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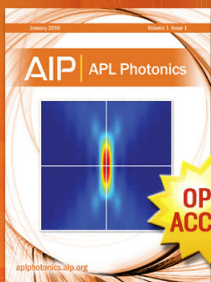
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Effect of high-temperature annealing on the residual strain and bending of freestanding GaN films grown by hydride vapor phase epitaxy

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The effect of high-temperature high-pressure annealing on the residual strain, bending, and point defect redistribution of freestanding hydride vapor phase epitaxial GaN films was studied. The bending was found to be determined by the difference in the in-plane lattice parameters in the two faces of the films. The results showed a tendency of equalizing the lattice parameters in the two faces with increasing annealing temperature, leading to uniform strain distribution across the film thickness. A nonmonotonic behavior of structural parameters with increasing annealing temperature was revealed and related to the change in the point defect content under the high-temperature treatment. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192149]

Freestanding (FS) hydride vapor phase epitaxy (HVPE) GaN films are currently considered as the most promising substitute for the native bulk nitride substrate because of the difficulties in the growth of bulk GaN. Freestanding GaN wafers have been demonstrated by several groups and have recently become even commercially available. However, a critical remaining question is the high and nonuniform distribution of dislocations,¹ impurities,^{2,3} native defects,⁴ and strain^{5,6} across the thickness. Residual strain,⁷ wafer bending,^{8,9} and cracking^{10,11} are the main drawbacks, hampering the reproducible production of large-area GaN substrates, and thus a proper understanding of the reasons for them is of crucial importance. The high-temperature annealing (HTA), as an important tool in materials research, is expected to lead to the redistribution of the defects and consequently to a change of electrical, optical, and structural parameters of the material. Thus, a study of the change of the defect content and distribution under the annealing treatment can provide useful insight into the defects responsible for the residual strain and bending of freestanding GaN films.

In this work we carry out a systematic investigation of the residual strain and bending of as-grown and high-temperature annealed HVPE-GaN freestanding films, aiming to reveal the effect of HTA treatment. The bending was determined by high-resolution x-ray diffraction (HRXRD), while the strain was assessed by lattice parameter determination on both the as-grown side (often called Ga face as determined to be under typical growth conditions¹) and interface side (N face) of the films by HRXRD and photoluminescence (PL) as well as by micro-Raman scattering (mRS) measurements in cross section of the films. The

grown-in point defects were investigated by positron annihilation spectroscopy (PAS) in order to clarify their relation to the strain redistribution caused by the HTA.

The HVPE growth of the GaN film with 270 μm thickness was performed at 1080 °C in a conventional horizontal reactor¹² on a metal-organic chemical vapor deposition (MOCVD) epitaxial lateral overgrown (ELOG) GaN template (supplied by Lumilog, France) in order to ensure a lower dislocation density in the overgrown layer. The template with 3-nm-thick SiN mask stripes subsequently overgrown with a fully coalesced GaN film of about 14 μm in thickness was grown by a two-step growth method.¹³ The selected samples for this study with sizes of about 6 \times 7 mm were crack-free GaN self-separated films from the sapphire substrate during cooling down from the growth temperature. Four freestanding HVPE-GaN samples, containing the MOCVD LEO template as confirmed by cathodoluminescence,¹² have been annealed at a high pressure of 10 kbars for 1 h in the temperature range of 1150–1450 °C. Nitrogen gas was used as the medium for the high-pressure annealing to avoid decomposition of GaN, which occurs at ambient pressure at temperatures above around 1000 °C.

