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S. W. King, R. F. Davis, C. Ronning, et al.

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Valence band discontinuity, surface reconstruction, and chemistry of (0001), (000 $\overline{1}$), and (1 $\overline{1}$ 00) 2H–AIN/6H–SiC interfaces

S. W. King and R. F. Davis^{a)}

Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7919

C. Ronning

II. Physical Institute, University of Göttingen, Bunsenstr. 7-9, 37073 Göttingen, Germany

M. C. Benjamin and R. J. Nemanich

Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

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A detailed examination of the valence band discontinuity (ΔE_v) formed at the (0001), (0001), and (1100) interfaces between 2H–AlN and 6H–SiC has been conducted using x-ray and UV photoelectron spectroscopies. The ΔE_v was observed to range from 0.6–2.0 eV depending on the growth direction (i.e., AlN on SiC vs SiC on AlN), as well as the crystallographic orientation, cut of the SiC substrate (i.e., on versus off axis), and SiC surface reconstruction and stoichiometry. A ΔE_v of 1.4–1.5 eV was observed for AlN grown on (3×3) (0001)_{Si}6H–SiC on-axis substrates; a ΔE_v of 0.9–1.0 eV was observed for off-axis substrates with the same surface reconstruction. The values of ΔE_v for AlN grown on ($\sqrt{3} \times \sqrt{3}$)R30°(0001) 6H–SiC on-and-off-axis substrates were 1.1–1.2 eV. A larger valence band discontinuity of 1.9–2.0 eV was determined for 3C–SiC grown on (0001) 2H–AlN. Smaller values of ΔE_v of 0.6–0.7 and 0.8–0.9 eV were observed for AlN grown on on-axis (0001)_C and (1100)6H–SiC substrates, respectively. © 1999 American Institute of Physics. [S0021-8979(99)01020-8]

I. INTRODUCTION

The moderately close in-plane lattice matching $(\Delta a/a_0)$ of 0.9% and 2.5%, respectively, to 6H silicon carbide (6H-SiC, $E_g = 3.2 \text{ eV}$) and gallium nitride (GaN, $E_g = 3.4 \text{ eV}$) allows monocrystalline aluminum nitride (AlN, $E_g = 6.2 \text{ eV}$) to be commonly employed as a buffer layer for growth of GaN on 6H-SiC substrates.^{1,2} The rather small difference in lattice constants also allows the consideration of AlN/SiC/AlN quantum well heterostructures and the growth of AlN_rSiC_v alloys.3,4 Epitaxial AlN/SiC metal-insulator-semiconductor (MIS) structures are additionally of interest due to lower interface state densities.⁵ Several detailed studies of the microstructure at the AlN/SiC interface and the physical defects formed therein have been conducted,^{6,7} but relatively few studies have been reported regarding the electronic structure of this interface. The valence band discontinuity formed at the AlN/SiC interface, in particular, is one fundamental parameter needed to predict and model the electrical properties of this interface.8,9

The first report of the valence band discontinuity between AlN and SiC was that of Lambrecht and Segal for the (110) interface between 3C–SiC and 3C–AlN.¹⁰ Their theoretical investigation using the linear muffin tin orbital (LMTO) method indicated a valence band discontinuity of 1.5 eV (see Table I). However, a lower value for the valence band discontinuity between 2H–AlN and 6H–SiC at the (0001) interface was later provided by Benjamin *et al.*¹¹ based on ultraviolet photoelectron spectroscopy (UPS) investigations. Knowing the dopant concentration in the 6H–SiC substrate and the position of the AlN valence band maximum (VBM) relative to the Fermi level, Benjamin *et al.* estimated the valence band discontinuity by aligning the Fermi level of the two semiconductors and ignoring the possibility of band bending at the interface. This calculation indicated that the discontinuity was 0.8 eV. This value was contradicted by a different estimate of 1.85 eV by Wang *et al.*¹² based on the theoretical differences in the Au Schottky barrier formed with AlN and 3C–SiC. The larger values of Wang *et al.* and Lambrecht and Segal,^{10,12} were later supported by x-ray photoelectron spectroscopy (XPS) measurements by King *et al.*,¹³ which determined the (0001) 2H–AlN/6H–SiC valence band discontinuity to be 1.4 ± 0.3 eV.

Clarification of the above apparent discrepancies has been potentially provided by more recent theoretical investigations. The plane-wave psuedopotential (PWP) calculations by Ferrara, Binggeli, and Baldereschi¹⁴ have shown that for the (111)/(0001) AlN/SiC interface, the valence band discontinuity can range from as high 2.26 to as low as 1.31 eV depending on the level and type of cation/anion intermixing at the interface. Similar effects have also been recently reported for the (001) 3C–AlN/3C–SiC and 3C–GaN/3C–SiC interface by Städele, Majewski, and Vogl.¹⁵ However, these results are not surprising. For other reactive interfaces such as CuBr/GaAs, ZnO/CdS, ZnSe/GaAs, etc.,^{16–18} ΔE_v has been observed to be strongly dependent on the number and types of bonds formed at the interface. Using the (001)

^{a)}Electronic mail: robert_davis@ncsu.edu

TABLE I. Published data for the valence band discontinuity ΔE_v of the AlN/SiC interface (UPS=ultraviolet photoelectron spectroscopy, XPS=x-ray photoelectron spectroscopy, LMTO=linear muffin tin orbital, PWP=plane-wave pseudopotential, Au Φ =Au schottky barrier, T=theory, E=experimental).

