

## Surface oxide relationships to band bending in GaN

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A trend of increased near-surface valence band maximum band bending with increasing O/Ga relative fraction was observed, extrapolating to 2.7 eV $\pm$ 0.1 eV for pristine GaN surfaces (0% O 1s peak area). This trend of apparent oxide overlayer coverage affecting the band bending linearly could lead to better understanding and characterization of oxidized GaN surfaces to control band bending for sensors or other devices. © 2006 American Institute of Physics.

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GaN and AlGaIn/GaN materials are of great interest to applications such as sensors because of their surface sensitivity, high mobility, low drift current, optical transparency, and high thermal breakdown. Its implementation in biosensors, ChemFETs, pH sensors, and other surface sensitive devices requires a thorough understanding of the surface and interfacial properties for optimal performance.<sup>1–7</sup> Optimization of the materials growth techniques, substrate surface preparation leading to improved device performance, and processing of the device components in general is still developing.<sup>8,9</sup>

Surface Fermi level band bending is particularly important to study because of its effects on semiconductor device properties.<sup>10</sup> The removal or addition of an electronic charge in the valence band due to changes in bonding state, such as through oxidation, will alter the electron shielding and cause changes in band bending at the surface.<sup>11</sup> Both the native and thermal oxide of GaN have been studied to assess phase formation and reaction kinetics, and to gauge its utility in electronics.<sup>12–18</sup> Prabhakaran *et al.* concluded that the native oxide on GaN is predominantly the monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which has been reported to be the stable form of Gallia.<sup>16,19</sup> The presence of an intermediate, oxynitride state has also been proposed.<sup>16,17</sup> Interestingly, Fu and Kang determined that the majority of fixed charge in the oxide to be negative, which would cause an upward band bending.<sup>10,14</sup>

In an effort to contribute to a greater understanding of the role of Gallia on the semiconductor attributes, we report on the relationship between the amount of apparent native oxide on GaN(0001) and its Fermi level band bending position. The study was conducted on molecular beam epitaxy (MBE) grown GaN on 4HN-SiC and 6HN-SiC substrates. This experimental set consisted of different substrate preparation treatments that were used in the MBE before film deposition, including high temperature nitridation (750 °C), low temperature nitridation (200 °C), and varying degrees of gallium flashing (0.5, 1, and 2 ML) to remove the SiC oxide and establish substrate surface reconstruction.<sup>8,9</sup> These varying substrates, GaN thicknesses and substrate preparation treatments, are speculated to lead to different fractions of

native oxide on the surface as characterized by x-ray photoelectron spectroscopy (XPS). No additional oxide has been intentionally grown on these samples. All surface oxide is assumed to be formed from exposure to the atmosphere when the samples are removed from the MBE after GaN epitaxial growth.

XPS was performed on samples from a previous study<sup>8,9</sup> using a Kratos Axis Ultra™ instrument. No additional chemical treatment of the samples was applied before they were placed into the XPS chamber after MBE growth. Survey scans (1200 to –5 eV), region scans of O 1s, Ga 3d, and C 1s core levels and valence band (+10 to –5 eV) scans were done with a monochromatic, Al K $\alpha$  source with a kinetic energy of 1486.6 eV. On a Ag calibration sample, the system has a full width at half maximum resolution of 0.6 eV at pass energy 20 eV for the Ag 3d<sub>5/2</sub> region and a Fermi edge resolution of <0.28 eV. The binding energies (BE) were calibrated to the adventitious hydrocarbon peak position at 285 eV. This peak position was determined from referencing to a Au 4f<sub>7/2</sub> BE at 84 eV with respect to the Fermi level (0 eV for Au).

The region area ratios of the O 1s and Ga 3d core levels (after division by the relative sensitivity factors provided by Kratos Analytical Inc.; 0.78 and 0.439, respectively) were used for O/Ga quantification in order to compare with the relative fraction computations of other research groups.<sup>12,15,17,18</sup> The valence band regions were linearly smoothed using CasaXPS™ processing software. The valence band maximums (VBMs) of the samples were then determined using the linear extraction method as suggested by Chambers *et al.*<sup>20</sup> An example of such a linear fit of a valence band can be seen in Fig. 1.

The results from quantification and linear extrapolation analysis provided a matrix of data, from which we looked for trends and correlations. One of the strongest trends in our data was a seemingly linear relationship between the valence band maximum and the O/Ga relative fraction presented in Fig. 2. Several groups suggested that there would be a correlation between the band bending and oxide formation, but it was not clear that the trend would be linear.<sup>13,15,18,21–23</sup> An interesting observation from this linear trend in Fig. 2 is that for O/Ga percentages extrapolated to ~0%, the predicted surface Fermi level  $E_{FS}$  is 2.70 eV $\pm$ 0.10 eV above the sur-

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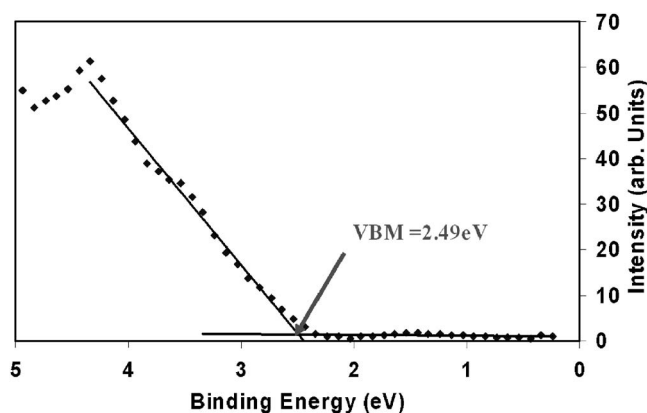


