Valence Band Discontinuity of the (0001) 2H-GaN / (111) 3C-SiC Interface

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X-ray and UV photoelectron spectroscopies were used to measure the valence band discontinuity at the interface between (0001) 2H-GaN films and 3C-SiC (111) substrates. For GaN films grown by NH₃ gas source molecular beam epitaxy on (1×1) 3C-SiC on-axis surfaces, a type I band alignment was observed with a valence band discontinuity of 0.5 ± 0.1 eV. A type I band alignment was also determined for GaN films grown on (3×3) 3C-SiC, but with a larger valence band discontinuity of 0.8 ± 0.1 eV.

Key words: GaN, SiC, valence band, discontinuity, gallium nitride, silicon carbide, x-ray photoelectron spectroscopy, ultra-violet photoelectron spectroscopy

The interface between selected polytypes of SiC $(E_{a} = 2.1 \text{ eV} (3C), 3.0 \text{ eV} (6H), \text{ and } 3.2 \text{ eV} (4H))$ and 2H-GaN (E = 3.5 eV) is of significant importance due to the rapid development of SiC and III-V nitrides for high-temperature, -power, and -frequency microelectronic devices and the latter for light-emitting devices.^{1–3} Due to moderately close lattice matching $(\Delta a/a_{o}(SiC/AlN) = 0.9\%, (GaN/AlN) = 2.5\%), a monoc$ rystalline AlN thin film is commonly grown on SiC substrates to provide a buffer layer for the growth of device quality GaN.⁴ Unfortunately, AlN is an insulator which prevents current injection from the SiC substrate into the GaN film; this necessitates the use of shorting rings or conducting Al_xGa_{1-x}N buffer layers to build top-down device structures.⁴ Growth of monocrystalline GaN directly on SiC is, therefore, more desirable; however, this has been difficult for chemical and thermodynamic reasons.^{5,6}

The employment of GaN/SiC heterojunction devices in a given application requires the knowledge of the band alignment between the two semiconductors. Of paramount importance in this regard is the value of the GaN/SiC valence band discontinuity (ΔE_v), which can control both current/charge transport across the interface, as well as quantum confinement of electrons and/or holes at the interface. Only a few theoretical predictions^{7,8} and one experimental investigation⁹ to date have been reported regarding the

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band alignments between GaN and SiC. To the authors' knowledge, the first prediction was that by Wang et al.⁷ Based on differences in the Au Schottky barriers formed between the two materials, these authors predicted a type II band alignment with a ΔE_{y} of 1.2 eV for the GaN/3C-SiC interface. The plane wave pseudopotential calculations of Städele et al.8 also predicted a type II band alignment for the (100) 3C-GaN/3C-SiC interface. These calculations showed that ΔE_{v} depended on whether the interface was composed of intermixed Si/Ga cations or C/N anions. $\Delta E_v = 1.4 \text{ eV}$ was determined for one monolayer of Si/ Ga intermixing; whereas for one monolayer of C/N intermixing, a $\Delta E_{v} = 0.5$ eV was calculated for the same interface. For two monolayers of both C/N and Si/Ga intermixing, a ΔE_v of 0.8 was reported. However, for the low ΔE_v values, the band alignment is of course Type I, considering the respective band gaps (3C-GaN = 3.25 eV). Recently, Torvik et al.⁹ have measured ΔE_v for 2H-GaN/6H-SiC using electrical measurements and reported a discontinuity of 0.48 ± 0.1 eV and a type II alignment.

In this letter, we report our results and conclusions from a x-ray/UV photoelectron spectroscopy (XPS, UPS) investigation of the (0001) 2H-GaN/(111) 3C-SiC interface. To our knowledge, this study provides the first experimental measurement of the valence band discontinuity between these two interfaces and its dependence on the 3C-SiC surface reconstruction.