ΔE_v AlN/SiC	Orientation	Technique	Author	
1.5 eV	(110) ZB	LMTO (T)	Lambrecht ^a	
0.8 eV	(0001) WZ	UPS (E) Benjamin ^b		
1.85 eV	ZB	Au $\Phi(T)$	Wang et al. ^c	
1.4±0.3 eV	(0001) WZ	XPS (E)	King et al. ^d	
1.71 eV	(110) ZB	PWP (T)	Ferrara, Binggeli, and Baldereschi ^e	
1.33 - (C-Si-N-Al)	(111)/(0001)	PWP (T)	Ferrara, Binggeli, and Baldereschi ^e	
1.31 - (Si-C-A-N)	C/N intermixing			
2.26 - (C-Si-N-Al)	(111)/(0001)	PWP (T)	Ferrara, Binggeli, and Baldereschi ^e	
2.54 - (Si-C-Al-N)	Al/Si intermixing			
1.78 - (C-Si-N-Al)	(111)/(0001)	PWP (T)	Ferrara, Binggeli, and Baldereshcie	
1.97 - (Si-C-Al-N)	C/N/Al/Si			
	intermixing			
2.4 eV	(001) ZB C/N	PWP (T)	Städele, Majewski, and Voglf	
1.5 eV	(001) ZB Al/Si	PWP(T)	Städele, Majewski, and Voglf	

^aSee Ref. 10.

^bSee Ref. 11.

^cSee Ref. 12.

^dSee Ref. 13.

^eSee Ref. 14.

^fSee Ref. 15.

GaAs/ZnSe interface as an example, ΔE_v (GaAs/ZnSe) was determined to be 0.40±0.05 eV when the GaAs/ZnSe interface was composed mostly of Ga–Se bonds and 1.01 ±0.05 eV when the GaAs/ZnSe interface was composed mostly of As–Zn bonds.¹⁸ Therefore, one could expect to observe a similar variation in ΔE_v for the AlN/SiC interface depending on the number of Si–N and/or Al–C bonds formed.

In this article, we report our findings on a more detailed XPS examination of the AlN/SiC interface in which we have manipulated the types of bonds formed at the AlN/SiC interface and the degree of intermixing of anions and cations at the interface. This manipulation was achieved by controlling: (i) the SiC surface reconstruction during surface cleaning, (ii) the atomic termination/orientation of the SiC substrate [i.e., $(0001)_{Si}$, $(000\bar{1})_{C}$, and $(1\bar{1}00)$], and (iii) pre-exposing the SiC (AlN) surface to either Al or NH₃ (SiH₄ or C₂H₄) prior to growth of the AlN (SiC) film.

II. EXPERIMENTAL PROCEDURE

A gas source molecular beam epitaxy (GSMBE) system with a base pressure of 3×10^{-10} Torr was designed and constructed specifically for the growth of III–V nitride thin films.¹⁹ The reactants were SiH₄ (99.9995%), C₂H₄ (99.9999%), Al(99.9999%), and NH₃ (99.9995%). The Al was evaporated from a 25 cm³ "cold lip" 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, C₂H₄, and NH₃ was achieved using "molecular beam" dosers similar to the design of Bozack *et al.*²⁰

The substrates used in this study were $1.5 \text{ cm} \times 1.5 \text{ cm}$ pieces of *n*-type $(N_d = 10^{18}/\text{cm}^3) \text{ 6H-SiC}(0001)_{\text{Si}}$ wafers cutoff-axis 4° toward $(1\overline{1}20)$ and containing a $\approx 1 \ \mu\text{m}$ *n*-type $(N_d = 5 \times 10^{17} \text{ cm}^3) \text{ 6H-SiC}$ epitaxial layer. On-axis $(0001)_{Si}$, $(000\overline{1})_C$, and $(1\overline{1}00)6H$ -SiC wafers without an epitaxial layer but with a thermally grown oxide were also investigated. All wafers were ultrasonically and sequentially rinsed in trichloroethylene, acetone, and methanol, dipped in 10:1 buffered HF for 10 min, and mounted to a Mo sample holder. The *in situ* procedure used for the final cleaning step of the 6H-SiC substrates was similar to that employed by Kaplan²¹ and Kern²² and is described in more detail in Ref. 23. Briefly, each SiC wafer was annealed in the GSMBE system in a flux of 10^{-6} – 10^{-5} Torr SiH₄ for 15–20 min at 1050 °C. Analysis via Auger electron spectroscopy (AES) and (XPS) revealed oxygen-free, silicon-terminated SiC surfaces which displayed (1×1) low energy electron diffraction (LEED) patterns. For the $(0001)_{Si}$ orientation, a (3 \times 3) reconstruction was generated by using longer SiH₄ exposures. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction was obtained for the (0001)_{Si} surface by annealing the wafer at 1000 °C in UHV without a flux of SiH₄. Non-SiC carbon was detected from this surface by XPS. We were not successful in generating surface reconstructions for the $(000\overline{1})_{\rm C}$ and $(1\overline{1}00)$ 6H–SiC surface orientations.

To initiate the deposition of AlN, each 6H–SiC wafer was first raised to 1050 °C. At this point, either the shutter to the Al cell or the NH₃ leak valve was opened first and the surface was exposed to the second component. This was done to generate a different degree of mixing at the AlN/SiC interface. Sustained growth of the AlN films occurred at a rate of ≈ 250 Å/h in 10^{-5} Torr NH₃. After a predetermined AlN thickness was obtained, the Al cell was shuttered and the sample was allowed to cool in ammonia until approximately 600–700 °C when the ammonia leak valve was closed. The AlN films displayed (2×2) reconstructed surfaces immediately after growth. Scanning electron microscopy (SEM) analysis showed the films to be free of surface topography at a magnification of 10 000X, and the films were too resistive for Hall or capacitance/voltage measurements.

