15$ ps could be separated from the data when the average lifetime is above 163 ps, indicating that the increased average lifetime in our samples is due to positron trapping at Ga vacancies, most likely decorated by oxygen.[5,11,12] In the samples measured on the N side and annealed below 1723 K, the average positron lifetime increases when the temperature decreases below 150 K, indicating that the oxygen-decorated Ga vacancies are in the negative charge state. The average positron lifetime measured on the Ga side of the as-grown material coincides with the bulk lifetime at room temperature, indicating a Ga vacancy related defect concentration of at most 10^{15} cm^{-3}, a value typical of thick undoped HVPE GaN.[1,5,13–15]

In the as-grown HVPE GaN sample, the average positron lifetime and hence the Ga vacancy related defect concentration is clearly higher on the N side than on the Ga side, as seen in Fig. 1(a), throughout the whole temperature range of the measurement. This is as expected, since the Ga vacancy concentration has been found to correlate with the O and dislocation density profiles in HVPE GaN.[5] Annealing of the material at 1523–1623 K decreases the average positron lifetime measured on the N side [Fig. 1(b)]. This implies that the concentration of the Ga vacancies near the N side decreases with increasing annealing temperature, most probably due to the dissociation of the Ga vacancy-oxygen complexes. No change in the positron lifetime was observed near the Ga side at annealing temperatures up to 1623 K. However, during the annealing at 1723 K the average positron

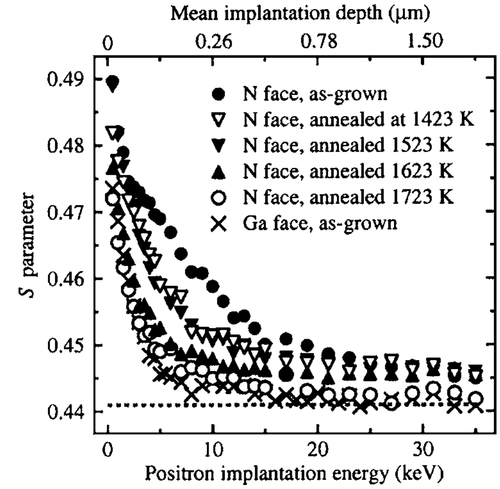

FIG. 2. The S parameter in the HVPE GaN layers as a function of positron implantation energy. The dashed line shows the S parameter in the defect-free GaN lattice.

lifetimes near both the N and Ga sides change noticeably and become almost equal, being slightly higher than that near the Ga side of the as-grown sample. This indicates a flattening of the Ga vacancy concentration depth profile, and it is important to notice that the Ga vacancy concentration increases near the Ga side after the annealing at 1723 K.

The S parameter in the HVPE GaN samples is shown as a function of positron implantation energy in Fig. 2. A Mg-doped p-type GaN sample was used to obtain the annihilation parameters in the free lattice.[16] At low implantation energies, the S parameter is affected by the annihilations at the surface due to the diffusion of thermalized positrons. The S parameter becomes constant at implantation energies above 25 keV. Plotting the layer-specific W parameter as a function of the S parameter results in a straight line with a slope that coincides with that obtained for the Ga vacancy in previous works.[5,11,16] Thus, as in lifetime experiments, the dominant positron trapping defect in the bulk of the samples (implantation energies 25–35 keV) is the Ga vacancy.

The annealing behavior of the Doppler broadening parameters S and W is similar to that of the average positron lifetime. Ga vacancies are present near the N side of the as-grown material, and their concentration is considerably reduced after the annealing at 1723 K. No positron trapping at vacancy defects could be observed near the Ga side of the as-grown HVPE GaN sample. The behavior of S and W vs E at implantation energies below 15 keV in the as-grown sample (N face) cannot be explained by the diffusion of positrons to the surface as in the other samples. Instead, it implies that large vacancy related clusters ($S_D \geq 0.47 \simeq 1.07 S_B$, while $S_{V,\mathrm{Ga}} \simeq 1.04 S_B$) are present in the 100–300 nm thick near-surface region. These defects disappear from the sample already in the first annealing at 1423 K.