FIG. 1. XPS valence band region of a GaN sample showing linear extrapolation for determining VBM.

face valence band  $E_{VS}$ . This value is in agreement with Hashizume, Wu, Kahn, and Bermudez for pristine GaN (not exposed to air or other contaminants after growth).<sup>13,15,18,23</sup> The error of  $\pm 0.1$  eV was calculated with the standard error of estimate method. In addition, many have found that after the GaN is exposed to air, the native oxide results in upward band bending, containing a negative fixed or interface charge (inducing positive charges in the GaN between the GaN/oxide interface).<sup>18,21,24</sup> Furthermore, also utilizing XPS valence band analysis, Wu *et al.* observed a  $+0.4$  eV upward band bending for exposed GaN surfaces. Ishikawa observed that the native oxide added  $0.2$  eV to the barrier height.<sup>18,21</sup>

The oxide overlayer is certainly not the only contributor to the Fermi level band bending. Dislocation densities, surface strain, other contaminants (such as adventitious carbon), surface states, surface relaxation, and/or dipole layer from charge leakage could contribute to band bending.<sup>11,22</sup> Although the native oxide overlayer may not be the only cause of band bending, this linear trend in Fig. 2 suggests it may be one of the main causes. Also, the surface photovoltage effect is minimal because of the high doping level in the GaN.<sup>25</sup> Other considerations that may affect Fermi level band bending among the samples are the surface roughness and oxide phase purity. Atomic force microscopy images of our samples showed all the surfaces to be topographically similar, with an average rms roughness of  $\sim 5.7 \text{ \AA}$ . Also, angle-resolved XPS, performed on the Ga  $3d$  regions of several samples, revealed that the BE peak position did not shift or

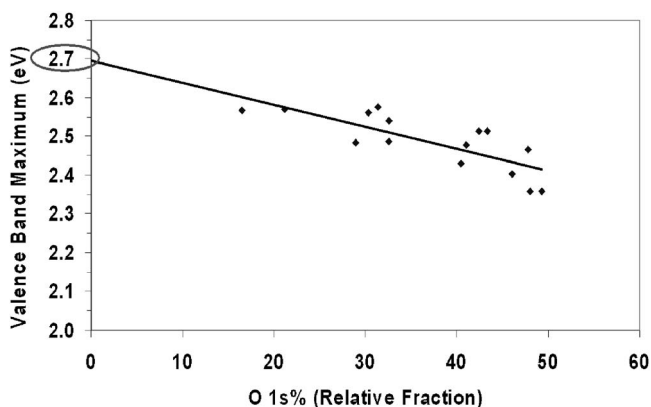


FIG. 2. Relationship between VBM and O  $1s$  relative fraction. The fitted data appear to be linear and extrapolates to  $\sim 2.7$  eV for a clean surface with no native oxide present.

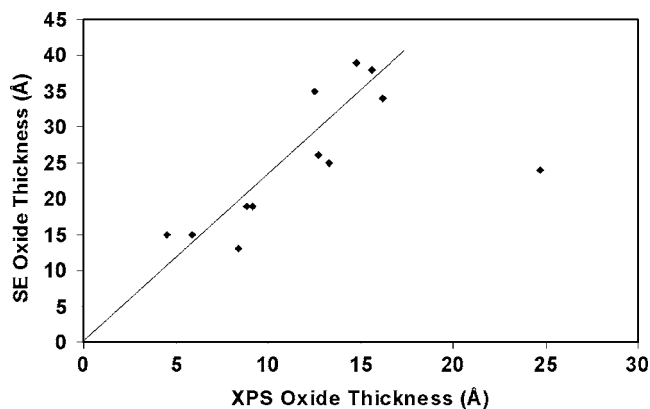


FIG. 3. Comparison of estimated native oxide thicknesses from SE vs XPS analysis.

change shape, indicating little or no change in the composition of the top  $\sim 2$  nm of the sample. There did not appear to be any correlation between the band bending and surface roughness or the C  $1s$  relative fraction.

However, as observed in Fig. 3, there does appear to be a correlation between the native oxide thicknesses calculated from spectroscopic ellipsometry (SE) and XPS models. This implies that the thickness of the native oxide on the GaN surface could be the major contributor to the surface band bending. The SE model calculates the native oxide thickness from the difference in the measured dielectric constants and the XPS model uses the relative fraction of oxide and GaN.<sup>26–29</sup> The values of the native oxide thickness themselves are offset, which could be caused by slight estimation errors in the SE and XPS models.

The variability of Fermi level with oxide concentration revealed in this study obviates problems of material inconsistencies. Efforts to limit native oxide formation through pre- and postdeposition treatments are thus warranted. This would be particularly useful for gateless field-effect transistor sensors where a GaN active area is exposed for electrochemical sensing of an environment. Corroborating studies could be attempted in the future to control the amount of native oxide and observe the band bending with other systems such as ultraviolet photoelectron spectroscopy or electron force microscopy.

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