The growth of SiC on AlN at 1050 °C was also investigated using equal flows of the reactants of SiH₄ and C₂H₄. The AlN surface was initially exposed to SiH₄ followed by C₂H₄. The growth rate was slow (i.e., ≤ 100 Å/h), and the grown films were used only for measuring the ΔE_v of SiC on AlN. The SiC films were assumed to be the 3C (beta) polytype based on Ref. 22.

The XPS and UPS experiments were performed *in situ* using a UHV transfer line. The XPS/UPS system had a base pressure of 2×10^{-10} Torr and was equipped with a dual anode x-ray source, a differentially pumped helium resonance UV lamp, and a 100 mm hemispherical electron energy analyzer. All XPS spectra were obtained using Al $K\alpha$ radiation $(h\nu = 1486.6 \text{ eV})$. Calibration of the binding energy was achieved by periodically measuring the positions of the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks from clean standard samples and correcting them to 83.98 and 932.67 eV, respectively. A combination Gaussian–Lorentzian curve shape with a linear background best represented the XPS data. All UPS spectra were acquired using the unmonochromated He I line $(h\nu = 21.2 \text{ eV})$.

The method used for calculating the AlN/6H-SiC valence band discontinuity was similar to that of Waldrop and Grant²⁴ and Kraut *et al.*²⁵ The basic scheme of this approach is to reference the valence band maximum energy to a core level (CL) 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. The energy position of one CL from the substrate (SiC) is measured with respect to the substrate valence band maximum (VBM), i.e., (VBM-CL)^{SiC}_{bulk}. Subsequently, a thin layer (≈15-20 Å) of the second semiconductor (AlN) is deposited on the substrate and the difference between the substrate and film core levels is measured, i.e., (CL^{SiC}-CL^{AIN})_{interface}. Finally, the thickness of the overlying film is increased beyond the sampling depth of XPS (≈ 250 Å) and the CL-to-VBM energy is measured for the deposited film, i.e., (VBM-CL)^{AIN}_{bulk}. The valence band discontinuity between the two semiconductors is given as

$$-\Delta_{v}(AIN/SiC) = (VBM-CL)^{SiC}_{bulk} - (VBM-CL)^{AIN}_{bulk} - (CL^{SiC}-CL^{AIN})_{interface}.$$
 (1)

In a previous study,¹³ only XPS was used to determine both the core level and valence band maxima energies. In this technique, core level peak positions can be measured with an accuracy of $\leq 0.1 \text{ eV}$,²⁶ but the cross section for ejection of valence band electrons is extremely low, and results in an inherently poor signal-to-noise ratio (S/N). This necessitated comparison of the XPS VB spectra with the theoretically calculated VB density of states (VBDOS) to determine the position of the VBM. In contrast, for the measurements described here, both UPS (He I, hv=21.2 eV) and XPS were used to determine the VBM, and XPS was used to determine the core level positions. The S/N ratio in UPS VB spectra is several orders of magnitude higher than that of XPS and, therefore, a direct determination of the VBM without comparison to the theoretically determined VBDOS was



FIG. 1. UPS spectra from $(0001)_{Si}$ 6H–SiC surface after (a) annealing in SiH₄ at 1000 °C to remove the surface oxide and (b) thermal desorption at 600 °C.

possible. The location of the VBM was achieved by extrapolating the high kinetic energy leading edge of the VB spectra with a straight line to the energy axis.^{16–18}

III. RESULTS

A. SiC_{CL}-VBM

Measurements of the SiC core level energies relative to the SiC VBM were complicated due to the appearance of surface states in the SiC band gap when oxygen was completely removed via SiH₄ cleaning or thermal desorption at 1000 °C [see Fig. 1(a)]. Johansson, Owman, and Martensson²⁷ experienced similar difficulties for the $(\sqrt{3})$ $\times \sqrt{3}$ R 30° reconstructed surfaces of (0001) 4H/6H SiC prepared by annealing in UHV at 1000 °C. However, these authors²⁷ estimated that the SiC VBM was $2.3\pm0.2\,\text{eV}$ below E_F and that $C1s - VBM^{SiC} = 283.3 - 2.3 = 281.0 \text{ eV}$ $(Si 2p - VBM^{SiC} = 99.0 \text{ eV}).$ Our estimation of C 1s-VBM^{SiC} from the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ surface was unrealistically 1.0 eV higher, i.e., 282.0 eV. Thus, we adopted the method of Grant and Waldrop²⁸ and measured $C 1s(Si 2p) - VBM^{SiC}$ from our SiC substrates after thermal desorption at 600 °C, as shown in Fig. 1(b). In this case, no surface states were observed due to the remaining monolayer of oxygen on the SiC surface. The values of 281.3 ± 0.1 and C1s-VBM^{SiC} $99.3 \pm 0.1 \, \text{eV}$ obtained for and $Si 2p - VBM^{SiC}$, respectively, were in excellent agreement with Refs. 28 and 29. Similar values for SiC_{CL}-VBM were obtained for the $(000\overline{1})_C$ surface; however, a value of 99.8 was measured for the $(1\overline{1}00)$ orientation.

