

Schottky barrier height and electron affinity of titanium on AlN

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Approximately 100 or 1000 Å of AlN was deposited on the (0001)Si-face of on-axis *n*-type 6H-SiC. The surfaces were examined by ultraviolet photoemission spectroscopy (UPS) utilizing the He I α (21.2 eV) and the He II α (40.8 eV) excitation. Experimental difficulties are discussed. Titanium was deposited on the clean surface of *in situ* grown AlN. The titanium–AlN interface was also characterized with UPS. Two approaches are presented to identify the valence band maximum (VBM) and the electron affinity χ of the clean surface of AlN was found to be either 0 to 1 eV depending upon the position of the valence band edge. The same assumptions were applied to the analysis of the Ti/AlN interface and, for the case of $\chi=0$ eV, the position of the valence band maximum is 3.4 eV below the position of the Fermi level. For the case of $\chi=1$ eV, the position of the valence band maximum is 4.4 eV below the position of the Fermi level. Therefore, the *p*-type Schottky barrier height of titanium on AlN is measured to be 3.4 ± 0.2 or 4.4 ± 0.2 eV for $\chi=0$ eV and $\chi=1$ eV, respectively. Independent of the selection of the valence band maximum, the observed Schottky barrier differed from that predicted by the Schottky–Mott model by 1.5 ± 0.2 eV. © 2000 American Vacuum Society. [S0734-211X(00)00104-9]

I. INTRODUCTION

The III-nitride wide band gap semiconductors of AlN–GaN–InN have been considered for a wide range of electronic and optoelectronic applications. Of this group, AlN exhibits the largest band gap with a value of 6.2 eV.^{1,2} Several studies have suggested the materials exhibit a low or negative electron affinity.^{3–5} Given this small or negative electron affinity of AlN, our interest in exploring the Schottky barrier to AlN is twofold. The first is to explore contacts that could supply electrons to the conduction band, and the second is to determine if a thin metal layer on AlN will result in an effective negative electron affinity as in the case of diamond.⁶

Photoemission spectroscopy has proven to be an indispensable technique in obtaining information about electronic structure. In particular, ultraviolet photoemission spectroscopy (UPS) is especially surface sensitive, making it possible to determine the electron affinity and the surface Fermi level as well as offering information about surface states. These material parameters will have a direct effect on the properties of the interface formed between a metal and a semiconductor. However, these are not the only effects that will determine the value of the Schottky barrier. The complex bonding at the interface contributes to the Schottky barrier through several different effects.

The Schottky barrier is often described in terms of two models. The Schottky–Mott model assumes that the bands are aligned with respect to the vacuum level of the metal and the semiconductor. The *n*-type Schottky barrier is just the difference between the metal work function and the semiconductor electron affinity. The alternative model is the interface dipole model, where the structure of the interface causes a

shift in the bands relative to the predictions of the Schottky–Mott model. This band shift may be interpreted as a change in the interface dipole due to the atomic bonding at the interface.

In understanding the electronic structure of interfaces of wide band gap semiconductors, it is useful to have knowledge of the electron affinity. The electron affinity of a semiconductor is defined as the energy difference between the vacuum level and the conduction band minimum. The value of the electron affinity at the surface of AlN has been the subject of debate in the literature. For example, thin layers of AlN deposited on 6H–SiC by organometallic vapor phase epitaxy (OMVPE) or by gas source molecular beam epitaxy (GSMBE) resulted in a negative electron affinity.^{3,4} In another study,^{7,8} AlN (0.2 μm thick) films were deposited on Si(111) by molecular beam epitaxy (MBE). The results of this study indicate a positive electron affinity of either 1.9 ± 0.2 or 2.1 ± 0.3 eV. In another study,⁹ an epitaxial structure consisting of a 30 nm AlN(0001) layer on GaN on the (0001) face of Al₂O₃ exhibited a positive electron affinity value of 3.2 eV. Another technique⁵ for depositing AlN involved first depositing a thick layer (2.7 μm) of *n*-type silicon-doped GaN and then depositing a thin Al layer via vapor deposition. This structure was then annealed in excess of 800 °C which is the temperature at which nitrogen was released from the underlying GaN. The nitrogen then combined with the Al to form AlN as verified by x-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES). The results indicate a positive electron affinity of 0.6 ± 0.3 eV. A more recent study¹⁰ of reactive magnetron sputtered AlN prepared *in situ* with the analysis indicates that oxygen plays a critical role in determining whether the value of the electron affinity at the surface will be negative or positive.

