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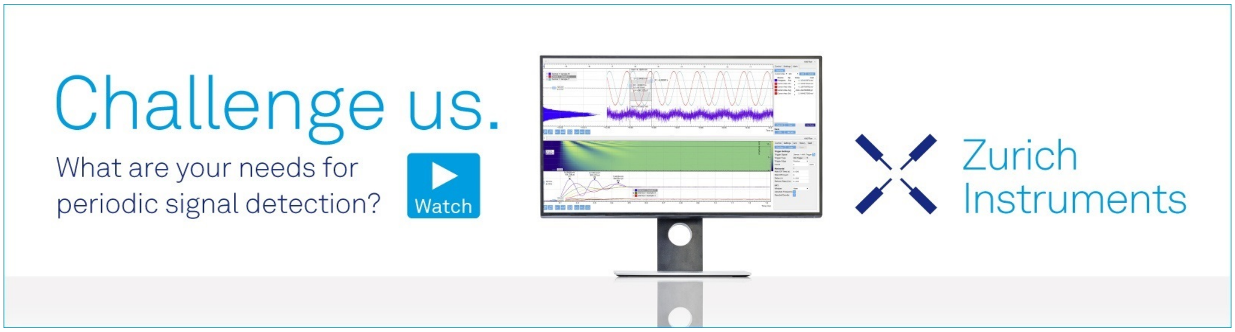

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Preparation and characterization of atomically clean, stoichiometric surfaces of *n*- and *p*-type GaN(0001)

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It is demonstrated that *in situ* exposure of the (0001) surface of *n*- and *p*-type GaN thin films to flowing ammonia at 860 °C and 10^{-4} Torr removes hydrocarbon and oxygen/hydroxide species below the detectable limits of x-ray and ultraviolet photoelectron spectroscopies (UPS) and decreases the Ga/N ratio from 1.3 to 1.0. Additional indications of the efficacy of this ammonia-based chemical vapor cleaning (CVC) process were the shifts in the Ga 3*d* and the N 1*s* core level positions from the as-loaded to the CVC surfaces of the *n*-type samples from 21.0±0.1 to 20.6±0.1 eV and from 398.3±0.1 to 398.0±0.1 eV, respectively, and the change in the UPS measured low energy spectrum turn on from 3.9±0.1 (as-loaded samples) to 3.0±0.1 eV (cleaned samples) below the Fermi level. Analogous changes in the *p*-type samples were from 19.6±0.1 to 18.9±0.1 eV and from 397.1±0.1 to 396.3±0.1 eV for the Ga 3*d* and the N 1*s* core levels, and from 3.0±0.1 to 1.1±0.1 eV for the UPS valence band maximum (VBM). The VBM values of the CVC samples indicate band bending of ~0.3 eV upward on *n* type and ~0.8 eV downward on *p* type. Electron affinities of 2.8±0.1 and 2.6±0.1 eV were determined for the clean *n*-type and *p*-type surfaces, respectively. Irrespective of doping, the CVC process left unchanged the (1×1) low energy diffraction pattern, the terraced microstructure, and the root mean square roughness observed for the surfaces of the as-loaded samples, i.e., the surface microstructure was not damaged during the high temperature exposure to ammonia at low pressure.
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I. INTRODUCTION

The group III nitrides of GaN, AlN, and InN and their related alloys have become the materials of choice for short-wavelength photonic devices for display and data-storage applications and UV detectors. These materials are also chemically inert and exhibit high avalanche breakdown fields and large high-field electron drift velocities, making them ideal for use in high-power and high-frequency applications.

At present, most devices are manufactured from GaN-based heterostructures grown on sapphire or silicon carbide substrates. However, selected GaN wafer technologies, e.g., those derived via laser liftoff of thick films grown on sapphire substrates[1] have advanced to commercial reality. Extensive processing of these wafers leaves the surfaces contaminated with hydroxides, hydrocarbons, and other chemical species. Experience gained from silicon and gallium arsenide technologies has shown that the surface chemistry of the wafers greatly affects device performance. Effectively cleaning the wafers significantly reduces the concentrations of point, line, and two-dimensional defects that affect in uncontrollable ways the electrical properties of films and device structures deposited on these substrates. These effects include increased resistance of ohmic contacts, increased leakage currents at Schottky barriers and *p*–*n* junctions, reduced dielectric breakdown, and reduced threshold voltages. As such, removal of surface contaminants has been and remains a subject of considerable research in the well-established semiconductor industries.

In addition to the surface chemistry, the electronic structure of a film surface and the surface microstructure are also important considerations when reviewing a cleaning process. The electronic structure is important when predicting device properties such as heterojunction band offsets or Schottky barriers. The relevant electronic features are the position of the valence band maximum (VBM), the band bending, and the electron affinity. These aspects are primarily investigated using a surface sensitive photoemission technique such as ultraviolet photoelectron spectroscopy (UPS) to investigate the valence band spectrum. It is also important that the surface microstructure be undamaged by the cleaning process to ensure that high quality epitaxial layers can be grown on the substrates. The surface microstructure is investigated through the use of *in situ* techniques such as low energy electron diffraction (LEED) or reflection high energy electron diffraction (RHEED), as well as through *ex situ* techniques such as atomic force microscopy (AFM).

Smith *et al.*[2] and Prabhakaran *et al.*[3] have reported that as-grown GaN films removed from vacuum acquire a contamination layer that contains oxygen and carbon. Thus, de-

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velopment of a technique to remove those contaminants, while preserving the as-grown electronic structure and microstructure, is important to the continued improvement of III nitride devices and commercialization of them. Previous *ex situ* and *in situ* studies devoted to the cleaning of GaN surfaces have achieved varying levels of success and are reviewed in the following paragraphs.