B. AIN_{CL}-VBM

We have previously reported our values for the positions of the Al and N core levels with respect to the AlN valence band maximum in a separate study of the (0001) GaN/AlN

TABLE II. Si 2p, C 1s, Al 2p, and N 1s core levels referenced to the SiC and AlN valence band maxima, respectively.

CL-VBM	
C 1s-VBM _{sic}	281.3±0.1 eV
Si 2 <i>p</i> -VBM _{sic}	99.3±0.1 eV
Al 2 <i>p</i> -VBM _{AlN}	71.4±0.2 eV
N 1 s – VBM _{AIN}	$394.7 \pm 0.2 \text{ eV}$

band alignment.³⁰ The AlN layers used in this study were the same films used in the previous GaN/AIN study; thus, these results are only summarized below.

The measurements of the AlN VBM energy positions were complicated by significant amounts of emission from HeI_{β} radiation in the UPS spectra. The location of the VBM in the UPS VB spectra was thus determined by extrapolating a straight line through the leading edge of the spectra to the energy axis. A value of 71.5 ± 0.1 was determined for $A12p-VBM^{AIN}$ using this analysis procedure for several AlN films with a (2×2) reconstructed surface. A slightly lower value of 71.3 ± 0.3 eV was determined from the XPS spectra. The intermediate value of 71.4±0.2 eV for $A12p - VBM^{AIN}$ and $394.7 \pm 0.2 \text{ eV}$ for $N1s - VBM^{AIN}$ were chosen for the calculations (see Table II). The value for $A12p - VBM^{AIN}$ is intermediate to the value of 71.9 eV reported by Bermudez et al.³¹ and 70.6 eV reported by Waldrop and Grant. 24 The AlN $_{CL}-VBM$ for the $(000\overline{1})_{C}$ orientation was also the same as for the (0001) orientation. The Al 2p – VBM^{AlN} for the (1100) orientation was larger at 71.9 eV.

C. $\Delta CL(AIN/SiC) = (CL^{SiC} - CL^{AIN})_{interface}$

The positions of the Al 2*p*, N1*s*, Si 2*p*, and C1*s* core levels were recorded as a function of AlN thickness on SiC. The values and deltas reported here and used to calculate ΔE_v were taken at an AlN thickness of 20–25 Å, which is below the reported critical thickness for AlN on SiC of \approx 45



FIG. 2. The measured N1*s*-C1*s* and calculated AlN/6H–SiC ΔE_v observed as a function of AlN thickness on (1×1) 6H–SiC off-axis (0001)_{Si}.

Å for the (0001) interface⁶ and ≈ 140 Å for the (100) interface.³² The thickness of 20–25 Å was selected as both the N1*s*-C1*s* and Si 2*p*-Al 2*p* values were observed to stabilize (see Fig. 2) at this thickness, as well as give the same ΔE_v . At smaller thickness values, the ΔE_v calculated using N1*s*-C1*s* differed from Si 2*p*-Al 2*p* by as much as 0.3–0.4 eV. The values of ΔE_v obtained for thicker AlN films (30–35 Å) were not different from those at 20–25 Å. Beyond 40 Å no SiC core levels were detected.

All the valence band discontinuities obtained for the different interfaces are summarized in Table III. A type I valence band discontinuity was observed in all cases, but the values ranged from 0.6 to 2.1 eV depending on orientation, cut, and the SiC surface cleaning method employed. The absolute values of ΔE_v are reported here with an accuracy of only ± 0.2 eV due to difficulties in determining the exact energy position of the AlN VBM. However, the actual differences in ΔE_v due to interface chemistry, reconstruction, etc., were measured with an accuracy of ± 0.1 eV. This information is completely nested within the $\Delta CL(AlN-SiC)$ term in Eq. (1), which we could measure with an accuracy of ± 0.1 eV. Thus, the differences we see in the ΔE_v for differ-

TABLE III. Measured values of Δ CL and respective valence band discontinuties (ΔE_v) for AlN deposited on various 6H–SiC surfaces and for SiC deposited on 2H–AlN.

On/off axis	Reconstruction (SiH ₄ /UHV)	Al/NH ₃	$\begin{array}{c} \operatorname{Si} 2p - \operatorname{Al} 2p \\ (\pm 0.1 \text{ eV}) \end{array}$	N 1 <i>s</i> -C 1 <i>s</i> (±0.1 eV)	$\frac{\Delta E_v}{(\pm 0.2 \text{ eV})}$
6H-SiC (00)01) _{Si}				
Off	$(3\times3)/SiH_4$	NH ₃	26.9	114.3	0.9-1.0
Off	$(1 \times 1)/SiH_4$	NH ₃	26.5-26.7	114.5-114.8	1.1 - 1.4
Off	(1×1) /SiH ₄	Al	26.6-27.0	114.3-114.7	0.9-1.3
Off	$(\sqrt{3} \times \sqrt{3}) R 30^{\circ}/\text{UHV}$	NH ₃	26.7	114.5	1.1 - 1.2
On	(3×3) /SiH ₄	NH ₃	26.5	114.9	1.4 - 1.5
On	$(\sqrt{3} \times \sqrt{3})R30^{\circ}/\text{UHV}$	NH ₃	26.7	114.6	1.2
On	(1×1) /SiH ₄	Al	26.5	114.7	1.3-1.4
6H-SiC (0	001) _C				
On	$(1 \times 1)/SiH_4$	NH ₃	27.3	114.1	0.6 - 0.7
On	$(1 \times 1)/UHV$	Al	26.8	114.4	1.0 - 1.1
6H-SiC (1	100)				
On	$(1 \times 1)/\text{SiH}_4$	NH ₃	27.0	114.3	0.9
On	$(1 \times 1)/UHV$	Al	27.0	114.2	0.8 - 0.9
2H-AIN ()001) _{Al}				
On	(2×2)	SiH_4	25.9	115.3	1.9-2.0 eV

AIN plasmon

Si 2p

(a) $(\sqrt{3}x\sqrt{3})R30^{\circ}$

(b) (3x3

106

Si-N

104



102

100

 $6H-SiC(0001)_{Si}$ interface and (b) $AlN/(3\times3)R$ $6H-SiC(0001)_{Si}$ interface.

ent orientations and reconstructions are real and within our experimental capabilities.