This study explores the electron affinity of AlN and the Schottky barrier with Ti. The metal Ti has a relatively low

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work function with a reported polycrystalline value of 4.3 eV.¹¹ Our previous studies of Ti on diamond have established that a thin layer of Ti results in an effective negative electron affinity.⁶ The results established that with the thin Ti layer the vacuum level is at or below the conduction band minimum of the diamond, and the *p*-type Schottky barrier to the diamond was ~ 1.0 eV. While other surface layers such as Cs have been considered to induce an effective negative electron affinity, Ti has a significant advantage in stability.

Our study will first explore the experimental difficulties in determining the electron affinity of AlN, and then examine the Schottky barrier of a thin layer of Ti on a clean AlN surface. Comparison of the results will allow the determination of the effect of the interface bonding on the interface dipole layer.

II. EXPERIMENT

The films prepared for this study were 100 and 1000 Å of AlN deposited on the (0001) Si-face of on-axis *n*-type 6H-SiC (hereafter referred to as 6H-SiC) by (GSMBE). The GSMBE is interconnected via a transfer tube with several analysis chambers [AES, low energy electron diffraction (LEED), and UPS] as well as an e-beam evaporation system. The base pressure of the entire system is $\sim 1.0\text{E}-09$ Torr. AES and LEED were employed before and after each process step in order to monitor any contamination that might result from transfer.

The SiC was received with a thermally grown oxide protective coating. This oxide can be removed with a 10:1 buffered HF dip for 10 min. Once the oxide is removed, a thick layer of tungsten is sputtered onto the backside of the wafer. This is necessary for the radiative heating of the SiC. After the tungsten deposition, the SiC is cleaned with solvents (trichloroethylene, acetone, and methanol), mounted to a molybdenum sample holder with Ta wire, and loaded into the GSMBE for the AlN film growth. The particulars of the GSMBE can be found elsewhere,¹² but certain aspects of the growth will be highlighted here. Once the SiC is loaded into the GSMBE, a final cleaning procedure for the SiC is employed. Each SiC wafer is annealed for 11 min at 1250 °C in a flux of SiH₄. The pressure in the chamber never exceeded $3.0\text{E}-05$ Torr during this procedure. For the AlN growth, the samples were annealed to 1250 °C. Once this temperature is achieved, the sample is exposed to Al from a Knudsen cell and NH₃ through a leak valve. The temperature of the Al Knudsen cell was 1250 °C. A sustained growth rate of ~ 1000 Å/h was achieved with a NH₃ leak rate that corresponded to a chamber pressure of $\sim 1.0\text{E}-05$ Torr. The AlN film was exposed to a constant flow of NH₃ until the sample cooled to a temperature of 600–700 °C.

After the growth process, the sample was transferred into the AES and LEED chamber, and then into the UPS chamber. For the AES measurements, a PHI model 10-155 single pass cylindrical-mirror analyzer was employed to study the chemical composition of the surface of the samples. For the AES measurements, a beam energy of 3 kV was employed for the incident electrons. The AES is operated in the pulse-

count, $N(E)$, mode. For the LEED images, a Princeton Research Instruments model RVL 6-120 was employed to image the surface of the samples. For the LEED images, an accelerating potential of 80 V was utilized.