The lattice parameters of the GaN samples were measured by HRXRD using a Philips triple axis diffractometer, following the alignment and calculation procedures described in Ref. 7. The dependences of the *c* lattice parameters in both faces of the FS films on the annealing temperature are shown in Fig. 1(a). One can see a small increase of the *c* lattice parameters with respect to that in the as-grown sample, and, respectively, of the tensile strain, in both faces of the annealed sample at the lowest temperature of 1150 °C, followed by a decrease of the strain with increasing temperature. Surprisingly, the sample annealed at the

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^{b)} Deceased

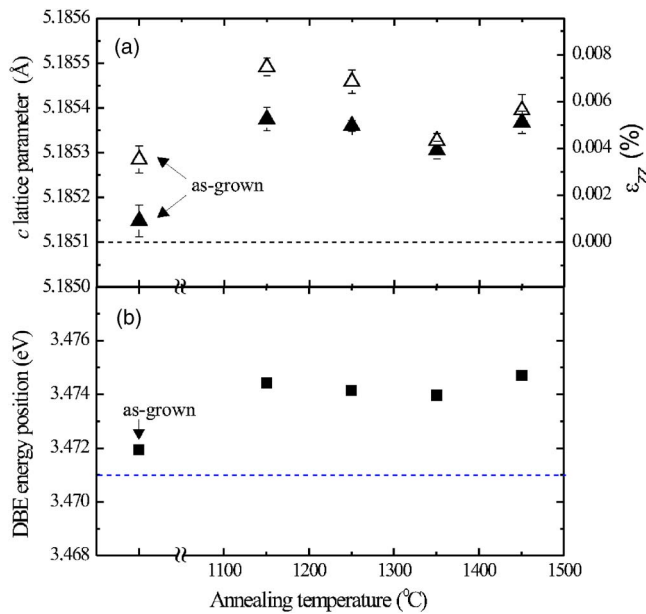


FIG. 1. (a) Out-of-plane lattice parameters and residual strain in growth direction vs annealing temperature in both sides of FS GaN films. (b) Energy position of the DBE line in 2K PL spectra vs the annealing temperature determined in the as-grown (Ga face) side of the FS films. Full symbols present the data for the Ga face, while the open symbols present the data for the N face. The dashed lines indicate the strain free positions for the respective parameters.

highest annealing temperature of 1450 °C shows again an increase of the c parameters and the strain.

The behavior of the residual strain in the FS films was independently studied by PL measurements at 2 K under excitation with the 266 nm laser line using an excitation power of 5 mW. The luminescence was detected with a charge-coupled device (CCD) camera with a spectral resolution better than 0.3 meV at 350 nm. All the spectra from the Ga face surfaces are dominated by the sharp donor bound exciton (DBE) peaks, previously attributed to Si and O residual impurities in HVPE grown GaN material.¹⁴ In addition, the A free exciton line X_A in the higher energy side, an acceptor bound exciton line A^0X in the lower energy side, as well as their phonon replicas are present in the PL spectra of both as-grown and annealed films. The narrow linewidths of the bound exciton related peaks down to 0.7 meV in all the films indicate high optical quality and nondestructive impact of the HTA treatment, although the surface roughness estimated by atomic force microscopy was found to increase from 0.5 nm in the as-grown sample up to 2.7 nm in the film annealed at 1450 °C. The energy position dependence of the DBE peak in the PL spectra from the Ga faces versus the annealing temperature is shown in Fig. 1(b). The same trend of non-monotonic change of the strain can be seen in full agreement with the alteration of the c lattice parameters in both faces of the annealed samples, despite that the XRD is measured at room temperature and the PL at 2 K.

Precise estimations of the in-plane a lattice parameters in both faces of the FS films versus the annealing temperature [Fig. 2(a)], show generally an opposite trend with respect to that for the c lattice parameters. However, the annealing at 1150 °C does not increase noticeably the compressive in-plane strain, contrary to that observed for the out-of-plane strain. This difference in the behavior could be attributed to the higher concentrations of all the defects in the N side of