D. Interface chemistry

WWW

96

98

ntensity [arb. units]

The AlN/SiC interface is heterovalent with different anions and cations on both sides of the interface. Thus, care was taken to separate chemically shifted peaks in the XPS spectra of the Al 2p, Si 2p, C 1s, and N 1s core levels due to formation of Si–N or Al–C bonds. A shifted Si 2p core level was not observed for AlN/SiC interfaces formed on $(\sqrt{3}\times\sqrt{3})R30^{\circ}$ 6H–SiC(0001)_{Si} and (000-1)C surfaces prepared by thermal desorption at 1000 °C as shown in Fig. 3(a). However, a small, chemically shifted Si 2p core level at 102.2-102.8 eV (indicative of Si-N bonding) was observed from all AlN/SiC interfaces in which the SiC surface was cleaned via annealing in SiH₄. The Si-N bonding was particularly prevalent for AlN deposited on (3×3) 6H-SiC $(0001)_{Si}$ surfaces, as shown in Fig. 3(b). The feature at 99.3 eV is from an AlN plasmon. As we have shown in separate articles,^{22,23} the SiH₄ cleaning step leaves a silicon-rich surface with excess silicon, whereas the thermal desorption clean leaves a silicon-depleted surface with excess carbon C-C bonded/graphite) at the surface. Thus, it is not surprising that Si-N bonding is observed at AlN/SiC interfaces in which the SiC surface is prepared by annealing in SiH₄. The presence or amount of Si-N bonding was not dependent on whether the SiC surface was pre-exposed to Al or NH₃ first. On the other hand, Al-C bond formation was not detected in either the Al 2p or C 1s spectra despite larger full width at half maximum (FWHM)] from AlN/SiC interfaces in which the SiC surface was prepared by simple thermal desorption at 1000 °C. Similar observations were also made for SiC/AlN interfaces prepared by growing SiC on AlN films.



FIG. 4. XPS of the Si2*p* core level from (a) (3×3) 6H–SiC(0001)_{Si} exposed to NH₃ at 1050 °C and (b) (2×2) AlN (0001) surface exposed to SiH₄.

For a better understanding of the interface chemistry and formation between AlN and 6H-SiC, the surfaces of these two materials were exposed to separate fluxes of SiH₄ and $C_2H_4(AIN)$ and Al and $NH_3(6H-SiC)$, at the growth temperature of 1050 °C. XPS was used to determine the chemical bonding at the surface. Silicon-N bond formation was clearly seen on SiH₄ cleaned (0001)_{Si} 6H-SiC surfaces which were exposed to NH3 at 1050 °C. The appearance of the N1s core level at 398.7 eV was observed and the chemically shifted Si2p core level at 102.5 eV is shown in Fig. 4(a). Analysis of the N 1s intensity was indicative of ≈ 1 ML of deposited nitrogen. Silicon-N bond formation was also observed for (0001) AlN surfaces exposed to SiH_4 at 1050 °C by the appearance of the Si 2p peak at 102.3 eV, as shown in Fig. 4(b). However, no chemically shifted C1score levels, indicative of Al-C bonds, were observed for SiH₄ cleaned (0001)_{Si} 6H-SiC surfaces exposed to Al at 1050 °C and quickly cooled to room temperature. Further, only a small Al 2p peak characteristic of <0.1-0.2 ML coverage was observed. The energy position of this peak may be indicative of Al-C bond formation based on the work of Bermudez.³³ However, the higher binding energy may be also due to band bending or due to Al-O bonding, as the oxygen surface coverage increased proportionally with the Al coverage. Finally, no deposition of carbon occurred on (0001) AlN surfaces exposed to C_2H_4 at 1050 °C. This indicates that this surface is unreactive with C2H4 at this temperature and that growth of SiC on this surface must be initiated with silicon via Si-N bond formation.

Exposure to NH_3 of SiC surfaces prepared by annealing at 1000 °C resulted in the formation of Si–N bonding. Unfortunately, we were not able to study the interaction of Al with these surfaces. However, we note that Bermudez³³ and Porte³⁴ have studied the interaction of Al with carbon-rich (0001) 6H–and (001) 3C–SiC films, respectively, and observed some Al–C bond formation via the appearance of a chemically shifted Al 2p core level at 0.71 eV higher binding energy than metallic Al. This explains our difficulty in observing Al–C bond formation in that the chemical shift is similar to that for Al–N bonding.

IV. DISCUSSION

The data in Table III show that the values obtained for the valence band discontinuity (ΔE_v) between 2H–AlN and 6H–SiC are clustered around 0.9–1.5 eV, irrespective of the orientation. Significant outliers for this distribution were observed only for AlN deposited on SiH₄ cleaned (000 $\overline{1}$)_C 6H–SiC with a NH₃ pre-exposure and 3C–SiC deposited on (2×2)(0001) 2H–AlN.