The UPS technique utilizes an Omicron HIS13 noble-gas-discharge lamp. Both the He I α (21.2 eV) and the He II α (40.8 eV) light are accessible with this excitation source. The He II α excitation is particularly useful because of the He I β (23.1 eV) line which can sometimes complicate the determination of the valence band maximum (VBM). The photoexcited electrons were collected by an energy analyzer which was positioned at surface normal. The 50 mm radius hemispherical electron analyzer has an energy resolution of 0.15 eV and a 2° angular resolution. The sample stage is electrically isolated from the rest of the chamber and was biased by up to 6 V. In order for the low-energy electrons to overcome the work function of the analyzer, which is 4.5 eV, a 3–4 V bias is necessary to realize the full width of the spectra. The reason for the higher bias value of 6 V is that, for AlN films, charging effects which will distort the UPS spectra and shift the spectra toward higher binding energies are often encountered. However, if a somewhat higher bias (6 V) is applied to the sample, the full width of the spectra can be realized depending upon the amount of charging. Unfortunately, in the case of charging, the peak positions will be shifted toward higher binding energies, and it is generally impossible to accurately determine the surface Fermi level relative to the valence band maximum (VBM).

Once UPS spectra have been collected from the clean surface of AlN, the sample is transferred to the e-beam evaporation system for titanium deposition. Data are presented for a metal film thickness of 2 Å. The sample is returned to the UPS chamber for further characterization.

III. RESULTS AND DISCUSSION

The results of AES and LEED indicate a clean, 1×1 surface. The carbon signal was at or below the detection limit while there is a small peak due to the presence of oxygen as indicated in Fig. 1.

Photoemission spectra for clean AlN having thicknesses of 100 and 1000 Å are shown in Fig. 2. Since both films were prepared identically, it is unlikely that there is a fundamental difference in the surface Fermi level position. The spectrum of the 1000 Å film is significantly shifted to higher binding energies, and the spectrum is distorted. These effects are attributed to charging of the highly insulating AlN film.

In order to determine the position of the VBM, and hence determine the electron affinity of the sample, it is necessary to find bulk AlN features in the spectra to which all values can be referenced. We consider now the spectra of the 100 Å AlN layer where charging effects are not directly evident. There are three identifiable bulk features in the spectrum shown in Fig. 2(a). The first and most dominant feature is located at ~ 6.1 eV below the Fermi level. The second feature is located at ~ 9.3 eV below the Fermi level. The 9.3 eV feature is more evident when the 40.8 eV excitation is employed as indicated in Fig. 3. The third feature, which ap-

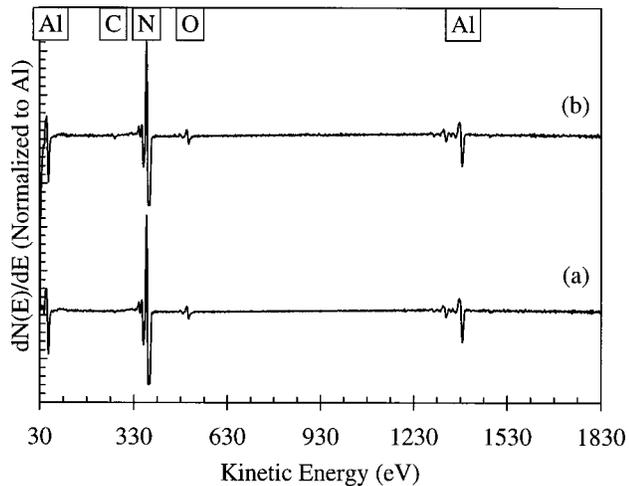


FIG. 1. AES survey spectra of (a) 100 Å AlN on 6H-SiC and (b) 1000 Å AlN on 6H-SiC. The spectra are normalized such that the absolute height of the dominant Al *KLL* peak is one. The peak due to carbon is at or below the detection limit while there is a small peak due to the presence of oxygen.

pears as a shoulder to the secondary electron peak, is located at ~ 13 eV below the Fermi level.

