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## Pd growth and subsequent Schottky barrier formation on chemical vapor cleaned *p*-type GaN surfaces

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Characterization of chemical vapor cleaned, Mg-doped, *p*-type GaN(0001) surfaces and Pd contacts sequentially deposited on these surfaces has been conducted using x-ray and ultraviolet photoelectron spectroscopies and low-energy electron diffraction. The band bending and the electron affinity at the cleaned *p*-GaN surface were  $1.4\pm0.1 \text{ eV}$  and  $3.1\pm0.1 \text{ eV}$ , respectively. A previously unidentified band of surface states was observed at ~1.0 eV below the Fermi level on this surface. The Pd grew epitaxially on the cleaned surface in a layer-by-layer mode and formed an abrupt, unreacted metal-semiconductor interface. The induced Fermi level movement with Pd deposition has been attributed to a complex interaction between extrinsic and intrinsic surface states as well as metal induced gap states. The final Schottky barrier height at the Pd/*p*-GaN interface was  $1.3\pm0.1 \text{ eV}$ ; the interface dipole contribution was  $0.4\pm0.1 \text{ eV}$ . © 2002 American Institute of Physics. [DOI: 10.1063/1.1424060]

#### I. INTRODUCTION

The achievement of *p*-type conducting GaN has led to the development of blue and green light-emitting diodes, blue emitting laser diodes, as well as nitride based heterojunction bipolar transistors and field-effect devices.<sup>1–5</sup> The future improvement of these devices rests in part on a detailed understanding of the metal/p-GaN interface and the development of approaches to reduce the specific contact resistivity, which has been consistently reported between 1  $\times 10^{-4}$  and  $6 \times 10^{-2} (\Omega \text{ cm}^2)$ .<sup>6,7–19</sup> The large specific contact resistivity proceeds directly from the inherent difficulties involved in acceptor doping with Mg, which is the most common method for achieving *p*-type conducting GaN. The current limitations in the quantity of Mg that can be incorporated during growth  $(\sim 1 \times 10^{20} \text{ cm}^{-3})^{20-22}$  as well as the large acceptor ionization energy ( $\sim 300 \text{ meV}$ ),<sup>23</sup> limits the carrier concentration/atomic concentration ratio for this dopant to a range of 0.1%-2.0%.<sup>20,24</sup> Both limitations make it difficult to fabricate a tunneling ohmic contact to p-GaN in a manner similar to that used in other metal-semiconductor systems.<sup>25</sup> The large work function of *p*-GaN ( $\sim$ 6.5 eV) and the absence of any metal with a work function greater than 5.8 eV, make it impossible to select a contact metal based on a minimization of the difference in work function. Additionally, there is a tenacious layer of native contamination on the as-grown surface, that is  $\sim 2$  nm thick and adds an additional 0.2 eV to the barrier height.<sup>26,27</sup>

In light of the aforementioned challenges, the Ni based contact schemes, which were previously employed in making ohmic contacts to GaAs<sup>28,29</sup> due in part to their ability to penetrate the native oxide, were subsequently applied to

p-GaN films. Several studies, which combined a Ni/Au scheme with a p-GaN surface that had been subjected to ex situ pretreatment, resulted in some of the lowest specific contact resistivities reported to date.<sup>6,30,31,9</sup> There have also been reports of Ni/Pt/Au (Refs. 8 and 9), Pt/Ni/Au (Ref. 10), Ni/ AuZn (Ref. 11), Cr/AuZn (Ref. 11), and Ni/Si/Ni/Au (Ref. 13) multilayer contact structures deposited on similarly treated surfaces which have had limited success. Several other studies demonstrate a lowered specific contact resistivity for Pd based structures on p-GaN surfaces, prepared with aquaregia,  $^{14-16}$  (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>,  $^{17,18}$  or KOH (Ref. 19) solutions prior to metallization. The authors<sup>6,30,31,7-19</sup> speculate that the improved contact properties are due to both a partial removal of the native surface contamination and a modification in the termination or bonding states at the p-GaN surface. The combined effects of the pretreatment as well as the large work function of Pd result in a lowering of the Schottky barrier height and a subsequent reduction of the specific contact resistivity. Although these results argue for the use of a pretreated p-GaN surface, there have been relatively few studies, 32-36 which systematically investigate the chemical and electronic properties of the pretreated surface, the evolution of those properties with sequential metal deposition, and the resulting Schottky barrier height.

