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Band offset measurements of the GaN (0001)/HfO₂ interface

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Photoemission spectroscopy has been used to observe the interface electronic states as HfO_2 was deposited on clean *n*-type Ga-face GaN (0001) surfaces. The HfO_2 was formed by repeated deposition of several monolayers of Hf followed by remote plasma oxidation at 300 °C, and a 650 °C densification anneal. The 650 °C anneal resulted in a 0.6 and 0.4 eV change in band bending and valence band offset, respectively. The final annealed GaN/HfO₂ interface exhibited a valence band offset of 0.3 eV and a conduction band offset of 2.1 eV. A 2.0 eV deviation was found from the electron affinity band offset model. © 2003 American Institute of Physics. [DOI: 10.1063/1.1618374]

I. INTRODUCTION

Properties such as high dielectric constant, low leakage current, and relatively low interface density suggest the promise of HfO₂ in electronic device fabrication. The large band gap of 5.8 eV would be consistent with applications on wide band gap semiconductors such as GaN. The use of HfO₂ and other high- κ dielectrics as a passivation layer on GaN-based high voltage devices and as a gate insulator in field effect transistor devices requires knowledge of the band alignment of this interface.

In our study, HfO_2 films are formed on clean GaN(0001) surfaces prepared by an *in situ* ammonia exposure at an elevated temperature.¹ While several studies^{2,3} have employed photoemission techniques to explore the Si-HfO₂ interface, there has been no similar report for the GaN-HfO₂ interface.

A first approach to describing a heterostructure interface is to apply the electron affinity model (EAM). This model holds in an ideal case, where there is no potential created as the heterostructure is formed. Alternatively, a deviation from the EAM can be represented as a change in the interface dipole. Tersoff⁴ suggested that the band alignment between two semiconductors is controlled by the charge transfer across the interface and the resulting interface dipole in a fashion similar to Schottky barrier models. Recently, Robertson⁵ employed charge neutrality levels (CNL) and dielectric screening to relate the relative contribution of the electron affinity model and the interface dipole in determining the band offset of oxides on Si.

The focus of our experiment is to use photoemission to measure the band offsets of HfO_2 on clean GaN (0001) and to compare the results to the EAM. The deviation will be discussed in terms of a change in the interface dipole.

II. EXPERIMENT

The GaN films were grown via metallorganic chemical vapor deposition (MOCVD) on 50 mm diameter on-axis Siface, 6H SiC (0001) substrates with a conducting AlN (0001)

buffer layer. The thickness of the GaN epilayer and the AlN buffer were 1.1 and 0.1 μ m, respectively. Prior research has established that MOCVD growth of GaN on Si face SiC (0001) results in Ga face GaN (0001).^{6,7} Silicon was used as the *n* dopant with a net donor concentration (N_d-N_a) of 1 $\times 10^{17}$ cm⁻³ determined by mercury probe capacitance–voltage measurements.

The in situ surface cleaning and the experimental procedures are essentially identical to those described in a previous study.8 X-ray photoemission spectra (XPS) and UV photoemission spectra (UPS) were obtained after each process step in a sequence of experiments. Shifts of the XPS peaks and the evolution of the valence band spectra were recorded. The spectra were measured after each of the following steps: a 4 Å Hf deposition, O₂ plasma at 300 °C, 4 Å Hf (8 Å total Hf) and O₂ plasma at 300 °C, 650 °C anneal for 15 min, a final 4 Å Hf deposition (12 Å Hf total) and O_2 plasma at 300 °C, and a 15 min 650 °C final anneal. We have established that similar films on Si are stable to ~900 °C indicating that at 650 °C the evaporation is not significant. For the 12 Å Hf total, the ultimate thickness of the HfO₂ film was calculated to be ~ 20 Å based on bulk densities. The attenuation of the GaN XPS core levels was consistent with this value.

III. RESULTS AND DISCUSSION

The evolution of the UPS spectra from the clean GaN through the oxidation and anneal of the 12 Å Hf is shown in Fig. 1. The valence-band maximum (VBM) of the clean GaN surface was determined from an extrapolation of a line fit to the leading edge of the spectrum and was measured to be at 3.0 ± 0.1 eV (referenced to the Fermi level). As a verification that our measured turn-on is indeed the VBM, we note that our results indicate that the Ga 3*d* is 17.7 eV below the VBM, which is consistent with the careful study by Waldrop and Grant.⁹ The electron affinity of the GaN and the HfO₂ were deduced from the UPS using the relation $\chi = h\nu - W - E_g$ where *W* is the spectral width from the VBM to the low energy cutoff, $h\nu$ is the photon energy (21.2 eV), and E_g is the band gap of the material. For the clean *n*-type GaN sur-

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Binding Energy

FIG. 2. Oxygen 1s XPS spectra for: (a) CVC clean *n*-GaN, (b) 4 Å Hf deposition, (c) 4 Å Hf and O₂ plasma, (d) 8 Å Hf, O₂ plasma, and 650 °C anneal, (e) 12 Å Hf and O₂ plasma, and (h) 650 °C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