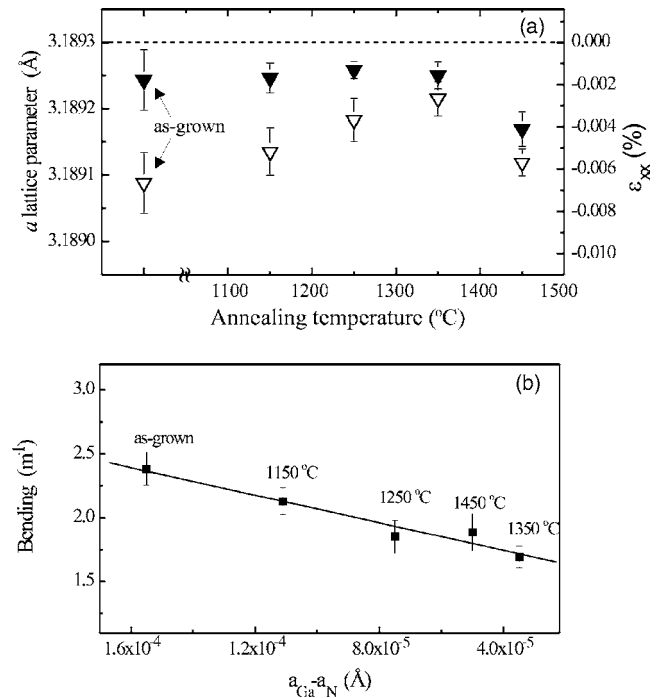


FIG. 2. (a) In-plane lattice parameters and residual strain vs annealing temperature in both sides of FS GaN films. Full symbols present the data for the Ga face, while the open symbols present the data for the N face; (b) bending vs the difference in the in-plane lattice parameters of the Ga and N face sides of the FS films.

the as-grown FS films as compared to the Ga side and thus the ratio c/a in the two sides is not expected to be influenced by the annealing in an identical way. Further increasing of the annealing temperature leads to a decrease of the compressive in-plane strain, and the annealing at the highest temperature of 1450 °C results in a similar increase of the in-plane compressive strain as for the observed increase of the out-of-plane tensile strain [Fig. 1(a)].

The curvature of the FS films was estimated by measuring the rocking curves using ω scans of the 006 reflection at two points separated by a certain distance on the as-grown surface.¹⁵ Figure 2(b) shows the bending of the FS films as a function of the difference in the in-plane lattice parameters of the Ga and N face sides for all the samples. A clear reduction of the bending in the annealed samples can be seen although it remains significant in all the FS films. One can see from Fig. 2(b) that the bending decreases with decreasing the difference in the lattice parameters of the Ga and N face showing a clear linear correlation. Note that in full agreement the film annealed at the highest temperature possesses a larger bending compared to that in the samples annealed at 1350 °C. Thus, we conclude that the difference in the in-plane lattice parameters has a determining effect on the bending of the FS films.

One can also see in Figs. 1(a) and 2(a) that increasing the annealing temperature results also in equalizing the lattice parameters in the two faces and thus leading to the flattening of the strain distribution along the film thickness. This was independently confirmed by micro-Raman measurements, performed at room temperature using the 514 nm line of Ar⁺-ion laser. The spectra were recorded with a Dilor XY 800 spectrometer in $x(yy)x$ backscattering configurations (with z direction oriented along the c axis of the GaN films), allowing the detection of the E_2 mode. Figure 3 shows the

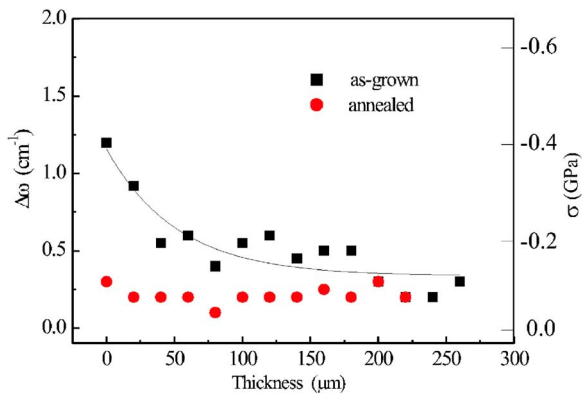


FIG. 3. Frequency shift of the E_2 mode and residual compressive in-plane stress as a function of the distance from the sapphire interface side of the as-grown and the annealed at 1350 °C HVPE-GaN freestanding films.