The present work is a comprehensive study of the chemical, structural, and electronic properties of Pd contacts deposited on the surfaces of *p*-GaN films, which have been pretreated using a NH<sub>3</sub>-based, high temperature chemical vapor clean (CVC). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were used to evaluate the chemical and electronic properties of the *p*-GaN surface in the as-loaded, pretreated, and metallized states. The growth mode and the crystal structure of the sur-

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face of the Pd film was evaluated using both low-energy electron diffraction (LEED) and XPS.

#### **II. EXPERIMENT**

The 1  $\mu$ m thick, Mg-doped GaN thin films used in this study were grown via organometallic vapor phase epitaxy on a 100 nm thick AlN buffer layer previously deposited at 1150 °C on an on-axis 6H–SiC(0001) substrate. The wurtzite films were oriented in the [0001] direction and were presumed to be Ga terminated.<sup>16,37</sup> Following growth, the films were annealed at 800 °C±10 °C for 30 s in an AG-Associates 610 rapid thermal annealing unit to activate the Mg dopant. This component is compensated by atomic hydrogen in the as-grown condition.<sup>38</sup> Capacitance–voltage (*C–V*) measurements made using a Hewlett Packard 4284A *C–V* measurement system and a MDC mercury probe station indicated a net ionized impurity concentration ( $N_A - N_D$ ) of (2±1)×10<sup>18</sup> cm<sup>-3</sup>.

Tungsten was subsequently sputtered onto the back side of the SiC substrates to assist in radiative heating of the samples throughout the in situ preparation process. Prior to loading, the films were cleaned sequentially in trichloroethylene, acetone, and methanol baths for 1 min each, followed by a 10 min dip in 49% hydrochloric acid and a 10 s rinse in deionized water (DI). The details of the effects of this cleaning process have been published elsewhere.<sup>26</sup> The samples were fastened to a molybdenum plate and subsequently attached to a molybdenum sample holder, which facilitated the transfer process throughout the experiment. There was an approximate 30 min lavover between pulling the sample from the DI rinse and loading into an integrated surface analysis and growth system operating at a base pressure of  $(1\pm2)\times10^{-9}$  Torr and equipped with XPS, UPS, LEED, electron beam metallization, and CVC facilities.

An ammonia-based high temperature chemical vapor process<sup>26</sup> was used to obtain clean, stoichiometric p-type GaN surfaces. To achieve these surfaces, the sample was initially heated to  $500 \pm 10$  °C, whereupon the ammonia flux was introduced. The sample was then heated to 825 °C  $\pm 25$  °C and held for 15 min at a process pressure of (9  $\pm 1$ )×10<sup>-5</sup> Torr. As the distance between the ammonia doser and the sample was  $\sim 5$  cm, the partial pressure of ammonia at the sample surface may have been as much as an order of magnitude greater than the system pressure. Upon cooling to  $200 \,^{\circ}\text{C} \pm 10 \,^{\circ}\text{C}$ , the sample was immediately transferred in an ultrahigh vacuum for photoelectron spectroscopy measurements and subsequent metallization. The surface temperature was monitored throughout the process with an Ircon infrared pyrometer at an emissivity ( $\epsilon$ ) setting of 0.5. Temperatures outside the operating range of the pyrometer (<600 °C) were measured using the thermocouple mounted immediately behind the sample.