In one study,¹³ these features are located at 6 and 8.5 eV below the Fermi level. The AlN samples in that study were prepared by N_2^+ ion beam bombardment of high-purity polycrystalline Al. In a similar study on samples prepared in the same manner by the same authors,¹⁴ these peaks are reported to be located at 5 and 8.5 eV below the Fermi level. These peak positions were located at 5.8 and 8 eV below the Fermi level for samples consisting of 1000 Å of Al deposited on (100) Si and subsequently bombarded by N_2^+ ions.¹⁵ In another study,¹⁶ XPS results of AlN prepared by N^+ ion bombardment of monocrystalline (111) aluminum indicates that these peaks are located at 5 and 9 eV. The XPS results were in excellent agreement with the UPS results in that study. These values were also obtained by Bermudez *et al.*⁵

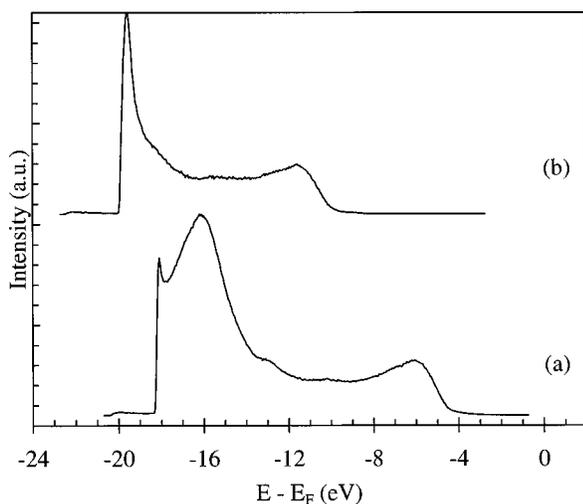


FIG. 2. UPS spectra of (a) 100 Å AlN on 6H-SiC and (b) 1000 Å AlN on 6H-SiC. In (b), the peak positions clearly indicate the presence of charging which will shift the spectrum to higher binding energies.

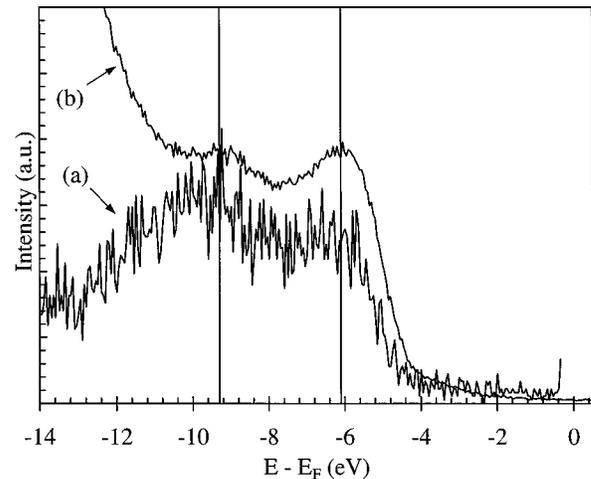


FIG. 3. UPS spectra of 100 Å AlN on 6H-SiC when (a) 40.8 eV excitation and (b) 21.2 eV excitation is incident upon the sample. For (a), the spectrum is multiplied by 45. The vertical lines are located at 9.3 eV below the Fermi level and 6.1 eV below the Fermi level. The peak at 9.3 eV below the Fermi level is enhanced by the 40.8 eV excitation.

In addition to surface charging there are several other effects that could lead to shifts in the spectra, which would be reflected as changes in the binding energy. These include band bending due to surface states, a different bulk Fermi level, polarization fields, and nonequilibrium processes such as surface photovoltage.

We note that the spectra plotted in Fig. 2(a) may also exhibit the characteristics of charging or one of the other above mentioned effects since the values for the peak positions disagree with the other reported values by as much as 1 eV. Given the obvious charging effect displayed in Fig. 2(b), it seems likely that surface charging may explain the smaller shifts observed in Fig. 2(a).