Ex situ cleaning of GaN grown by both metalorganic vapor phase epitaxy (MOVPE) and gas source molecular beam epitaxy (GSMBE) was investigated using HCl, HF, ultraviolet/ozone (UV/O_3), BHF, BHF vapor, NH_4OH, $NH_4OH{:}H_2O_2$, NH_4F, $H_2SO_4{:}H_2O_2{:}DI$, H_3PO_4, RCA SC1, and RCA SC2 chemistries.[2,4–6] Reductions in the concentrations of carbon and oxygen were observed; however, no wet chemical treatment produced a surface free of either of these contaminants, as was determined by subsequent *in situ* x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) investigations. It was found that HCl-based techniques produced the lowest oxygen and carbon coverages.[4] Lee *et al.*[6] reported that ultraviolet light/ozone exposure removed carbon from the surface, but with a concurrent increase in oxygen concentration on the surface. While most *ex situ* processes did not affect the surface morphology, exposure to H_3PO_4 increased the surface root mean square (rms) roughness as measured by AFM.[4]

In situ cleaning studies of vacuum annealing have been undertaken by several authors. King *et al.*[4] and Smith *et al.*[2] found that *ex situ* HF processing and subsequent thermal annealing of the GaN(0001) surfaces resulted in the most efficient removal of contamination, however, complete desorption of contaminants was only obtained at 950 °C. The former group presented temperature programmed desorption results that indicated that Ga evaporation begins to occur above ~800 °C when heating in vacuum. When they annealed both MOVPE- and GSMBE-grown GaN films in 5×10^{-6} Torr of ammonia at 800 °C, they found complete removal of carbon, reduction of oxygen to ~1/10 of a monolayer, and LEED patterns that showed (2×2) reconstruction. Similarly, Machuca *et al.*[7] combined an *ex situ* dip in 4:1 $H_2SO_4{:}H_2O_2$ with an *in situ* vacuum anneal at 700 °C to clean 0.1 μm thick *p*-type GaN films grown by molecular beam epitaxy (MBE) on AlN buffer layers on *c*-axis sapphire. The authors reported carbon and oxygen contamination was reduced to a few percent of a monolayer. Further investigation of *in situ* vacuum annealing was undertaken by Lee *et al.*[6] After capping the cleaned surface with ~1000 Å of GaN, AES and secondary ion mass spectroscopy were used to analyze the resulting interface. The authors found that thermal cleaning at 900 °C was insufficient to remove contamination from GaN surfaces, and that surface roughness was unaffected by the cleaning process.

Additional studies have examined *in situ* treatment of GaN films with reactive ion plasmas. Plasmas of Ar,[8–10] Xe,[8] and Ne (Ref. 9) have been found to be ineffective in completely removing contamination from GaN(0001) surfaces grown by various methods. Furthermore, it was reported[9] that both Ar and Ne ions generated surfaces that were gallium rich after the ion bombardment process. This excess gallium on the surface after the ion treatment then formed metallic Ga clusters when annealed at temperatures above 350 °C.

By contrast, it has been reported[8,9] that sputtering with N_2^+ ions resulted in a much smaller decrease in nitrogen concentration. Both groups also found that subsequent annealing in this reactive atmosphere produced a N/Ga ratio that approached unity. When compared with surfaces sputtered by Ar^+, Hunt *et al.*[8] observed improved (1×1) RHEED patterns and Lai *et al.*[9] observed improved (1×1) LEED patterns. It was proposed by Lai *et al.*[9] that N_2^+ or N^+ reacts with free Ga at the surface and reforms GaN, and that N_2 in the background adsorbs on the surface during sputtering and is activated and reacts with the surface by ion bombardment. Lee *et al.*[6] reported similar results that showed removal within the detection limits of AES of carbon and oxygen contamination after *in situ* exposure to N_2 plasma at 750 or 900 °C or to H_2/N_2 plasma at 750 °C.

Several researchers have reported[11–14] using nitrogen sputter and anneal techniques to produce GaN(0001) films that are free of oxygen and carbon contamination. Bellitto *et al.*[11] used N_2 ion sputtering with subsequent vacuum annealing to prepare GaN(0001) that had been grown on *a*-plane sapphire. They found (1×1) LEED images that showed evidence of faceting, indicating surface damage.

Wu and Kahn[12] investigated nitrogen sputtering (10 min at 500 eV) and annealing at 900 °C for 10 min on both *n*(Si-doped)- and *p*(Mg doped)-GaN films grown via MOVPE techniques on SiC substrates. The sputter and anneal technique produced nearly stoichiometric surfaces with ordered (1×1) LEED images, and with ~0.75 eV band bending, upward on *n*-type and downward on *p*-type films. Dhesi *et al.*[13] have used nitrogen ion sputtering and subsequent 900 °C anneals to prepare clean surfaces for angle resolved photoemission studies of the valence band structure of GaN surfaces. Their studies showed upward band bending of ~0.9 eV, as well as a nondispersive feature near the VBM which they attributed to a surface state. A similar feature was predicted in theoretical calculations by Rapcewicz *et al.*[15] that appears to be related to a filled dangling bond state for a nitrogen surface atom which is not bonded to an adsorbed hydrogen atom. Surface states were also observed by Plucinski *et al.*[16] and by Chao *et al.*[17] using valence band spectroscopy.