XPS measurements were made using a Fisons XR3 dual anode x-ray source coupled to a Fisons CLAM II hemispherical electron energy analyzer with a mean radius of 100 mm operating at a base pressure of  $(5 \pm 1) \times 10^{-10}$  Torr. The resolution of the analyzer was 1.0 eV, although the absolute peak positions could be measured to within 0.1 eV. All core level spectra were fit using linear background subtraction and a mixed Gaussian–Lorentzian peak type. UPS measurements were made using an Omicron HIS13 gas discharge lamp together with a hemispherical electron energy analyzer whose mean radius was 50 mm. A -4 V bias was applied to the sample throughout the measurement to overcome the work function of the spectrometer. The resolution of the analyzer was approximately 0.1 eV. All spectra were acquired at an operating pressure of  $(7\pm3)\times10^{-9}$  Torr while the base pressure of the system was  $<3\times10^{-10}$  Torr. The Fermi level position was determined from UPS measurements made on clean 500 Å thick Pd films. All Pd depositions were conducted using an electron-beam evaporation system equipped with a quartz crystal thickness monitor operating at a base pressure of  $(2\pm1)\times10^{-10}$  Torr.

#### **III. RESULTS**

#### A. Chemical vapor cleaning of the GaN(0001) surface

The XPS spectrum of the surface of an as-loaded GaN film is shown in Fig. 1. It indicates that the C 1s core level, located at  $285.5\pm0.1\,\text{eV}$  with a full width at half maximum (FWHM)=1.6 eV, lies near the 284.8-285.3 eV range reported in the literature for adventitious carbon.<sup>26,39,40</sup> These results and the evidence presented in later sections indicate that charging effects were negligible. Following the CVC process, the C signal at the surface was reduced beyond the detectable limit of the XPS, which is approximately 0.3 at. %.<sup>40</sup> The O 1s core level spectra from the as-loaded surface shown in Fig. 1(b) was fit with a single broad peak located at  $532.7 \pm 0.1 \text{ eV}$  (FWHM=3.1 eV). A significant reduction in the peak intensity and a shift to a lower binding energy occurred following the CVC process, as shown by the final peak location at  $531.5\pm0.1 \text{ eV}$  (FWHM=1.1 eV). The O concentrations on both the as-loaded and CVC treated surfaces; were 15 at. % and  $2\pm 1$  at. %, respectively, as calculated using the integrated intensities and corresponding sensitivity factor (O 1s, 0.660).

Figure 2 shows the Ga 3d spectra obtained from the as-loaded and CVC treated surfaces, which were fit with single peaks located at  $20.5\pm0.1 \text{ eV}$  (FWHM=1.5 eV) and  $19.5\pm0.1 \text{ eV}$  (FWHM=1.5 eV), respectively. An equivalent shift was observed for the N 1s core level, as shown in Fig. 3, whose peak locations on the as-loaded and CVC treated surfaces were  $398.1\pm0.1 \text{ eV}$  (FWHM=1.2 eV) and  $397.1\pm0.1 \text{ eV}$  (FWHM=1.2 eV) and  $397.1\pm0.1 \text{ eV}$  (FWHM=1.2 eV), respectively. The magnitude and direction of the shifts are in excellent agreement with the shift observed for the core level feature identified in the valence band spectra shown in Fig. 4. The Ga/N ratios, determined from the peak areas of the Ga 3d and N 1s core levels and the corresponding sensitivity factors (Ga 3d, 0.310 and N 1s, 0.420), were calculated to be 1.5 and 1.0 for the as-loaded and CVC treated surfaces, respectively.