frequency shift of the E_2 phonon mode along the growth direction with respect to the strain free E_2 mode position of 566.2 cm^{-1} (Ref. 16) and the respective compressive stresses estimated using a stress factor of 2.9 GPa/cm^{-1} (Ref. 17) for two HVPE-GaN samples, as-grown FS, and annealed FS at 1350 °C. It is clearly seen that the typical exponential dependence of the residual stress in the as-grown GaN films is flattened to the minimum value in the annealed sample. This uniformity and the small value of the residual stress of only $\sim 0.1 \text{ GPa}$ are indicative of the improving effect of the HPA treatment and point to the important role of the point defects on the stress. The remaining stress could be explained by grown-in defects, which are not strongly influenced by the HTA, most likely dislocations, stacking faults, or even voids in our case of using two-step ELOG templates.¹²

Having in mind the results of point defect distributions in FS HVPE-GaN films, two experimental facts are of importance for explaining the strain variation with increasing the annealing temperature: (i) The oxygen impurity with nonuniform distribution versus the thickness of our as-grown HVPE-GaN thick films³ decreases exponentially by more than two orders of magnitude with increasing distance from the interface, being consistent with results reported with other groups.² It is likely that the O diffuses and/or dissociates under the HTA treatment and thus, its density decreases in the N side and increases in the near Ga face surface region as compared to that in the as-grown sample. This result also correlates with previously reported observation of increasing the c lattice parameters with increasing the impurity (O and/or Mg) concentration¹⁸ and explains the observed increase of the out-of-plane strain in the film annealed at 1150 °C. (ii) Positron annihilation spectroscopy of Ga-vacancy (V_{Ga}) related defects in these films revealed a significant density ($3 \times 10^{16} \text{ cm}^{-3}$) of $V_{\text{Ga}}\text{-O}_N$ complex defects in the N face near surface region, which was decreased down to $8 \times 10^{15} \text{ cm}^{-3}$ after the HTA at 1450 °C (Fig. 4). The defect density is much less in the as-grown Ga face ($1 \times 10^{15} \text{ cm}^{-3}$) and surprisingly is significantly increased up to $6.5 \times 10^{15} \text{ cm}^{-3}$ in the sample after the HPA at the highest temperature of 1450 °C, indicating a formation of the Ga vacancy at this temperature. More details on this topic are published separately,¹⁹ but what is needed for the consideration here is the evidence for the effect of the HTA on the point defect redistribution in the FS HVPE-GaN films and especially the significant alteration of the defect density in the film annealed at 1450 °C, which could be related to the

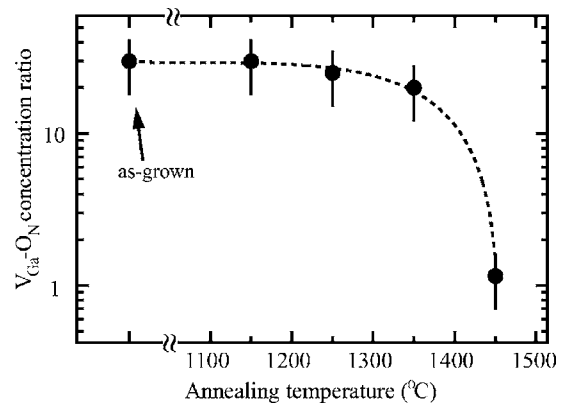


FIG. 4. $V_{\text{Ga}}\text{-O}_N$ defect concentration ratio between N and Ga faces vs the annealing temperature of the FS GaN films.

change of the lattice parameters, strain distribution, and consequently to the bending of the FS GaN films.

In summary, we have studied the effect of high-temperature annealing on the residual strain and bending of freestanding GaN films grown by HVPE. We have shown that the difference in the in-plane lattice parameters of the two faces of the FS films has the determining effect on the bending of the FS films. The HTA leads to equalizing of the lattice parameters in the two faces and to uniform strain distribution across the film thickness. We propose that point defects redistribution, dissociation, and generation have a strong contribution to the residual strain and, respectively, to the bending of the FS films.

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