Much theoretical and experimental work has been conducted on the surface reconstructions expected for GaN grown by MBE techniques. Papers by Smith *et al.*[18] and by Feenstra *et al.*[19] provide excellent reviews of experimentally observed reconstructions using LEED and RHEED and expected surface structures for both bare GaN surfaces as well as adsorbate covered surfaces. The surfaces investigated by these authors were grown and transferred for analysis completely *in situ*, and, therefore, represent the as-grown MBE films. Smith *et al.* found (1×1) patterns for *N*-polar (0001) surfaces, whereas (0001) GaN surfaces showed (1×1) reconstruction with satellite lines just outside the integral order lines.[18] Theoretical calculations by both groups[18,19] indicate that an adsorbate free and ideally terminated (1×1) surface is unstable for GaN. The (1×1) reconstruction can be stabilized by surface adsorbates, by vacancies, or by faceting. It was concluded that the MBE grown (1×1) surface is stabilized by a layer of adsorbed Ga resulting from the growth process.[19]

For GaN prepared by metalorganic techniques, there are fewer studies, experimental or theoretical, regarding the surface structure. Munkholm *et al.*[20] studied GaN *in situ* in an MOVPE reactor using grazing incidence x-ray scattering. They reported (1×1) and $(\sqrt{3}\times 2\sqrt{3})R30°$ reconstructions. Based on the theoretical work of Smith *et al.*[18] and of Feenstra *et al.*,[19] it is likely that the (1×1) surface is stabilized by adsorbates that remain after the MOVPE growth process.

As an alternative to reactive ion processing, other researchers have utilized deposition and subsequent desorption of Ga metal to clean GaN(0001) films. Using 3.5 μm thick MOVPE GaN(0001) films grown in a MBE system, Khan *et al.*[21] cleaned the films by annealing at 600–900 °C in a Ga flux or by sequentially depositing several monolayers of Ga at room temperature and flashing the metal from the surface at 900 °C. *In situ* AES studies showed the oxygen signal to be near the limit of sensitivity and 2% of the nitrogen signal. These surfaces also showed (1×1) LEED patterns. Similar results were obtained by Maffeis *et al.*[22] who used soft XPS to study Ga deposition and vacuum desorption cleaning of GaN grown on sapphire by MBE.

Bermudez[14] has compared the cleaning efficacy of a Ga deposition and desorption technique with a N_2^+ ion sputter process followed by a vacuum anneal at 900 °C on surfaces of GaN grown by MOVPE on *a*-plane and *c*-plane sapphire.[23] Bermudez[14] reported the techniques to be equivalent, with both producing oxygen free surfaces, sharp (1×1) LEED patterns, and ~0.9 eV of upward band bending.[14] Bermudez *et al.*[24] subsequently investigated cleaning GaN via (1) vacuum annealing at temperatures from 200 to 1000 °C, (2) dosing the surface with $1.4\times10^{18}\,NH_3\,cm^{-2}$ during annealing between 750 and 900 °C, (3) Ga deposition, and (4) N_2^+ sputter/anneal process routes. The ultrahigh vacuum (UHV) annealing and ammonia flux techniques were not effective in cleaning, but annealing an ion-bombarded surface in ammonia impeded the formation of N vacancies that can occur when heating in vacuum. Additionally, the annealing temperature affected surface band bending by up to 0.7 eV over the range of 300–700 °C.[24]

Bermudez and his colleagues have investigated contamination and the effects on electronic structure by studying the adsorption of oxygen,[14] hydrogen,[24] ammonia,[25] H_2O,[26] and XeF_2 (Ref. 27) on GaN surfaces. In each study, the presence of adsorbate molecules removed surface states from the valence band spectra. This was observed by examining spectra obtained from UPS and electron loss spectroscopy (ELS) before and after exposure to the adsorbates. Band bending was affected differently by different adsorbates, with oxygen reducing band bending by ~0.5 eV,[14] ammonia leaving the band bending unchanged,[25] H_2O reducing the band bending only by ~0.14 eV,[26] and F chemisorbed from XeF_2 reducing the band bending by ~0.6 eV.[27] The effects of H adsorption on band bending were not reported.[24]

In the following we present results, discussion, and a summary of several integrated investigations with the overall objective being the removal of oxygen/hydroxide and hydrocarbon contaminants from *n*(Si-doped)- and *p*(Mg doped)-type GaN(0001) surfaces to below the detection limits of XPS, AES and UPS without measurable changes in the structure or the microstructure of the surface, as determined by LEED and AFM.

II. EXPERIMENTAL PROCEDURES

The 1 μm thick, *n*-type (Si-doped; $N_d=2.0\times10^{17}$ from van der Pauw measurements) and *p*-type (Mg-doped; $N_a-N_d=3\times10^{18}$ from $C-V$ measurements) epitaxial GaN thin films used in this research were grown via MOVPE on 0.1 μm thick AlN(0001) buffer layers previously deposited on 50 mm diam, on-axis $6H$-SiC(0001) substrates. Tungsten was sputtered onto the backs of the SiC wafers to allow radiant heating of the transparent samples in the vacuum system. The wafers were then diced into ~15 mm squares; sequentially degreased in ultrasonic baths containing trichloroethylene (TCE), acetone, and methanol for 10 min in each solvent; dried in flowing nitrogen and stored in Teflon™-based containers. Prior to *in situ* processing, the samples were immersed in TCE, acetone, and methanol for 1 min in each solvent; in 37% hydrochloric acid (HCl) for 10 min and in de-ionized water for 10 s. Within 20 min of the last cleaning procedure, the samples were fastened to molybdenum holders using tantalum wires and placed into a load lock that was evacuated to $<5\times10^{-8}$ Torr. They were subsequently transferred into the UHV system for *in situ* analysis and processing.