A gas source molecular beam epitaxy (GSMBE)



Fig. 1. XPS spectra of Si 2p and $Ga3p_{5/2,3/2}$ core levels from a 2H-GaN and (a) (3 × 3) 3C-SiC interface, and (b) (1 × 1) 3C-SiC interface.

system with a base pressure of 3×10^{-10} torr was designed and constructed for the growth of III-V nitride thin films.¹⁰ The source materials for this study were SiH₄ (99.9995%), Ga (99.9999%), and NH₃ (99.9995%). Gallium was evaporated from a 25 cc dual filament Knudsen cell. The NH₃ was further purified via an inline metalorganic resin purifier connected directly to a leak valve mounted on the GSMBE chamber. Sample exposure to the SiH₄ and NH₃ was obtained using "molecular beam" dosers similar to the design of Bozack et al.¹¹

The substrates were 1.5×1.5 cm² squares cleaved from on axis, n-type (N_d = 10^{18} /cm³) 6H-SiC (0001)_{Si} wafers with a 1 μ m thick, n-type epitaxial layer of 3C-SiC ($N_d = 5 \times 10^{17} \text{ cm}^3$) supplied by Cree Research, Inc. (Durham, NC). All substrates were ultrasonically and sequentially rinsed in trichlorethylene, acetone, and methanol, dipped in 10:1 buffered HF for 10 min and mounted on a Mo sample holder. The final in situ cleaning procedure is described in detail in Ref. 12. Briefly, each SiC wafer was annealed in the GSMBE system in a flux of 10^{-5} – 10^{-6} torr SiH₄ for 15–20 min at 950–1050°C. Auger electron spectroscopy (AES) and XPS revealed oxygen-free, Si-terminated SiC surfaces which displayed (1×1) LEED patterns. The (3×3) surfaces were prepared by using longer SiH₄ exposures at the same temperature.

To initiate the deposition of GaN, each cleaned 3C-SiC sample was heated to 650°C at which the shutter to the Ga cell was opened. The surface was exposed to NH₃ 5 seconds later. Sustained growth of the GaN film was achieved at ≈ 100 Å/hr in 10^{-5} Torr NH₃. After a predetermined GaN thickness had been reached, the Ga cell was shuttered and each sample cooled in ammonia down to approximately 400°C where the ammonia valve was closed. The prepared samples were transferred under a UHV environment to the LEED and XPS/UPS systems via a transfer line mechanism.¹⁰ The GaN films displayed (1×1) unreconstructed LEED patterns immediately after growth. Scanning electron microscopy of 500–1000 Å thick films revealed the surfaces to be extremely rough (>50–100 Å rms in AFM), indicative of three dimensional growth. The films were too conductive for Hall or capacitance/voltage measurements indicative of a very high concentration of background donors $(N_d > 10^{20}/cm^3)$. The XPS and UPS experiments were performed in

The XPS and UPS experiments were performed in a UHV chamber (base pressure = 2×10^{-10} Torr) equipped with a x-ray source, a differentially pumped helium lamp, and a 100 mm hemispherical electron energy analyzer (VG CLAM II). All XPS spectra were obtained using Mg K α radiation (hv = 1253.6 eV). Calibration of the binding energy was achieved by periodically measuring the positions of the Au 4f_{7/2} and Cu 2p_{3/2} lines from clean standard samples and correcting them to 83.98 eV and 932.67 eV, respectively. A combination of Gaussian-Lorentzian curves with a linear background best represented the XPS data. All UPS spectra were acquired using the unmonochromated He I line (hv = 21.2 eV) from the UV lamp.