Ferrara, Binggeli, and Baldereschi¹⁴ predicted much larger valence band discontinuities of 2.26 and 2.54 eV for (111) 3C-AlN/3C-SiC interfaces with intermixing of Al and Si only and Al-N-Si-C and N-Al-C-Si stacking, respectively. These values are in reasonable agreement with the valence band discontinuity of 1.9-2.0 eV measured from the (0001) 3C-SiC/2H-AlN interface formed by growing SiC on a 2H-AlN/(0001)_{Si} 6H-SiC on-axis substrate. Predominantly Al/Si intermixing can be expected for this interface based on the preparation of the AlN surface prior to SiC growth *[i.e., the (0001)* AlN film should be Al terminated based on crystallography and the growth of the SiC film was initiated by first exposing the AlN surface to SiH₄]. However, the measured value of 1.9-2.0 eV for the 3C-SiC/2H-AlN interface is in better agreement with the values of 1.78 and 1.97 eV calculated by Ferrara, Binggeli, and Baldereschi¹⁴ for the (111) 3C-AlN/3C-SiC interface with both Al/Si and C/N intermixing and Al-N-Si-C and N-Al-C-Si stacking, respectively. Even better agreement is found when the stacking for the 3C-SiC/2H-AlN interface is taken into consideration. As mentioned above for the (0001) 3C-SiC/2H-AlN interface prepared in this study, Si-C-Al-N stacking is expected based on the crystallography of the underlying (0001) 6H-SiC substrate. This consideration yields excellent agreement between the experimental ΔE_{v} of 1.9–2.0 eV and that of theory –1.97 eV.

For AlN deposited on silicon-rich (0001)_{Si} 6H-SiC surfaces, we observed much smaller valence band discontinuities of 0.9-1.5 eV. Again based on crystallography and the stoichiometry of the starting growth surface, predominantly Al/Si intermixing could also be expected, but the ΔE_v values observed here are clearly much lower than the theoretical values of 2.26 and 2.54 eV reported by Ferrara, Binggeli, Baldereschi¹⁴ for this scenario. As for the 3C-SiC/2H-AlN interface mentioned above, intermixing of both Al/Si and N/C could be responsible for the lower ΔE_{v} . The larger values of 1.4-1.5 eV obtained for 2H-AlN grown on (3 $\times 3$)(0001)_{Si} on-axis 6H–SiC surfaces are close to the value of 1.78 eV reported by Ferrara, Binggeli, and Baldereschi¹⁴ for the (111) 3C-AlN/3C-SiC interface with Al-N-Si-C stacking. This is reasonable as this stacking is expected for AlN growth on $(0001)_{Si}$ 6H–SiC substrates. The ΔE_{V} values for $2H-AlN/(3\times3)$ 6H-SiC are also in extremely close agreement to the ΔE_v of 1.5 eV reported by Lambrecht and Segal¹⁰ for the neutral (110) 3C-AlN/3C-SiC interface which has an equal number of both Al-C and Si-N bonds at the interface.

However, the ΔE_{v} 's obtained for AlN grown on siliconrich (0001)_{Si} 6H-SiC surfaces are equally close or closer to the ΔE_v of 1.33 eV reported by Ferrara, Binggeli, and Baldereschi14 for the (111) 3C-AlN/3C-SiC interface with Al-N-Si-C stacking and intermixing of C and N only at the interface. Initially, this commonality may seem surprising given the extenuous attempts to produce Al/Si intermixing by starting with Si-rich surfaces and using Al pre-exposures. However, the extremely low sticking coefficient of Al on silicon-rich SiC surfaces at 1050 °C observed in this study indicates that very little intermixing of Al and Si is likely to occur initially. Instead, nitrogen is likely to first react with the excess Si on the SiC surface to form a Si-N bilayer. The stacking sequence for the AlN/SiC interface in this case is likely to proceed as Al-N-Si-N-Si-C. The net effect can be viewed as essentially a predominate intermixing of N on "C" sites of SiC. Alternatively, the excess Si can be viewed as causing intermixing of Al/Si and C/N at distances of 2-4 atomic planes (1-2 bilayers) as opposed to the 1-2 atomic planes considered in the study by Ferrara, Binggeli, and Baldereschi.¹⁴ Intermixing at distances greater than two bilayers is unlikely given the low growth temperature, the reported low solubility of AlN in SiC at this temperature,⁴ and the absence of any observations of interdiffusion of Al and N in SiC in transmission electron microscopy (TEM) at 1600–1750 °C.⁶

Unfortunately, the above discussion still fails to explain the low ΔE_v values of 0.9–1.1 eV observed for the 2H-AlN/(0001)_{Si} 6H-SiC interfaces. Closer examination of the data set, however, does reveal that values of ΔE_{v} in the range of 0.9-1.1 eV are only observed from AlN/6H-SiC interfaces prepared on silicon-rich $[(3 \times 3) \text{ and } (1 \times 1)]$, off-axis 6H–SiC substrates. Further, a larger range in ΔE_{v} of 0.9-1.4 eV was observed for AlN/SiC interfaces prepared on off-axis 6H–SiC substrates. This larger spread in ΔE_v for off-axis substrates may be related to the nature and types of defects formed at the AIN/SiC interface due to the presence of steps and the relaxation of strain. TEM studies of the growth of AlN on off-axis 6H-SiC substrates have shown an increased density of misfit dislocations and double position boundaries.⁶ These defects could influence ΔE_{v} in two different ways: (i) they allow the AlN films grown on off-axis 6H-SiC substrates to relax at thicknesses less than the onaxis substrates; thus, the observed differences in ΔE_{v} could be a result of strain. Or (ii) the defects formed at the AlN/SiC surface could be charged and, therefore, help to neutralize/ balance the charge formed at the (0001) interface due to the unbalanced C-Si-N-Al dipole which occurs along the [0001] direction. This explanation is similar to the cation/ anion intermixing proposed by Ferrara, Binggeli, and Baldereschi¹⁴ to neutralize the interface charge. This may explain why the ΔE_{v} values obtained for on-axis substrates are in much better agreement with the theoretical results, since these (0001) AlN/SiC interfaces are less defective.