The GaN(0001) surfaces were cleaned in a GSMBE chamber with a base pressure of 7×10^{-10} Torr. The thermal output of a coiled wire resistive heater placed in close proximity to the sample was controlled by a thermocouple located in the center of the heater. The surface temperature of the sample was directly measurable above 600 °C using an Ircon infrared (IR) thermometer with an emissivity setting of 0.5. Lower temperatures were determined using the thermocouple.

The *in situ* chemical vapor cleaning (CVC) process involved annealing each sample in ammonia that was introduced via a leak valve into the GSMBE when the thermocouple temperature reached 500 °C. The chamber was maintained at an ammonia pressure of $1.0\pm0.1\times10^{-4}$ Torr during the CVC process. Once the pressure was stabilized, the sample temperature was increased to 865 °C at a rate of 30 °C/min, held for 15 min, decreased at a rate of 40 °C/min to 500 °C, held at this temperature for 1 min during which the ammonia leak valve was closed, and further decreased until the thermocouple indicated <200 °C. The system pressure was then decreased to $<2.5\times10^{-8}$ Torr at which point the sample was transferred to an analysis chamber.

The GSMBE chamber was connected to other chambers via a ~14 m long UHV transfer line. *In situ* surface analysis capabilities included XPS, UPS, and LEED instruments located in separate chambers connected by the transfer line. The base pressure of each chamber was $<3\times10^{-10}$ Torr, and the pressure of the transfer line was typically $\sim8\times10^{-10}$ Torr.

A Fisons Clam II hemispheric analyzer with a mean radius of 100 mm was used to collect the XPS spectra. The resolution of the analyzer was determined from the full width half maximum (FWHM) of a gold $4f_{7/2}$ spectral peak to be approximately 1.0 eV; however, through curve fitting, spectral peak positions (centers) could be resolved to ±0.1 eV. The settings for the x-ray source were 5 A filament current, 20 mA emission current, 13 kV accelerating voltage and 3.0 kV channeltron voltage. Survey scans and core level spectra were collected using pass energies of 50 and 20 eV, respectively. The linear background was subtracted from the core level spectra, and the resulting spectra were fitted with a mix of Gaussian–Lorentzian functions, discussed by Briggs and Seah.[28] While fitting of the background could lead to improved accuracy, particularly for line shape analysis, subtraction of the linear background was considered sufficient for peak positions and linewidths within our specified 0.1 eV uncertainty.

Spectra were collected from the as-loaded surfaces and the CVC surfaces for the Ga $3d$, N $1s$, O $1s$, C $1s$, as well as survey regions using both magnesium (1253.6 eV) and aluminum (1486.6 eV) anodes. Survey scans with both anodes were required due to the overlap of Auger and photoemission transitions. When the Mg anode is used, the Ga LMM lines mask the C $1s$ signal, making it difficult to deconvolute the carbon from the Ga Auger series. When the Al anode is used, the N $1s$ core level is masked by the Ga Auger transition lines.

Ultraviolet photoelectron spectra were obtained with the analyzer entrance at normal incidence with the sample surface. An Omicron HIS13 discharge lamp was employed to generate a maximum amount of He I (21.2 eV) radiation and minimize the amount of He II (40.8 eV) radiation. The lamp voltage and discharge current were set to 520 V and 50 mA, respectively. The electron multiplier was set to 2.6 kV, and a pass energy of 10 eV was used. A negative 4 V bias was applied to the sample to overcome the work function of the analyzer. The resolution of the 50 mm hemispheric analyzer was approximately 0.1 eV. The system was set to scan kinetic energies from 0 to 24 eV, which includes the valence band region of GaN.

Low energy electron diffraction images were obtained using an extraction current of 0.4 mA, a screen voltage of 4 kV and a gun voltage of approximately 80 eV. Photographs of the different patterns were acquired using a Kodak DS-120 digital camera.

Atomic force microscopy was performed using a Park Scientific Instruments autoprobe M5 system. The scans were acquired over a $2\ \mu\mathrm{m}\times 2\ \mu\mathrm{m}$ region using a probe with a silicon tip.

III. RESULTS

The XPS survey spectra acquired from the as-loaded and the CVC n-GaN surfaces for the 1100–0 eV binding energy region are shown in Figs. 1(a)–1(d). Both XPS and Auger features are identified. Figure 1(a), obtained from the as-loaded sample using the magnesium anode, shows the Auger transitions for an as-loaded sample for carbon KVV at a binding energy of 1000 eV, nitrogen KLL at 875 eV, oxygen KLL at 750 eV, and gallium LMM transitions over the range of 150–364 eV. Core level transitions are also shown in this spectrum, including that of oxygen $1s$ at a binding energy of ~530 eV, nitrogen $1s$ at ~400 eV, gallium $3p$ at ~105 eV, and gallium $3d$ at ~20 eV. In contrast, the spectrum of the GaN surface acquired after the CVC presented in Fig. 1(b) shows only the nitrogen $1s$, gallium $3p$, and gallium $3d$ core levels; carbon and oxygen Auger transitions and a core level signal from oxygen were not detected. Similar behavior is observed in analogous spectra [Figs. 1(c) and 1(d)] obtained using the aluminum anode. When the aluminum anode was used, the nitrogen KLL Auger signal has shifted beyond the range of Fig. 1, and the N $1s$ core level signal is obscured by the Ga LMM Auger transitions. For the as-loaded surface, Fig. 1(c), the oxygen KLL Auger transitions were observed at a binding energy of 980 eV and those of the gallium LMM were acquired over the range of 390–590 eV; core level signals were observed from carbon $1s$ at ~285 eV, gallium $3s$ at ~160 eV, gallium $3p$ at ~105 eV, and gallium $3d$ at ~20 eV. As before, the survey scan acquired following CVC revealed no detectable signals for carbon or oxygen. Similar results were obtained for the p-type GaN surfaces (not shown).