Another set of studies^{7,8} has focused on the electron affinity and electronic structure of AlN (0.2 μm thick) films deposited on Si(111) by MBE. Their results indicate spectral peaks located at ~ 7 and ~ 11 eV below the Fermi level. Comparing their spectra to those presented here and to the prior reports may suggest that the spectra are shifted ~ 2 eV accordingly to higher binding energies. After shifting the spectra, the peak positions of the 7 eV peak and the 11 eV peak should then be 5 and 9 eV. We note this difference since this study^{7,8} had noted a significantly larger electron affinity than prior studies from our laboratory and from other reports.³⁻⁵

We continue to explore effects in our spectra that are apparently related to charging. Even if the spectrum in Fig. 2(a) is shifted to higher binding energies due to charging, we expect the width (W) of the spectrum to be the same as long as there is enough bias applied to be able to discern the entire spectrum. For Fig. 2(a), a series of scans were collected at different applied sample bias. The spectra were biased up to 5 V in increments of 0.5 V. At a bias value of 3.5 V, the width of the spectra stopped increasing. The spectra presented in Fig. 2(a) were obtained with a bias value of 4 V, and the full width is discernible.

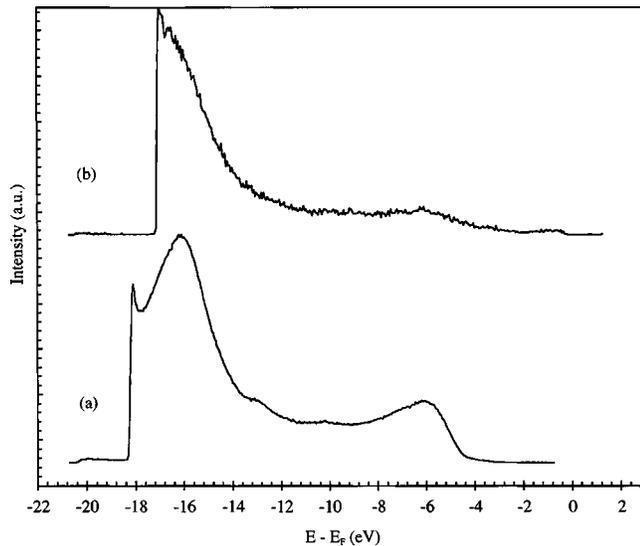


FIG. 4. UPS spectra of (a) AlN (100 Å thickness) deposited on 6H-SiC and (b) 2 Å Ti deposited on 1000 Å AlN deposited on 6H-SiC. Note that as a result of the Ti deposition, the charging effects that were evident in Fig. 2(b) appear to be reduced.

Charging in itself does not necessarily affect the width of the spectra unless not enough bias is applied to discern the entire width of the spectra. For example, in Fig. 2(b), a bias of 6 V was applied to the sample, and the full width of the spectra is still not discernible because the spectrum is shifted to higher binding energies by as much as 6 V (the peak that should be located 5 eV below the Fermi level is located at 11 eV below the Fermi level). Therefore, if we were to determine the electron affinity from the spectrum presented in Fig. 2(b), we would erroneously come to the conclusion that the surface has a positive electron affinity of 4.5 eV.

The electron affinity as determined by photoemission has the following relationship:

$$\chi = h\nu - E_g - W, \quad (1)$$

where χ is the electron affinity, $h\nu$ is the energy of the excitation source, E_g is the band gap of the material, and W is the measured width of the spectra from the position of the onset of the emission to the position of the low energy end of the spectra. In all calculations in this study, a value of 6.2 eV is used for the band gap of AlN. Note that this relationship does not apply to the case of a negative electron affinity. In that case, the low energy end of the spectrum defines the position of the conduction band minimum and not the position of the vacuum level. If a surface exhibits a negative electron affinity, this analysis would yield a value of $\chi = 0$. Therefore, the value of an electron affinity which is less than zero cannot be determined from photoemission without other supporting measurements.