FIG. 5. XPS of the O 1s core level from (a) (2×2) AlN (0001) surface after growth and (b) after exposure to SiH₄ at 1000 °C.

An alternative explanation for the low ΔE_v 's of 0.8–1.1 eV and the discrepancy with theory can also be provided based on the one significant difference observed in the XPS spectra obtained from 3C-SiC/2H-AlN and 2H-AlN/6H-SiC interfaces. For AlN deposited on 6H-SiC, a small O1s signal was always detected which increased with the number and time of the AlN depositions, as shown in Fig. 5(a). On the other hand, the O1s signal was eliminated after the initial SiH₄ exposure for SiC deposited on AlN [Fig. 5(b)]. This observation indicates that the SiC/AlN interface formed by SiC growth on AlN is of higher purity than the AlN/SiC interface formed by growth of AlN on 6H-SiC. Obviously, the presence of significant amounts of oxygen at the AlN/SiC interface could influence the amount and type of anion/cation intermixing needed to neutralize the interface charge. In the case of SiC grown on AlN, less oxygen was present at the interface and, hence, the ΔE_v observed for this interface was in closer agreement with that predicted by theory.

For AlN/SiC interfaces prepared by growing AlN on carbon-rich $(\sqrt{3} \times \sqrt{3})R30^{\circ}(0001)_{Si}6H-SiC$ surfaces, our ΔE_v results of 1.1–1.2 eV are equally close to the value of 1.33 eV reported by Ferrara, Binggeli, and Baldereschi¹⁴ for the (111) AlN/SiC interface with intermixing of C/N only. In this case, predominant C/N intermixing was expected based on the free carbon existing on the starting SiC growth surface and the NH₃ pre-exposure prior to AlN growth. Interestingly though, essentially the same results were obtained for both on-and-off-axis 6H–SiC substrates. Slightly lower values of 1.0–1.1 eV were also obtained for 2H–AlN/6H–SiC interfaces prepared on carbon-rich (0001)_C on axis 6H–SiC surfaces. In this case, the slightly lower ΔE_v could be due to the Al pre-exposure used instead or due to the larger coverage of free carbon on the surface.

At this point, it is worth noting that some of the discrepancies observed here between the theoretically calculated and experimentally measured ΔE_v 's for the AlN/SiC interface could be due to the differences in the polytypes examined (i.e., theory=3C/3C, exp.=2H/6H). However, the calculations of Ferrara, Binggeli, and Baldereschi¹⁴ found that the ΔE_v for the (111) 3C-AlN/3C-SiC interface differed from the (0001) 2H-AlN/2H-SiC interface by less than 0.1 eV with the differences in band gap being made up entirely in the conduction band discontinuity. Further, the LMTO calculations of Ke *et al.*³⁵ indicate that the ΔE_v between 2H/3C interfaces of SiC and AlN are also both less than 0.1 eV.

Finally, within the sample set examined for the (0001)and $(1\overline{1}00)$ orientations, no dependence on ΔE_v was observed with NH₃ vs Al pre-exposure. Again, this is related to the extremely low sticking coefficient of Al- to Si-terminated SiC surfaces. As mentioned previously, less than 0.1-0.2 ML of Al was observed on (0001)Si 6H-SiC surfaces exposed to an Al flux for 5-10 min at 1050 °C and quickly quenched to room temperature. This means that a large fraction of the Si-terminated SiC surface is directly exposed to NH₃ when it is introduced into the growth chamber; thus, the Al pre-exposure does not influence the degree of Al/Si intermixing. The flux needed to maintain a 1 ML coverage of Al on Si-terminated 6H-SiC at 1050 °C is three-to-four orders of magnitude larger than can be delivered in a typical molecular beam epitaxy (MBE) system, but could be easily achieved in chemical vapor deposition (CVD).

V. CONCLUSIONS

The above variations in ΔE_v AlN/SiC with orientation, cut, and interface chemistry are important as they indicate that the valence band and conduction band discontinuities can be manipulated and tailored for a particular device application. Large value of ΔE_v are desired as they would closely align the SiC/AlN conduction bands and aid in injection of electrons from SiC across AlN and into GaN or vacuum. In this case, our results show that one should choose on-axis 4H–SiC substrates and adopt growth schemes which would minimize the amount of oxygen left at the AlN/SiC interface.

Our detailed examination of the valence band discontinuity (ΔE_v) formed between 2H–AlN and 6H–SiC at $(0001)_{Si}$, $(000\bar{1})_C$, and $(1\bar{1}00)$ interfaces has been conducted using x-ray and UV photoelectron spectroscopies. Values for ΔE_v AlN/SiC from 0.6–2.0 eV were determined. The data indicate that the valence band discontinuity formed between these two different materials is dependent on the density and types of defects formed at the interface. These defects can be modulated by substrate cut, surface termination/reconstruction, and the presence of point defect and impurities such as oxygen.