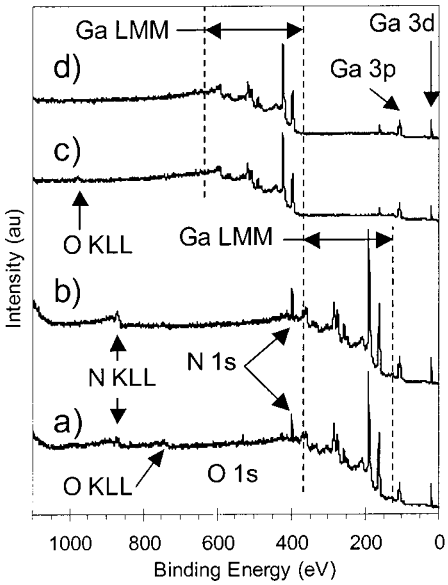

FIG. 1. (a) XPS spectra of as-loaded n-GaN(0001) and (b) CVC n-GaN(0001) surfaces obtained using Mg K_α x-rays ($h\nu=1253.6$ eV). Analogous spectra acquired using Al K_α x-rays ($h\nu=1486.6$ eV) of (c) as-loaded n-GaN(0001) and (d) CVC n-GaN(0001).

Figures 2(a) and 2(b) contain plots of the gallium $3d$ and the nitrogen $1s$ core level spectra, respectively, acquired using the magnesium anode for as-loaded and cleaned n-type GaN(0001) surfaces [spectra (i) and (ii) in Figs. 2(a) and 2(b)]. The positions of the peaks of the gallium $3d$ core level spectra shown in Fig. 2(a) for the as-loaded and CVC surfaces were 21.0 ± 0.1 eV (FWHM$=1.3\pm0.1$ eV) and 20.6 ±0.1 eV (FWHM$=1.3\pm0.1$ eV), respectively. Similar results were observed for the spectra obtained using the aluminum anode. The nitrogen $1s$ peaks for the as-loaded and CVC surfaces were centered at 398.3 ± 0.1 eV (FWHM

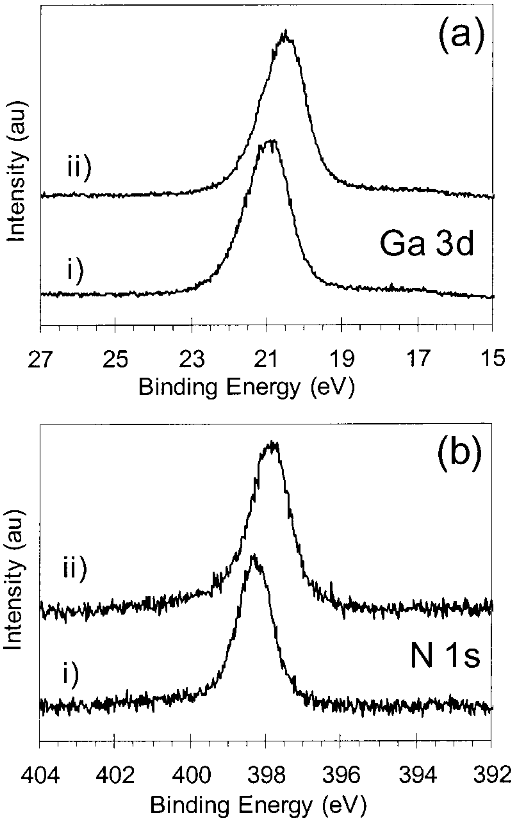

FIG. 2. Core level XPS spectra of (a) gallium 3*d* and (b) nitrogen 1*s* for as-loaded GaN(0001) [spectrum (i) in (a) and (b)] and CVC GaN(0001) [spectrum (ii) in (a) and (b)] surfaces. The spectra were obtained using Mg K_α x-rays. The spectra were offset vertically for ease in viewing.

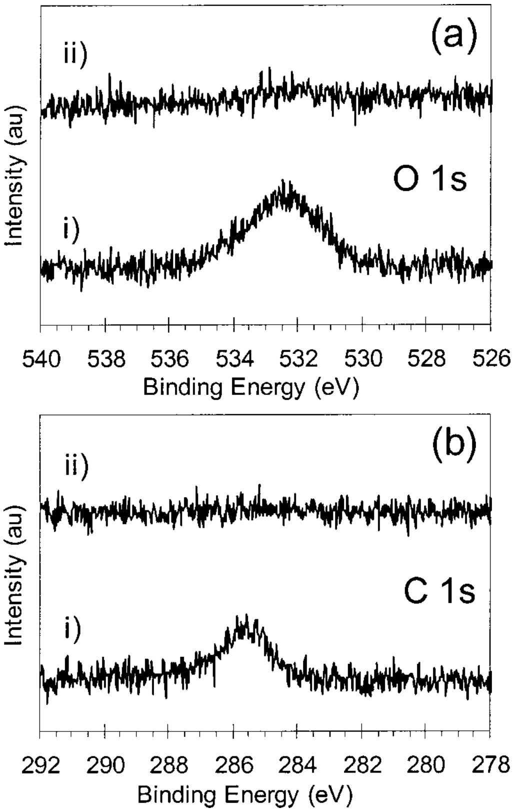

FIG. 3. Core level spectra of (a) oxygen 1*s* (acquired using Mg K_α x-rays) and (b) carbon 1*s* (acquired using Al K_α x-rays) for as-loaded GaN(0001) [spectrum (i) in (a) and (b)] and CVC GaN(0001) [spectrum (ii) in (a) and (b)] surfaces.