The Fermi level is pinned well above the valence band maximum (VBM) on the as-loaded surface. The exact position of the VBM on this surface is difficult to determine due to the exponential nature of the turn on due to the heavy contamination. Following the CVC process, there is a significant shift in the VBM to  $1.7\pm0.1$  eV below the Fermi



FIG. 1. XPS (a) C 1s and (b) O 1s and core level photoelectron peaks from the as-loaded and CVC *p*-GaN surface. The O 1s and C 1s spectra were acquired using Mg  $K\alpha$  ( $h\nu$ =1253.6 eV) and Al  $K\alpha$  ( $h\nu$ =1486.6 eV) radiation, respectively.

level, as determined by taking a linear fit of the high kinetic energy side of the spectrum shown in Fig. 4. The subsequent downward band bending and electron affinity were calculated to be  $1.4\pm0.1$  eV and  $3.1\pm0.1$  eV, respectively, assuming the Mg acceptor level lies ~300 meV above the VBM and a room temperature band gap of  $3.4 \text{ eV.}^{23}$  A schematic of the proposed energy band diagram for the CVC surface is shown in Fig. 5(a). A second interpretation of the valence band spectra presented by Wu *et al.*<sup>34</sup> and Bermudez *et al.*<sup>41</sup> argues that the true position of the VBM on the clean surface is obscured by a band of surface states located at or near the VBM. These authors identified emission from this band of states as a shoulder located at the high kinetic energy side of the spectrum, which is indicated with an asterisk at the inset



FIG. 2. XPS Ga 3*d* core level photoelectron peaks as a function of Pd deposition on a CVC *p*-GaN surface. The as-loaded spectrum is included as a reference. All spectra were acquired using Mg  $K\alpha$  ( $h\nu$ =1253.6 eV) radiation.

of Fig. 4. According to these studies, the band of surface states may extend as far as  $0.6\pm0.1$  eV above the true VBM. If this interpretation is correct, the adjusted values for the band bending and electron affinity cited above would be  $2.0\pm0.1$  eV and  $3.7\pm0.1$  eV, respectively.



FIG. 3. XPS N 1s core level photoelectron peaks as a function of Pd deposition on a CVC p-GaN surface. The as-loaded spectrum is included as a reference. All spectra were acquired using Mg  $K\alpha$  ( $h\nu$ =1253.6 eV) radiation.



FIG. 4. UPS valence band spectra from the (a) as-loaded and (b) CVC *p*-GaN surface. The dashed lines indicate the shift of the core level feature. A linear fit of the high kinetic energy side of spectra (b) and the subsequent position of the valence band maximum on the clean surface are shown within at the inset. The vertical arrow labeled  $ss_2$  indicates surface state related emission. All spectra were acquired using the He–I photon line ( $h\nu$ =21.2 eV). The binding energy is measured with respect to the Fermi level ( $E_F$ =0 eV).

### B. Growth mode of Pd and the characterization of the Pd/GaN interface

The attenuation in the intensity of the Ga 3*d* core level spectra with sequential Pd deposition was used to evaluate the characteristic growth mode of the Pd overlayer on CVC treated *p*-GaN in a manner similar to that of Wolter *et al.*,<sup>39</sup>



FIG. 5. Energy band diagrams for the (a) unmetallized, CVC *p*-GaN surface and the (b) Pd 20 Å/CVC *p*-GaN contact structure (assuming a band gap  $(E_g)$  of 3.4 eV). The band bending and subsequent Schottky barrier height remained unchanged following additional metal depositions.

and Sitar *et al.*<sup>42</sup> The three possible growth modes considered in this study were (i) Frank–van der Merwe (FM) (twodimensional, layer-by-layer growth), (ii) Volmer–Weber (VW) (three-dimensional growth of discrete islands), and (iii) Stranski–Krastanov (SK) (a combination of the two previous models wherein the initial film growth occurs in a layer-by-layer fashion and is subsequently followed by the onset of island growth). The prevailing growth mode is a strong function of the substrate, film, and interfacial surface energies. FM growth is described by

$$\frac{I_S}{I_o} = e^{(-t/\lambda_o)},\tag{1}$$

where  $I_o$  is the baseline core level intensity from the clean *p*-GaN substrate with no overlayer,  $I_s$  is the core level intensity for a given overlayer thickness (*t*), and  $\lambda_o$  is the attenuation length of the Ga 3*d* photoelectron. The VW model is described by

$$\frac{I_S}{I_o} = (1 - \theta) + \theta \times e^{(-t/\lambda_o)},$$
(2)

where  $\theta$  is the surface coverage of the islands, valued between 0 and 1. SK growth is described by

$$\frac{I_S}{I_o} = (1 - \theta) \times e^{(-q/t)} + \theta \times e^{(-t/\lambda)},$$
(3)

where q is the deposited film thickness prior to the onset of the nucleation or three-dimensional island growth.