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- ¹T. W. Weeks, M. D. Bremser, K. S. Ailey, E. P. Carlson, W. G. Perry, and R. F. Davis, Appl. Phys. Lett. **67**, 401 (1995).
- ²S. Tanaka, S. Iwai, and Y. Aoyagi, J. Cryst. Growth 170, 329 (1997).
- ³L. B. Rowland, R. S. Kern, S. Tanaka, and R. F. Davis, Appl. Phys. Lett. **62**, 3333 (1993).
- ⁴A. Zangvil and R. Ruh, J. Am. Ceram. Soc. **71**, 884 (1988).
- ⁵M. O. Aboelfotoh, R. S. Kern, S. Tanaka, R. F. Davis, and C. I. Harris, Appl. Phys. Lett. **69**, 2873 (1996).
- ⁶S. Tanaka, R. S. Kern, J. Bentley, and R. F. Davis, Jpn. J. Appl. Phys., Part 1 **35**, 1641 (1996); J. Cryst. Growth **163**, 93 (1996); Appl. Phys. Lett. **66**, 37 (1995).
- ⁷Q. Tian and A. V. Virkar, J. Am. Ceram. Soc. **79**, 2168 (1996).
- ⁸A. Morgan and J. Williams, *Physics and Technology of Heterojunction Devices* (Wiley, New York, 1985), pp. 241–244.
- ⁹G. Margaritondo and P. Perfetti, in *Heterojunction Band Discontinuities: Physics and Device Applications*, edited by F. Capasso and G. Margaritondo (Elsevier, New York, 1987), pp. 59–113.
- ¹⁰W. R. L. Lambrecht and B. Segal, Phys. Rev. B 43, 7070 (1991).
- ¹¹ M. C. Benjamin, C. Wang, R. F. Davis, and R. J. Nemanich, Appl. Phys. Lett. **64**, 3288 (1994).
- ¹² M. W. Wang, J. O. McCaldin, J. F. Swenberg, T. C. McGill, and R. J. Hauenstein, Appl. Phys. Lett. **66**, 1974 (1995).
- ¹³ S. W. King, M. C. Benjamin, R. J. Nemanich, R. F. Davis, and W. R. L. Lambrecht, in *Gallium Nitride and Related Materials*, Mater. Res. Soc. Proceedings (Materials Research Society, Pittsburgh, 1996), Vol. 395, pp. 375–380.
- ¹⁴P. Ferrara, N. Binggeli, and A. Baldereschi, Phys. Rev. B 55, R7418 (1997).

- ¹⁵M. Städele, J. A. Majewski, and P. Vogl, Phys. Rev. B 56, 6911 (1997).
- ¹⁶A. D. Katnani, in Ref. 9, pp. 115–165.
- ¹⁷ M. Ruckh, D. Schmid, and H. W. Schock, J. Appl. Phys. 76, 5945 (1994).
- ¹⁸G. Bratina, T. Ozzello, and A. Franciosi, J. Vac. Sci. Technol. B **14**, 2967 (1996).
- ¹⁹J. van der Weide, Ph.D. dissertation, North Carolina State University, 1994.
- ²⁰ M. J. Bozack, L. Muehlhoff, J. N. Russel, W. J. Choyke, and J. T. Yates, J. Vac. Sci. Technol. A 5, 1 (1987).
- ²¹R. Kaplan, Surf. Sci. 215, 111 (1989).
- ²²R. S. Kern and R. F. Davis, Appl. Phys. Lett. **71**, 1356 (1997).
- ²³ S. W. King, C. Ronning, R. F. Davis, R. S. Busby, and R. J. Nemanich, J. Appl. Phys. 84, 6042 (1998).
- ²⁴J. R. Waldrop and R. W. Grant, Appl. Phys. Lett. 68, 2879 (1996).
- ²⁵ E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, Phys. Rev. Lett. 44, 1620 (1980).
- ²⁶ R. W. Grant, E. A. Kraut, J. R. Waldrop, and S. P. Kowalczyk, in Ref. 9, pp. 167–206.
 ²⁷ L. I. Johansson, F. Owman, and P. Martensson, Surf. Sci. 360, L478
- ²⁷L. I. Johansson, F. Owman, and P. Martensson, Surf. Sci. **360**, L478 (1996); **360**, L483 (1996).
- ²⁸J. R. Waldrop and R. W. Grant, Appl. Phys. Lett. **62**, 2885 (1993); J. R. Waldrop, R. W. Grant, Y. C. Wang, and R. F. Davis, J. Appl. Phys. **72**, 4757 (1992).
- ²⁹L. M. Porter, R. F. Davis, J. S. Bow, M. J. Kim, R. W. Carpenter, and R. C. Glass, J. Mater. Res. **10**, 668 (1995).
- ³⁰S. W. King, C. Ronning, R. F. Davis, M. C. Benjamin, and R. J. Nemanich, J. Appl. Phys. 84, 2086 (1998).
- ³¹ V. M. Bermudez, T. M. Jung, K. Doverspike, and A. E. Wickenden, J. Appl. Phys. **79**, 110 (1996).
- ³²M. E. Sherwin and T. J. Drummond, J. Appl. Phys. **69**, 8423 (1991).
- ³³ V. M. Bermudez, J. Appl. Phys. **63**, 4951 (1988); Appl. Phys. Lett. **42**, 70 (1983).
- ³⁴L. Porte, J. Appl. Phys. **60**, 635 (1986).
- ³⁵S. Ke, J. Zi, K. Zhang, and X. Xie, Phys. Rev. B 54, 8789 (1996).