The method used for calculating the 2H-GaN/3C-SiC valence band discontinuity was similar to that of Grant et al.¹³ which has been successfully used for AlAs/GaAs, ZnO/CdS, ZnSe/GaAs and numerous other interfaces.^{13–15} The basic scheme of this approach is to reference the valence band maximum energy to a core level energy from each semiconductor and then use the measured difference between the two core level energies from a junction between the two semiconductors to determine the discontinuity. In the present study, the position of one core level (CL) from the SiCsubstrate was measured with respect to its valence band maximum (VBM); i.e., (VBM-CL)^{SiC}_{bulk}. Subsequently, a thin layer (\approx 15–20 Å) of GaN was deposited on the substrate, and the difference between the substrate and film core levels was measured; i.e., $(CL^{SiC}-CL^{GaN})_{interface}$. Finally, the thickness of the overlying film was increased to ≈ 250 Å (beyond the sampling depth of XPS) and the CL-to-VBM energy measured for the film; i.e., (VBM-CL)^{GaN}_{bulk}. The valence band discontinuity between the two semiconductors is given as:

$$-\Delta E_{v}(GaN/SiC) = (VBM-CL)^{SiC}_{bulk} - (VBM-CL)^{GaN}_{bulk} - (CL^{SiC}-CL^{GaN})_{interface}$$
(1)

Core level peak positions can be measured via XPS

Table 1. ACL and ΔE_{v} values for 2H-Gain Films Grown on (1 × 1) and (3 × 3) 3C-SIC Surfaces			
Si2p-Ga3p _{5/2}	Si2p-Ga3d	C1s-N1s	$\Delta \mathbf{E_v}$
4.4 4.7	80.9 80.5	114.6114.9	$0.5\pm0.1 \text{ eV} \\ 0.8\pm0.1 \text{ eV}$
	$\frac{\text{Si2p-Ga3p}_{5/2}}{\frac{4.4}{4.7}}$	$\frac{\operatorname{Si2p-Ga3p}_{5/2}}{4.4} \qquad \qquad$	$\frac{\frac{\text{Si2p-Ga3p}_{5/2}}{4.4}}{4.7} \qquad \frac{\frac{\text{Si2p-Ga3d}}{80.9}}{80.5} \qquad \frac{\text{C1s-N1s}}{114.6}}{114.9}$

a) an a:n a TACT 1 (0

with an accuracy of $\leq 0.1 \text{ eV}$ (limited by the line width of the x-ray source).¹⁴ However, the cross section for ejection of valence band electrons in this technique is extremely low, which causes a poor signal to noise ratio (S/N) in the valence band spectra and complicates the location of the VBM. The S/N ratio in the UPS VB spectra is several orders of magnitude higher compared to XPS, which allows a better determination of the VBM by extrapolating the high kinetic energy leading edge of the VB spectra with a straight line to the energy axis.¹⁵ As such, XPS was used for locating the energy position of the core levels, and UPS was used to locate the VBM of SiC and GaN. In order to ensure the reproducibility of these results, three separate interfaces for each SiC surface reconstruction were prepared and measured with 1-2 weeks separating each run. Across wafer variability was not addressed due to the comparable size of the wafer and the spot size of the x-ray source.

We have previously measured values for (VBM- $CL)^{SiC}_{bulk}$ and $(VBM-CL)^{GaN}_{bulk}$ in separate studies of the (0001) 2H-AlN/3C-SiC^{16} and (0001) 2H-GaN/2H-AlN¹⁷ valence band discontinuities. Since the same values were obtained and used in this study, we will only briefly summarize our results. The location of the SiC VBM was obtained after annealing the SiC wafer in UHV at 650°C but before annealing in SiH₄ at 1050°C. Location of the VBM for the SiC surfaces annealed in SiH_4 was complicated by the appearance of surface states in the UPS spectra due to removal of the monolayer of oxygen terminating the SiC surface.^{12,16} The values of 99.3 and 281.3 eV obtained for Si2p-VBM^{SiC} and the C1s-VBM^{SiC}, respectively, from the SiC surface prepared by thermal desorption are in excellent agreement with the values reported by Grant and Waldrop¹⁸ and Porter et al.¹⁹ for surfaces prepared in a similar fashion. The determination of the location of the GaN VBM was less complicated (due to the lack of surface states in the band gap) and the measured values of 17.9, 103.2, and 395.4 eV for the Ga 3d, 3p, and N 1s core levels relative to the GaN VBM are in excellent agreement with the previously reported ones.^{17,20}