=1.0±0.1 eV) and 398.0±0.1 eV (FWHM=1.2±0.1 eV), as shown in Fig. 2(b). For the *p*-type GaN surfaces, the core level peaks (not shown) showed similar behavior, with the position of the Ga 3*d* core level spectra observed at 19.6 ±0.1 eV (FWHM=1.6±0.1 eV) in the as-loaded samples and at 18.9±0.1 eV (FWHM=1.6±0.1 eV) after CVC. The nitrogen 1*s* peak position was observed at 397.1±0.1 eV (FWHM=1.3±0.1 eV) from the as-loaded surface and at 396.3±0.1 eV (FWHM=1.4±0.1 eV) from the CVC surface.

The oxygen 1*s* and the carbon 1*s* core level spectra obtained using the magnesium and the aluminum anodes, respectively, are shown in Figs. 3(a) and 3(b). The peak of the oxygen 1*s* spectrum for the as-loaded surface is centered at 532.2±0.1 eV (FWHM=3.0±0.1 eV); this peak was not detected after CVC, as shown in Fig. 3(a). The carbon 1*s* core level peak shown in Fig. 3(b) is centered at 285.1±0.1 eV (FWHM=1.6±0.1 eV); this signal was also not detected after the *in situ* cleaning step in ammonia atmosphere. The position of the carbon peak is in very good agreement with that of adventitious carbon; thus, sample charging was not a problem on the as-loaded surface.[29] Carbon 1*s* and oxygen 1*s* signals were similarly detected from the as-loaded *p*-type GaN film, with positions of 284.8±0.1 eV (FWHM=1.6 ±0.1 eV) and 531.9±0.1 eV (FWHM=2.7±0.1 eV), respectively.

It was reported by Cheng *et al.*[30] and by Ptak *et al.*[31] that Mg dopant can accumulate on the surface of GaN films during MBE growth processes. When analyzing the Mg-doped, MOVPE grown samples in this study, the Mg 2*p* core level spectral region was scanned using XPS. No evidence of Mg was detected on either the as-loaded or the CVC surfaces. Table I contains a summary of the peak positions observed and the FWHMs of the XPS spectra.

Figures 4(a) and 4(b) show the full width of the valence band spectra of the Si-doped GaN films and expansion of the region around the VBM, respectively, acquired via UPS of surfaces of the as-loaded GaN and the CVC GaN samples. All spectra are plotted on a binding energy scale with zero energy corresponding to the Fermi level (E_F), which had previously been determined from emission spectra from an *in situ* deposited gold surface. The main features in the as-loaded UPS spectrum in Fig. 4(a) are the high energy turn on, beginning at ~4 eV, a feature at 14.1±0.1 eV, and the secondary electron peak at 15.9±0.1 eV. The linear portions of the UPS energy turn on were fitted, represented by dashed lines in Fig. 4(b), and extrapolated to the abscissa to determine the position of the VBM. For the as-loaded spectrum, the VBM was fitted so as to be 3.9±0.1 eV below the Fermi level [see spectrum (i) in Fig. 4(b)]. *In situ* cleaning of the *n*-type GaN surface in ammonia caused changes in the position and shape of the VBM, with the turn on now determined to be 3.0±0.1 eV below the Fermi level [see spectrum (ii) in Fig. 4(b)]. The secondary electron peak was again located at 15.9±0.1 eV, but the feature on the shoulder of this peak was located at 13.5±0.1 eV after CVC. Both peaks are markedly

TABLE I. XPS results for the as-loaded and CVC GaN(0001) surfaces.

	n type (Si doped)				*p* type (Mg doped)			
	As loaded (±0.1 eV)		After CVC (±0.1 eV)		As loaded (±0.1 eV)		After CVC (±0.1 eV)	
	Center	FWHM	Center	FWHM	Center	FWHM	Center	FWHM
Oxygen 1*s*	532.2	3.0	⋯	⋯	531.9	2.7	⋯	⋯
Carbon 1*s*	285.1	1.6	⋯	⋯	284.8	1.6	⋯	⋯
Nitrogen 1*s*	398.3	1.0	398.0	1.2	397.1	1.3	396.3	1.4
Gallium 3*d*	21.0	1.3	20.6	1.3	19.6	1.6	18.9	1.6

more defined than those for the as-loaded surface. Again, similar results were obtained from *p*-doped GaN surfaces, with a shift present due to the different Fermi level position in the band gap. For *p*-type GaN, the VBM were determined to be 3.0±0.1 and 1.1±0.1 eV below the Fermi level after loading and after CVC, respectively. Table II contains the UPS spectral features for the as-loaded and the CVC *n*- and *p*-type GaN (0001) surfaces.