We now consider one of the critical aspects in determining the electron affinity from photoemission, namely the determination of the width of the spectrum. In Fig. 4(a), we present the results for the clean surface of AlN (100 Å thickness) deposited on 6H-SiC and in Fig. 5(a) we present an expanded view of the same spectrum. Examination of the

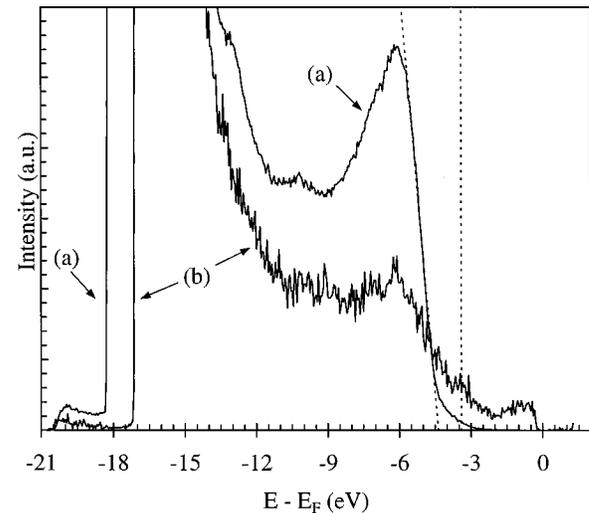


FIG. 5. Expanded view of the spectra shown in Fig. 4(a) AlN (100 Å thickness) deposited on 6H-SiC and (b) 2 Å Ti deposited on 1000 Å AlN deposited on 6H-SiC. The y axis of (b) is scaled with respect to (a) so that the features of the clean surface and the features of the titanium-covered surface can be compared. The dashed lines represent the models utilized in determining the VBM.

spectra shows a strong feature at 6.1 eV with scattering extending up to ~ 3 eV. We have compared this spectrum to a spectrum from a clean Ni film. In this comparison it is evident that the scattering extending above the 6 eV peak is indeed real and attributable to electronic states of the sample. This scattering is neither broadening due to the instrument nor spectral features associated with the weak 23.1 eV He I β radiation. This additional scattering may or may not be representative of the bulk states of the AlN. We therefore consider two different methods to define the VBM. In the first method, we ignore the additional scattering and line fit the leading edge of the 6.1 eV feature. The extrapolation of this line fit will give the VBM with this approach. The dashed line extrapolated to 4.4 eV below the Fermi level is the result of this analysis.

In the second approach we consider that the scattering extending above the 6.1 eV feature is due to bulk states of the AlN. Rather than a spectral analysis of this feature, we have instead drawn a vertical line on the graph that would indicate the position of the VBM if the surface had a negative electron affinity. This line is drawn at 15.0 eV from the low energy cutoff [as predicted from Eq. (1)]. Visual inspection indicates that this is a reasonable extrapolation under the assumption that these are indeed bulk states.

Wu and Kahn have proposed that this feature is due to contamination related states, particularly oxygen contamination in excess of a few percent as determined by XPS, on their samples.^{7,17} However, many of the spectra presented in the literature contain this feature.^{5,13-16,18,19} In one study,²⁰ this feature is attributed to the He I β (23.1 eV) radiation. However, if it were the 23.1 eV radiation, this feature should mimic the corresponding part of the spectra that is lower in energy by 1.9 eV. Indeed, the origin of this feature is difficult to understand.

Given that the low energy cutoff is well defined at 18.4 eV below the Fermi level as indicated in Fig. 5(a), the width of the spectrum can now be determined for these two possible assumptions. We find $\chi=1$ eV for case 1 where the leading edge of the 6.1 eV feature is extrapolated to zero intensity, and we find $\chi=0$ eV for the second case where we consider the weak emission extending up to 3 eV.