FIG. 1. UPS spectra of the valence band maximum of: (a) CVC clean *n*-GaN, (b) 4 Å Hf, (c) 4 Å Hf and O_2 plasma, (d) 8 Å Hf and O_2 plasma, (e) 8 Å Hf, O_2 plasma and 650 °C anneal, (f) 12 Å Hf and O_2 plasma, and (g) 650 °C anneal.

face, the width of the UPS spectrum was measured to be 14.8 eV, and using 3.4 eV as GaN band gap, we find an electron affinity of 3.0 eV, which is in agreement with prior reports.^{10,11} Similarly, the turn-on for the annealed HfO₂ is observed at \sim 3.3 eV below the Fermi level, and the spectral width is measured to be 12.5 eV. The valence band spectra observed for the HfO₂ film are qualitatively similar to those observed by others.^{12,13} Assuming a band gap of 5.8 eV, we obtain an electron affinity of 2.9 eV for the annealed film, which is within the experimental error of the estimated value reported by Robertson.⁵

The evolution of the Ga 3*d*, Ga 3 $p_{3/2}$, N 1*s*, Hf 4*f*, and O 1*s* core levels are summarized in Table I. The core level spectra indicate two significant effects. The first is the level of band bending in the GaN. Here, it is found that both the clean surface and the annealed HfO₂/GaN interface exhibited 0.3 eV upward band bending. The second effect is that we find a ~0.9 eV shift of the O 1*s* and Hf 4*f* core levels upon annealing to 650 °C. The evolution of the O 1*s* core

level is displayed in Fig. 2. This shift is attributed to combined changes in band bending and band offset. We note that a shoulder appears at \sim 532 eV after the first oxidation, which we attribute to the formation of a Ga oxide at the interface. This feature does not increase in intensity once formed and becomes difficult to distinguish with further HfO₂ depositions.

The method for determining the valence band offset is similar to that of Waldrop and Grant⁹ and Kraut *et al.*¹⁴ Their basic approach is to reference the VBM to a core level in the XPS spectra for each semiconductor and to use the measured difference between the core level energies to discern the band discontinuities. In our study, we have employed UPS to measure the energy of the VBM, and XPS to measure core level energies. We can then express the VBO (φ_{VBO}) as

$$\varphi_{\rm VBO} = E_{\rm VBM}^f - E_{\rm VBM}^i + E_{\Delta}, \quad E_{\Delta} = E_c^i - E_c^f, \tag{1}$$

where E_{VBM}^i and E_{VBM}^f are the measured VBM of the initial clean GaN and the oxide grown on GaN, respectively, and E_{Δ} is the change in band bending as defined from the shift of the Ga or N core levels. Here, E_c^i and E_c^f are the values of the

TABLE I. XPS core level curve fitting results for the Ga $3p_{3/2}$, Hf 4f, O 1s, Ga 3d, and N 1s energy levels. (Oxygen plasma is represented as O–Pl.)

Process Step	Ga 3 <i>d</i>		Ga 3 <i>p</i> _{3/2}		N 1 <i>s</i>		Hf 4f		O 1 <i>s</i>	
	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)
CVC	20.6	1.6	105.8	2.7	398.0	1.7				
4 Å Hf	20.3	2.0	105.5	3.2	397.5	2.0	17.4	2.0		
O–Pl	20.1	1.7	105.2	3.3	397.3	2.4	18.4	1.7	529.9	2.1
8 Å Hf, O–Pl, anneal	20.7	1.5	105.8	3.1	397.9	1.6	19.2	1.5	530.8	1.9
12 Å Hf, O–Pl	20.1	1.6	105.2	3.3	397.4	2.4	18.3	1.6	529.9	2.2
Final	20.7	1.4	105.8	3.1	397.9	1.7	19.1	1.4	530.7	1.9



FIG. 3. Deduced bands for the clean *n*-type GaN surface (left) and the interface between *n*-type GaN and HfO₂ before annealing. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

core level of the initial clean surface and the deposited oxide surface, respectively. An increase in upward band bending is defined as positive.

Figure 3 displays the deduced band lineup for the asdeposited GaN-HfO₂ interface. The upward band bending of the clean surface increases by 0.6 eV as the interface is formed. The valence band offset is then the measured UPS turn-on for the HfO_2 on the GaN (2.3 eV), minus the GaN turn-on (3.0 eV), plus the increase in upward band bending (0.6 eV), resulting in a value of -0.1 eV. With this value and the knowledge of the band gap of the material, the conduction band offset is obtained. The band gap of HfO₂ has been reported to be 5.7-6.0 eV.^{2,5} A value of 5.8 eV was used for our conduction band offset and electron affinity calculations. The valence band offset is deduced to be -0.1 eV, and the conduction band offset is 2.5 eV for our as deposited GaN/HfO₂ interface. The interface represents type II band alignment where the valence band maximum of the GaN lies below that of HfO₂ valence band.