The Ga 3d photoelectron attenuation length was calculated to be 1.6 nm using<sup>40</sup>

$$a_M = \left(\frac{A_M}{1000 \times \rho_M \times N}\right)^{1/3},\tag{4}$$

$$\lambda_o = 538 \times E^{-2} + .41 \times (a_M \times E)^{1/2}, \tag{5}$$

where  $A_M$  is the molecular weight of the overlaying film,  $\rho_M$  is the density of the overlying film, N is Avogadro's number, and E is the kinetic energy of the ejected photoelectron. Assuming the surface coverage of the islands and the deposited film thickness to be 0.5 and 0.5 nm, respectively, a plot of the attenuation  $(I/I_o)$  described by the three aforementioned models as well as the experimental data, as shown in Fig. 6, indicates that the growth mode of Pd on CVC treated *p*-GaN is layer by layer.

Changes in the band bending at the surface with subsequent Pd depositions were monitored using the Ga 3d core level. An increase in the downward band bending was observed following the deposition of 0.2 nm of Pd, as indicated by the  $0.2\pm0.1$  eV increase in the Ga 3d peak energy shown in Fig. 2. An identical shift was observed in the position of the N 1s core level and provided further evidence for the interpretation of the observed shifts as changes in band bending rather than chemically induced shifts. Subsequent Pd depositions resulted in a decrease in the downward band bending until a thickness of 2 nm was reached. The shifts observed in the Ga 3d and N 1s core level feature located at  $\sim -12$  eV in the valence band spectra shown in Fig. 7. The correlation between the shifts observed using two



FIG. 6. Attenuation of the Ga 3*d* core level photoelectron peak as a function of the overlying Pd thickness. The experimental  $I/I_o$  data is indicated by the solid diamonds. The dashed, dashed-dotted, and solid lines indicate VW, SK, and FM growth modes, respectively.

separate techniques was a good indication that charging effects were negligible. The final position of the Ga 3d core level indicates a total reduction in the downward band bending of  $0.4\pm0.1$  eV. Therefore, the subsequent reduction in the initial band bending, previously calculated to be  $1.4\pm0.1$  eV, indicates that the final Schottky barrier height and contact potential at the Pd/*p*-GaN interface are  $1.3\pm0.1$  eV and  $1.0\pm0.1$  eV, respectively. A schematic of the proposed



FIG. 7. UPS valence band spectra from the *p*-GaN surface following both CVC and sequential Pd metallization. The Pd induced band bending is indicated by the movement of the core level feature located at  $\sim -12$  eV. All spectra were acquired using the He–I photon line ( $h\nu$ =21.2 eV). The binding energy is measured with respect to the Fermi level ( $E_F$ =0 eV).



FIG. 8. LEED images taken from (a) 20 Å and (b) 500 Å Pd films on CVC p-GaN surfaces. The primary beam energies were (a) 78 eV and (b) 84 eV, respectively.

energy band diagram for the Pd/CVC *p*-GaN contact structure is shown in Fig. 5(b). Alternatively, using the VBM as proposed by Wu *et al.*<sup>34</sup> and Bermudez *et al.*<sup>41</sup> would suggest that the Schottky barrier may be as large as 1.9  $\pm 0.1 \text{ eV}$ . The apparent disagreement with the barrier height predicted by the Schottky–Mott model will be discussed in a later section.