We note that independent of our assumptions of the VBM, our data yield a larger spectral width and consequently a smaller electron affinity than those reported by Wu et al.^{7,8} One possibility that may account for this difference is that the polarity of the films is different (Al or N face), and the different surfaces may have a correspondingly different electron affinity. It remains for future work to determine if the different orientations of AlN exhibit different values of the electron affinity.

The Schottky barrier height (SBH) (Φ_b) can be measured from the photoemission spectra by locating the valence band edge (E_v) of the semiconductor and the Fermi level (E_F) of the metal. The position of the valence band edge is determined as described above. The *p*-type SBH is defined as the energy difference between the Fermi level and the VBM at the interface between the metal and the semiconductor under equilibrium conditions. In the photoemission spectra, this is the value that can be directly measured. The value of the *n*-type SBH can be determined with a knowledge of the band gap. In order to determine the SBH with UPS, it is necessary to deposit an appropriate thickness of metal such that features of the underlying semiconductor are evident in the spectra. It is also extremely difficult to discern the position of the valence band maximum for a metal layer deposited on a semiconductor. Thus, it is necessary to obtain at least two spectra; one spectra obtained from the clean surface of the semiconductor and another spectra obtained from the semiconductor with a thin layer of metal deposited.

In Figs. 4(b) and 5(b), we present the results for the 2 Å Ti deposited on 1000 Å AlN deposited on 6H-SiC. Note that as a result of the Ti deposition, the charging effects that were evident in Fig. 2(b) appear to be reduced. Comparing Figs. 5(a) and 5(b), only the AlN feature located at 6 eV below the Fermi level can be discerned in both spectra.

We consider now the Schottky barrier determined from the spectra presented in Figs. 4 and 5. The width of the combined spectrum now extends from the Fermi level to the low energy cutoff at 17.2 eV. The vacuum level is then determined to be 4.0 eV above the Fermi level (i.e., $E_{vac}=21.2$ eV - 17.2 eV). To complete a picture of the band alignments, it is necessary to determine the position of the VBM. Here again we will consider both possibilities noted in the discussion above. The band relations for the two cases, for $\chi=0$ and $\chi=1$, are illustrated in Figs. 6(a) and 6(b), respectively. In constructing this picture, we have also used a value of 4.3 eV for the work function of Ti.

The first aspect to note is that the surface has an increase in the effective electron affinity rather than the hoped for decrease. Here again we note that we define the effective electron affinity as the relationship between the semiconduc-

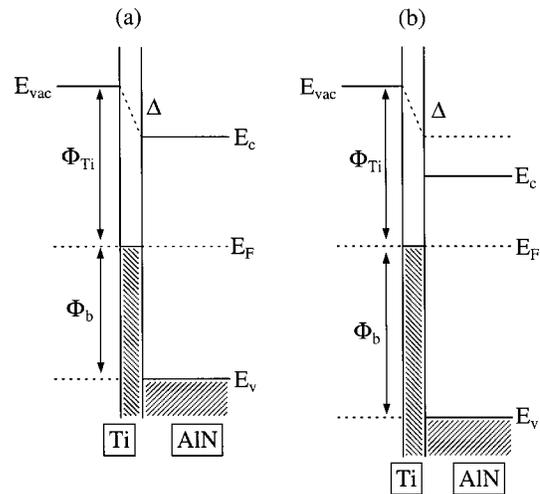


FIG. 6. Schematic of the band relations of the Ti/AlN interface. The two schematics were obtained from different approaches for the analysis of the VBM of the AlN spectrum: (a) is obtained from the analysis yielding χ of 0 eV, and (b) is obtained from the analysis assuming χ is 1 eV. The work function of titanium (Φ_{Ti}) is 4.1 eV. The *p*-type Schottky barrier height (Φ_b) is 3.4 ± 0.2 and 4.4 ± 0.2 eV in (a) and (b), respectively. The amount of band shifting (Δ) is independent of the choice of VBM and is determined to be 1.5 ± 0.2 eV.

tor conduction band minimum (CBM) and the vacuum level with the metallic overlayer. Thus, depending upon the determination of the VBM, the effective electron affinity after Ti deposition is 1.5 or 2.5 eV. In contrast, to the effect of Ti on diamond, which lowers the effective electron affinity, Ti on AlN results in an increase in the electron affinity.