Figure 4 shows the proposed band lineup for the *n*-type $GaN-HfO_2$ interface after annealing at 650 °C. The upward band bending is essentially the same as that of the clean

surface. The valence band offset determination is then the measured UPS turn-on for the HfO₂ on the GaN (3.3 eV), minus the GaN turn-on (3.0 eV). The valence band offset is deduced to be 0.3 eV, and the conduction band offset is 2.1 eV. We note that neither Fig. 3 nor Fig. 4 show a significant field in the HfO₂ layer. Such a field would be manifested as a broadening of the Hf 4*f* as well as the O 1*s* core levels was not observed. Here we have also assumed that there is no space charge in the HfO₂, and the Fermi level is determined by the value at the interface.

The Ga face GaN (0001) is a polar surface, and the spontaneous polarization will lead to a negative bound charge at the GaN film surface. The polarization bound charge screened by the ionized donors would lead to upward band bending at the GaN surface, consistent with our observations of the clean surface. It is possible that some changes in the band bending observed during formation of the oxide are due to compensation or screening of the polarization surface bound charge. But the measurements of the band offsets will not be affected by these changes.

Our results indicate a deviation from the electron affinity model of 2.0 eV for the before and after annealing cases of



FIG. 4. Deduced bands for the clean *n*-type GaN surface (left) and the interface between *n*-type GaN and HfO₂ after annealing at 650 °C. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

the GaN-HfO₂ interface. As an alternative to the electron affinity model, it has been proposed that heterojunction band alignments are determined by alignment of the CNL of the two materials. The charge neutrality levels represent the branch point of the surface or interface states related to the valence or conduction band. The presumption is that charge can transfer between the interface states of the two materials, which will cause an interface dipole. If the density of interface states is high, then the band offset will be determined by the relative position of the CNL of the two materials.

Recently, Robertson⁵ adapted the Schottky barrier interface defect model presented by Cowley and Sze¹⁵ to employ the CNL as the pinning levels for heterojunction interfaces. The model was applied to analyze the band alignment of a range of oxides on silicon, and the model seems consistent with most experimental results. In this model, the band lineup is described by the relation

$$\varphi_{\text{CBO}} = (\varphi_{\text{CNL},a} - \varphi_{\text{CNL},b}) - (E_{g,a} - E_{g,b}) + S[(\chi_a - \chi_b) + (E_{g,a} - E_{g,b}) - (\varphi_{\text{CNL},a} - \varphi_{\text{CNL},b})], \quad (2)$$

where φ_{CBO} is the CBO, χ and φ_{CNL} are the electron affinities and charge neutrality levels for each semiconductor (aand b), and S is a pinning factor based on the dielectric properties of the materials. Here, the φ_{CNL} are defined relative to the VBM of each semiconductor. A value of S=1represents the EAM while a value of 0 represents pinning at the CNL levels.

Our measured electron affinities are 3.0 and 2.9 eV for the GaN and HfO₂, respectively. Robertson⁵ has reported the CNL of HfO₂ to be 3.7 eV, and the CNL of GaN has been assigned as 2.37 eV.16 Thus, the EAM would predict a VBO of 2.3 eV and CBO of 0.1 eV. In the limit of strong pinning at the CNL, the model would predict a VBO of 1.3 eV and a CBO of 1.1 eV. It is evident that the observed VBO falls outside of the range that can be explained with the model (i.e., VBO between 1.3 and 2.3 eV) and the noted values of the CNL of GaN and HfO₂.

While we have attempted to minimize interface reactions, Hf–Ga site exchange, and the formation of complex Ga-Hf oxides at the interface cannot be excluded from contributing to the formation of an interface dipole.

The instability observed after annealing at 650 °C is noteworthy. The results indicate a change in the interface dipole and an increase in upward band bending. We suggest that these effects may be due to excess O atoms in a negative ion state that have diffused towards the interface. The negative ions would form from charge from the GaN conduction band, which would result in upward band bending and an interface dipole that would lower the electronic bands of the oxide with respect to the GaN. Based on the 0.6 eV change in band bending and the GaN doping level, we estimate an excess charge of $\sim 3 \times 10^{11}$ e/cm².

IV. CONCLUSION

In summary, the band alignment of an HfO₂ layer on *n*-type GaN has been investigated. The electron affinities for the clean n-type GaN and HfO₂ were measured to be 3.0 and 2.9 eV, respectively. After careful formation of the GaN-HfO₂ interface, upward band bending of 0.9 and 0.3 ± 0.1 eV existed for the as-grown and annealed interface, respectively. A valence band offset of -0.1 ± 0.1 eV (type II) was obtained for the as-grown interface, with a conduction band offset of $2.5 \pm 0.1 \text{ eV}$ (assuming $E_{gHfO2} = 5.8 \text{ eV}$). For the annealed interface, a valence band offset of 0.3 ± 0.1 eV was obtained, while the conduction band offset was determined to be 2.1 ± 0.1 eV. This result suggests the thermal stability of the hafnium oxide film significantly affects the electronic properties at the GaN-HfO2 interface. An interface dipole of 2.0 eV was deduced from comparison with the electron affinity model for both the before and after annealing cases of the GaN-HfO₂ interface. Moreover, the charge neutrality model does not accurately predict the band alignment of the GaN-HfO₂ interface.

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