The LEED patterns obtained for the as-loaded and CVC *n*-type GaN surfaces are shown in Figs. 5(a) and 5(b), respectively. The spots in the 1×1 hexagonal pattern obtained from the as-loaded sample are broad and diffuse with a bright background and are indicative of a disordered and/or contaminated surface. By contrast, a well-defined LEED pattern with sharp spots on a dark background was obtained from the cleaned *n*-type GaN. The LEED pattern was observed at beam energies of 60–195 eV. This beam energy was sufficient to observe up to third order spots, and the pattern remained sharp over the whole range of energy. These results are consistent with an unfaceted, flat surface. Similar results (not shown) were obtained from a *p*-type GaN(0001) sample.

AFM micrographs for the as-loaded and *in situ* cleaned *n*-type GaN surfaces are shown in Figs. 6(a) and 6(b), respectively. The rms roughnesses of these respective surfaces were determined to be 0.69 and 0.61 nm, respectively. Similar microstructural results were obtained from the surfaces of the *p*-type samples.

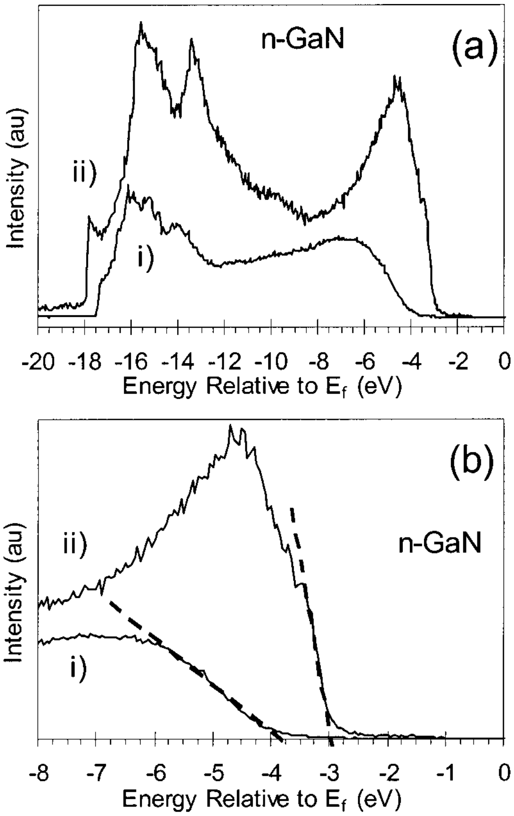

FIG. 4. UPS spectra showing (a) the full width of the valence band spectra and (b) an expanded view of the VBM region for as-loaded *n*-GaN [spectrum (i) in (a) and (b)] and CVC *n*-GaN surfaces [spectrum (ii) in (a) and (b)]. The dashed lines in (b) represent the fits used to determine the positions of the valence band maximum of the surfaces. All spectra were obtained using He I ($h\upsilon = 21.2$ eV) radiation.

IV. DISCUSSION

A. Surface chemistry

Since the majority of the results reported in the literature for GaN(0001) have been presented for *n*-type samples, the following discussion is conducted for *n*-type samples, unless noted otherwise. The Ga 3*d* core level peak positions measured in the current study agree well with those of previous investigators. Our measured as-loaded position of 21±0.1 eV matches the reported positions of 21.2 (Ref. 3) 21.0 and 20.8 eV (Ref. 4) from as-loaded surfaces, and our value of 20.6±0.1 eV from the CVC surface is in agreement with the reported range of 19.6–20.7 eV.[10]

The N 1*s* core level peak measured on the as-loaded surface in the current study was located at 398.3±0.1 eV. This is similar to the value of 398.2 eV for nitrogen on an as-loaded surface reported by both Prabhakaran *et al.*[3] and King *et al.*[4] After the CVC process, the N 1*s* core level was located at 398.0±0.1 eV, close to the value of 397.4 eV obtained by Prabhakaran *et al.*[3] The magnitude and direction of the shift of the N 1*s* core level are identical to those of the Ga 3*d* core level, indicating that the shift is related to a change in band bending.

The gallium-to-nitrogen ratio for the as-loaded surface, determined by the ratio of the Ga 3*d* to N 1*s* core level integrated peak areas and appropriate elemental sensitivity factors,[28,29] was approximately 1.3, indicating a gallium rich (or N-deficient) surface. It is believed that a fraction of the nitrogen atoms on the surface were replaced by adsorbed oxygen and/or OH$^-$ radicals. After cleaning, the gallium-to-

TABLE II. UPS based results for the as-loaded and CVC GaN(0001) surfaces. The electron affinities for the as-loaded samples are not reported due to uncertainties in the band gap energy of the contaminated surfaces and in the as-loaded VBM positions.

	n type (Si doped)		*p* type (Mg doped)	
	As loaded (eV below E_F)	After CVC (eV below E_F)	As loaded (eV below E_F)	After CVC (eV below E_F)
Turn on (VBM) (±0.1)	3.9	3.0	3.0	1.1
Shoulder peak (±0.1)	14.1	13.5	12.9	11.6
Cutoff (±0.1)	17.5	18.0	17.0	16.3
Width (±0.2)	13.4	15.0	14.0	15.2
χ (±0.2)		2.8		2.6

nitrogen ratio decreased to 1.0, indicative of a stoichiometric surface. While the photoelectron attenuation lengths of Ga and N make XPS somewhat less sensitive to surface stoichiometry, we submit the result here as an indication that the stoichiometry of the material is improved by the CVC process.