Figures 8(a) and 8(b) reveal LEED patterns from 2 nm and 50 nm thick Pd overlayers, respectively. The  $(1 \times 1)$ hexagonal pattern for both the thin and thick Pd overlayers provided evidence for the epitaxial nature of the film, which is consistent with reported studies of other face-centeredcubic metals on GaN.<sup>43</sup> The patterns clearly indicate that it is the (111) plane which is crystallographically matched to the (0001) oriented *p*-GaN substrate. The pattern from the 50 nm Pd film reveals sharp spots with excellent contrast indicating a well-ordered surface. The spots were considerably more diffuse with a brighter background for the 2 nm Pd film which indicates a less ordered film structure, possibly with smaller grains with a larger distribution in orientation.

#### **IV. DISCUSSION**

Nakamura *et al.*<sup>44</sup> have suggested that annealing *p*-type GaN in an ammonia atmosphere within the temperature range employed in this study will result in hydrogen "compensation" of the Mg acceptors (reformation of Mg–H complexes actually occurs). As the ammonia pressure used in the present work is at least four orders of magnitude smaller than that used in the aforementioned study,<sup>44</sup> the degree to which Mg is again bonded to hydrogen diffusing from the surface should not be significant. King *et al.*<sup>26</sup> provided further evidence for the limited reformation of Mg–H complexes under similar conditions.

There has been considerable disagreement regarding the nature of the native contamination at the surface. Several studies suggest that the  $\sim 2$  nm thick layer is composed of a gallium oxide as well as hydrocarbons and their related oxides.<sup>27,45–48</sup> However, other studies indicate that the native oxide may contain an ordered oxynitride phase.<sup>39,49,50</sup> In this present work, the Ga 3*d* and N 1*s* core level spectra of the as-loaded GaN film indicated the presence of Ga–O and N–O bonding states, as shown by the weak features in the high binding energy regions of the spectra located at  $\sim 21.4$  eV and  $\sim 400$  eV, respectively. The position of each feature is consistent with previously published values for oxygen induced chemical shifts in the Ga 3*d* (Ref. 48) and N 1*s* (Ref.

26) core levels. Although both the Ga–O and N–O bonding states are too weak to be separated from the core level spectra, the reduction in intensity at the high binding energy side of each spectrum following the CVC process suggests the presence of each state. Therefore, the features observed in the as-loaded core level spectra and the changes in these features following the CVC process, indicate the presence of a thin oxynitride phase. A detailed discussion of the material properties of this oxynitride has been presented elsewhere.<sup>39</sup>

Figure 1 indicates that a small amount of O is still detected following the CVC process. The authors of a previous study suggested Mg–O bonding at the surface,<sup>51</sup> which is exceedingly stable even at the  $\sim$ 825 °C temperature used during the cleaning. However, in the present study there was no detectable Mg on either the as-loaded or the CVC treated surfaces making Mg–O bonding very unlikely in the near surface region.

The Fermi level pinning on the as-loaded surface is attributed to a combination of contamination-induced surface states located in the lower portion of the band gap and intrinsic surface states located at or near the VBM.<sup>52,53</sup> In addition to eliminating a large portion of the native surface contamination and corresponding surface states, the CVC process leaves a stoichiometric surface as shown by the resulting Ga:N ratio of 1. The removal of contaminationinduced surface states results in an ~1.3 eV reduction in the downward band bending, as indicated in Fig. 4.

An additional feature, which is labeled  $ss_2$  within the inset to Fig. 4, appears to be emission from a broad band of partially filled surface states located in the lower portion of the band gap. Prior to attributing this emission to a new band of surface states, several experimental artifacts were individually considered and then eliminated as a possible emission source. A previous study<sup>41</sup> attributed this weak emission to the Ga 3d electrons excited by the He–II  $\alpha$  (40.81 eV) line. However, the Ga 3d core level was previously found to have a binding energy of  $19.5\pm0.1\,\text{eV}$ , which would center the He–II  $\alpha$  emission at approximately  $E_f$  in the He–I spectrum. Therefore, this additional feature centered at  $\sim 1 \text{ eV}$ below the Fermi level is not consistent with He–II Ga 3demission. The possibility that this feature is a satellite peak due to the He–I  $\beta$  (23.09 eV) line was also considered. Although the satellite peak from the large feature located at  $\sim 3$ eV would lie in the region where surface state emission is being considered, the relative intensity of the  $ss_2$  emission is approximately twice as intense as that which could be attributed solely to the He–I  $\beta$  line. The precise origin of these new surface states located in the lower portion of the band gap requires further study.