For the measurement of $\Delta CL = (CL^{SiC}-CL^{GaN})_{interface}$, the positions of the Ga 3p, 3d, N 1s, Si 2p, and C 1s core levels were recorded at GaN on SiC thicknesses of 15–20 Å as shown in Fig. 1. This thickness was selected as it is greater than the reported critical thickness of 7 Å for GaN on (100) 3C-SiC²¹ thus minimizing any possible strain effects, and in a separate study of the AlN/SiC interface, the valence band discontinuity was observed to have stabilized at \approx 15–20 Å thus minimizing any potential effects from polarization fields.¹⁶ The measured Δ CL data and the



Fig. 2. Schematic illustrating the flat band alignment for a (1×1) and (3×3) (111) 3C-SiC/(0001) 2H-GaN interface.

respective calculated ΔE_{u} are listed in Table I. These are $0.5 \pm 0.1 \, eV$ (Type I) for GaN grown on (1×1) 3C-SiC and 0.8 ± 0.1 eV (Type I) for GaN grown on (3×3) 3C-SiC (see Fig. 2).

The differences in ΔE_{v} for the different surface reconstructions are likely due to a slightly different intermixing of the interface layers. The (3×3) reconstruction represents the formation of an incomplete bilayer of Si on the SiC surface whereas (1×1) reconstruction consists of $< 1/10^{\text{th}}$ monolayer of excess Si on the surface.¹² For the (1×1) interface, one would ideally expect a Ga-N-Si-C stacking sequence based on the surface preparation and substrate orientation. However for the (3×3) reconstruction, a stacking sequence of Ga-N-Si-N-Si-C can be expected due to the presence of excess Si on the initial growth surface. A careful analysis of the N, C, Si, and Ga core levels (data not shown) indicated the presence of only Ga-N, Si-C, and Si-N bonding at the (3×3) interface which is consistent with the proposed stacking sequence and results obtained from similarly prepared (3×3) AlN/ SiC interfaces.¹⁶

Our measured valence band discontinuities fit well into the regime of theoretical values calculated by Städele et al.⁸ for two monolayers of intermixing (see above). However, the calculations of Städele et al. were made for a different orientation of the SiC substrate and a different polytype of GaN film. This coincidence in ΔE_v can be easily explained by the linear muffin tin orbital calculations by Ke et al.,²² which showed that the valence band discontinuities between the 3C and 2H polytypes of SiC, AlN, and GaN are ≤ 0.1 eV. This is also supported by the electrical measurements of Torvik et al.,⁹ which showed that the valence band discontinuity at the 2H-GaN/ 6H-SiC interface is closely matched to the ΔE_v reported in this study for the 2H-GaN/(1 × 1) 3C-SiC interface. Furthermore, plane wave pseudopotential calculations of the ΔE_v for 3C/2H-AlN/3C/2H-SiC interfaces by Ferrara et al.²³ have also shown similar valence band discontinuities for both (001) and (111)/ (0001) interfaces when intermixing of anions and cations occurs.

In summary, the valence band discontinuity for (0001) 2H-GaN/(111) 3C-SiC interfaces prepared by NH₃ GSMBE has been measured using x-ray and UV photoelectron spectroscopies. For GaN grown on (1 × 1) 3C-SiC surfaces a Type I ΔE_v of 0.5 ± 0.1 eV was measured, whereas for GaN grown on (3 × 3) 3C-SiC a Type I ΔE_v of 0.8 ± 0.1 eV was measured. These values are in excellent agreement with recently reported theoretical values for (2 × 2) (001) interfaces formed between the 3C polytypes of these materials.

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