An indication that the deposition of a metal overlayer may result in a reduction of the effective electron affinity can be obtained with a comparison of the electronegativity values for the atoms. The electronegativity is defined as the tendency of an atom to attract bonding electrons. Therefore, the difference between the values of the electronegativity for two atoms can provide a useful indicator of the polarity of the resulting dipole that is formed.¹¹ For an adsorbate atom that has a lower electronegativity value than the surface atoms on the semiconductor, the resulting dipole field that is formed will be directed outward from the semiconductor. Thus, the effective electron affinity would be reduced. In the case of AlN, Ti has a lower electronegativity than either Al or N (1.54 eV for Ti as compared to 1.61 eV for Al and 3.04 eV for N).¹¹ This is the reason that it was proposed that the deposition of Ti would result in a reduction of the effective electron affinity. This trend was not observed in this experiment.

Independent of the choice of the VBM, the amount of shift in the bands due to the interface dipole (Δ) is 1.5 ± 0.2 eV. This shift then represents the change in the band alignment due to the interface dipole. This change in band alignment is the difference between our measured results and those predicted from the Schottky-Mott model of the barrier. There is a slight discrepancy (almost within the experimental uncertainty) between this analysis shown in Fig. 6 and the amount of shift in the low energy end of the UPS spectra

between the clean and titanium-covered surface which is indicated in Fig. 5. From Fig. 5, the amount of shift in the low kinetic energy end of the spectra is 1.2 ± 0.2 eV toward lower binding energies. One possible explanation for this discrepancy is that if we were to use a lower value for the work function of titanium, we would obtain a correspondingly lower value for the interface dipole in the calculation illustrated in Fig. 6. The justification for using a lower value for the work function of titanium could be reactive bonding of titanium with nitrogen from the AlN. Another possible explanation results from a closer examination of Fig. 5(b). In Fig. 5(b), the spectrum extends to the Fermi level of the system. In fact, the turn-on for the spectrum in Fig. 5(b) is located ~ 0.2 eV below the Fermi level. The spectrum could be shifted toward higher binding energies by 0.2 eV due to the presence of charging. If this is the case, then the shift in the low kinetic energy end of the spectra should be 1.4 ± 0.2 instead of the observed 1.2 ± 0.2 eV. Both of these explanations would result in values that are in closer agreement with each other.

IV. CONCLUSIONS

We have explored the experimental aspects of photoemission measurements of epitaxial AlN films grown on 6H-SiC. Significant surface charging was observed for 1000 Å films. The choice of the position of the VBM was complicated by the presence of weak scattering that extends beyond the 6.1 eV feature. We have explored two possible methods to analyze the spectra, and we find a value for the VBM that differs by 1 eV depending upon the assumptions. Based on this analysis, we conclude that 100 Å of AlN grown on 6H-SiC has an electron affinity value of either 0 or 1 eV depending upon the choice of the position of the VBM.

Titanium was deposited on the clean surface of *in situ* grown AlN, and was characterized with UPS. For the case of $\chi = 0$ eV, the position of the VBM is 3.4 eV below the position of the Fermi level. For the case of $\chi = 1$ eV, the position of the valence band maximum is 4.4 eV below the position of the Fermi level. Therefore, the *p*-type Schottky barrier height of titanium on AlN is measured to be 3.4 ± 0.2 or 4.4 ± 0.2 eV for $\chi = 0$ and $\chi = 1$ eV, respectively. Independ-

ent of the selection of the VBM, the observed Schottky barrier differed from that predicted by the Schottky-Mott model by 1.5 ± 0.2 eV. This value of the interface dipole is independent of the choice of the VBM.

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