The Pd/*p*-GaN interface appears to be abrupt and unreacted as evidenced by the constant FWHM of the Ga 3*d* core level spectra shown in Fig. 2. This is consistent with the results of previous studies in the literature,<sup>54</sup> which indicated a Pd–Ga phase only after prolonged annealing at temperatures greater than 800 °C. There have been no reports of a Pd–N or Pd–Ga–N phase within the temperature range considered in this study. The upward movement of  $E_f$  and the corresponding increase in band bending following the initial deposition of 0.2 nm Pd may be attributed to a complex interaction between the existing surface states on the clean surface and the metal induced gap states, which arise as a result of the Pd deposition. The downward movement of  $E_f$ and the subsequent decrease in band bending with further Pd deposition is consistent with both the large work function of Pd ( $\Phi$ =5.6 eV)<sup>55</sup> and the observed onset of strong Fermi level emission in the UPS spectra shown in Fig. 7, that occurred at a total Pd thickness of 0.3 nm.

We consider now the barrier predicted from the Schottky–Mott model using the electron affinity obtained in this study and Eq. (1), which is consistent with the Schottky–Mott model. Substitution of the values of the GaN band gap ( $E_g$ ) at room temperature, the Pd work function ( $\Phi_{Pd}$ ), and the electron affinity of 3.4 eV, 5.6 eV, and 3.1 eV, respectively, into Eq. (6) results in a calculated value of the Schottky barrier of 0.9 eV

$$\Phi_{Bp} = E_G - \Phi_{Pd} + \chi_{GaN}. \tag{6}$$

The fact that this value is significantly smaller than that observed in the described experiment above suggests that there is an additional interface dipole contribution to the Schottky barrier, which results in the added  $0.4\pm0.1$  eV to the barrier height. It is important to note that if the VBM of Wu *et al.*<sup>34</sup> and Bermudez *et al.*<sup>41</sup> were used, a similar result would be obtained, since both the measured Schottky barrier and the electron affinity would be increased. The interface dipole term arises as a result of the complicated interaction between extrinsic and intrinsic surface states as well as the contribution from metal induced gap states.

#### V. SUMMARY

A NH<sub>3</sub>-based CVC process was used to obtain a stoichiometric *p*-GaN surface without detectable C and a significantly reduced O concentration. A significant reduction in the downward band bending and a corresponding downward movement of the Fermi level was observed at the cleaned surface. This resulted from the removal of contaminationinduced surface states located in the lower portion of the band gap. The downward band bending at the clean surface may be attributed to (a) intrinsic surface states, which include a band of previously unidentified surface states centered at approximately 1.0 eV below the Fermi level, as well as (b) the effects of extrinsic surface states.

The epitaxially deposited Pd film was observed to grow in a layer-by-layer mode. The difference between the measured Schottky barrier height  $(1.3\pm0.1 \text{ eV})$  at the Pd/*p*-GaN interface and that predicted by the Schottky–Mott model (0.9 eV), is attributed to an additional interface dipole term (0.4  $\pm0.1 \text{ eV}$ ), which arises as a result of the complex interaction between the aforementioned states on the cleaned *p*-GaN surface and the metal induced gap states placed in the band gap by the Pd overlayer. An alternate interpretation of the band structure at the clean surface, which identifies an additional band of surface states located at the VBM and places  $E_f$  at an even greater distance from the VBM, would result in a larger Schottky barrier height  $(1.9\pm0.1 \text{ eV})$ .

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