The Ga vacancy concentrations in the samples could be estimated by assuming a specific trapping coefficient of $\mu_V = 3\times10^{15}$ s^{-1} at 300 K (see Ref. 17), varying with temperature as $T^{-1/2}$, as observed previously in GaN.[5] Figure 3 shows the Ga vacancy concentrations calculated as the average

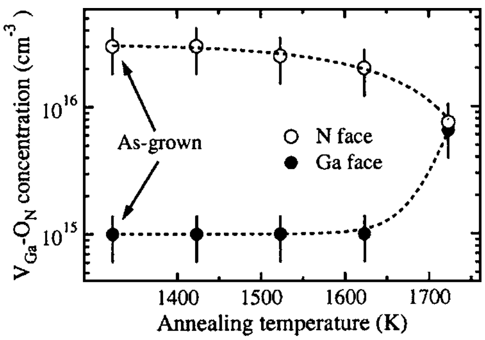

FIG. 3. The Ga vacancy related defect concentrations determined from the N and Ga polar sides of the HVPE GaN layers as a function of annealing temperature. The dashed lines are guides to the eye.

from those obtained from both the Doppler broadening and positron lifetime parameters.

The O concentration near the N face of the HVPE GaN samples is relatively high due to the higher dislocation density in the heteroepitaxial interface region, even when a buffer layer is used. The Ga vacancies, that are more easily formed in the region of high O content (high *n*-type conductivity) during growth, survive the cooling down by forming complexes, most likely with the O impurities.[1,12] Hence the decrease in the Ga vacancy concentration is due to the dissociation of the V_{Ga}-O_N pairs. An activation energy (E_A) fit to the Ga vacancy concentrations as a function of annealing temperature gives $E_A=3.1(2)$ eV, which can be interpreted as the sum E_M+E_B of the migration energy of V_{Ga} and the binding energy of the V_{Ga}-O_N complex. Taking the migration energy $E_M=1.5(2)$ eV determined from electron irradiation data in Ref. 17, we obtain a binding energy of $E_B=1.6(4)$ eV, in good agreement with the value of $E_B=1.8-2.1$ eV predicted by theory.[6,7]

The increase of the Ga vacancy concentration after the annealing at 1723 K measured near the Ga side of the sample indicates that thermally formed vacancies are present in the material. The flattening of the vacancy concentration profile suggests that also the O impurities are redistributed during the annealing, and the sample has reached thermal equilibrium. The present results show that the V_{Ga}-O_N pairs become unstable at 1523 K, and hence the Ga vacancy concentration observed after cooling down of the sample is determined by the equilibrium concentration at 1423–1523 K. This is in good agreement with previous experiments,[17] where the dissociation temperature of the V_{Ga}-O_N pairs has been estimated to be 1300–1500 K. In addition, our previous results[1] on in-grown vacancy defects in HVPE GaN indicate that the Ga vacancies are formed as isolated and the final concentration is determined by the ability of the Ga vacancies to diffuse and bind to O impurities.

The O concentration near the N polar face of the free-standing GaN samples is about 2×10^{19} cm^{-3}, and it decreases by two orders of magnitude to its value of about 1×10^{17} cm^{-3} in the bulk within the first 10 μm from the surface.[18] Assuming that the O concentration becomes completely flat during the annealing at 1723 K, it increases in the bulk of the material to a value of about 3×10^{17} cm^{-3}. This is in agreement with preliminary photoluminescence (PL) results,[19] which show an increase in the O concentration near the Ga side of the sample. Assuming that all the O donors are ionized, this increase in concentration shifts the Fermi level up toward the conduction band from $E_C-0.7$ eV to $E_C-0.5$ eV at 1723 K, at which temperature the Ga vacancies are stabilized by the O impurities. This shift is sufficient to decrease the formation energy of the negative Ga vacancies enough for them to be formed at concentrations detectable by positrons. Taking a typical value for the formation entropy of $S=(5-10)k_B$, the formation energy of the isolated Ga vacancy can be estimated from the equilibrium concentration at 1723 K to be $E^f=2.5-3.2$ eV at Fermi level position $E_C-E_F=0.5$ eV, in perfect agreement with the theoretical results[6,7] of $E^f=2.5-3.5$ eV.

In summary, we have used positron annihilation spectroscopy and high pressure annealing to study the thermal stability of in-grown vacancy defects in HVPE GaN. The V_{Ga}-O_N pairs present near the N polar face recover at annealing temperatures 1523–1723 K, from which we obtain a binding energy of $E_B=1.6(4)$ eV. Thermally formed Ga vacancies and flattening of the O impurity and Ga vacancy profiles are observed after the annealing at 1723 K. We obtain an estimate for the formation energy of $E^f=2.5-3.2$ eV at Fermi level position $E_C-E_F=0.5$ eV. Our results demonstrate that Ga vacancies are created thermally at the high growth temperature, but their ability to form complexes such as V_{Ga}-O_N determines the fraction of vacancy defects surviving the cooling down.

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