Bermudez[25] has reported that ammonia chemisorbs dissociatively on GaN(0001), yielding NH_2 and H species bonded to the surface. Given this fact, it is proposed that (1) carbon and oxygen are removed by surface reaction with ammonia and/or ammonia fragments and atomic H and (2) atomic nitrogen from the ammonia and/or an ammonia fragment replaces the contamination and results in a stoichiometric GaN surface.

Similar results were obtained for *p*-type GaN surfaces. The shift in the Ga 3*d* and N 1*s* core levels was observed to be 0.7±0.1 and 0.8±0.1 eV, respectively. As with the *n*-type surface, this shift is attributed to a change in band bending caused by removal of the carbon and oxygen contamination from the surface. The XPS measured stoichiometry of the *p*-type surfaces changed from 1.2 for the as-loaded surface to 0.9 for the CVC surface. These results are similar to those found by Hartlieb *et al.*[32] for CVC treated *p*-type GaN which retained 2±1% oxygen on the surface. The presence of excess ammonia or ammonia fragments on the surface could cause the nitrogen rich conditions observed in the current work.

B. Electronic structure

The bulk Fermi level of the *n*-type GaN samples was calculated to be 0.1 eV below the conduction band minimum. The value was calculated using standard expressions (see, e.g., Ref. 33) for the concentration of electrons in the conduction band, the effective density of states, a temperature of 300 K, the effective mass of electrons, $0.20m_0$ in GaN,[34] where m_0 is the mass of an electron in free space. An ionized dopant concentration of 1×10^{17} donors was used to find this value. Subtracting the Fermi level position from the room temperature band gap of 3.4 eV indicates that the VBM should be located 3.3 eV below the Fermi level, as shown on the left in Fig. 7(a) for *n*-type GaN. This is considered the flat band condition for *n*-type GaN. Mg dopants in GaN have an activation energy of ~0.3 eV,[35] consequently flat band *p*-type GaN should have the Fermi level positioned 0.3 eV above the VBM, as shown on the left in Fig. 7(b).

The low photon energy used in UPS makes the technique very surface sensitive; thus the VBM determined from these

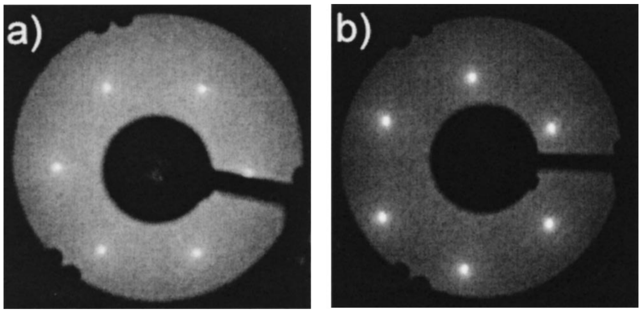

FIG. 5. LEED images of (a) as-loaded *n*-GaN and (b) clean *n*-GaN surfaces. The beam energy was 80 eV for both images.

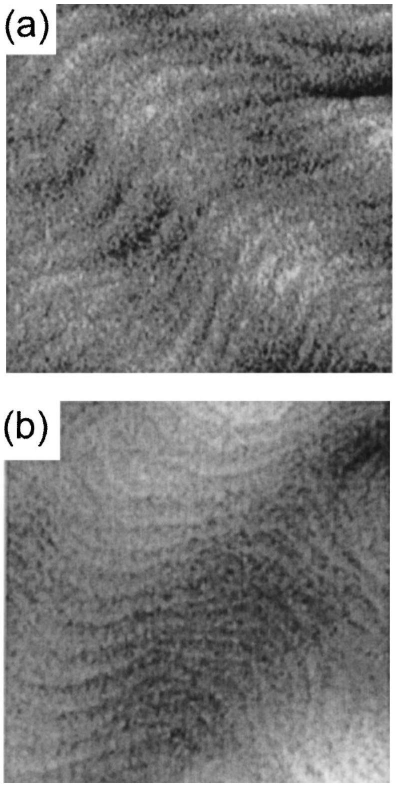

FIG. 6. AFM scans of (a) as-loaded GaN and (b) clean GaN surfaces. The rms roughness values measured were 0.69 and 0.61 nm for (a) and (b), respectively. The AFM scan is 2 μm×2 μm.

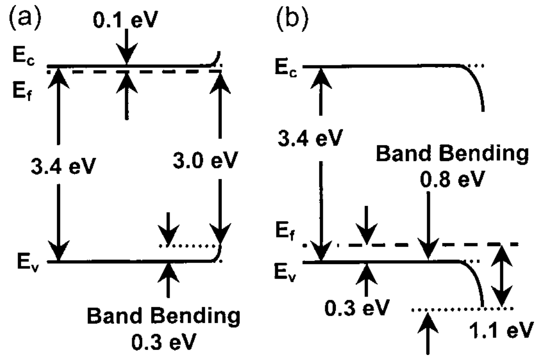

FIG. 7. Schematics of the bands of (a) n-GaN and (b) p-GaN. On the left side is the flat band condition, and on the right side is the band bending measured from the CVC surfaces in this study.

UPS spectra is strongly affected by surface contamination. Expansion of the VBM region of the UPS spectra acquired from an as-loaded sample and presented in Fig. 4(b) shows the linear fit used to determine the spectrum turn on at 3.9 ±0.1 eV below the Fermi level. This position is farther from the Fermi level than expected from calculations and is indicative of both oxide formation and similar to the values obtained by King *et al.*[4] for GaN(0001) surfaces rinsed only in HCl. As such, the as-loaded surface of GaN should not be considered representative of the bulk material based on the UPS results.

In Fig. 4(b), the VBM after ammonia CVC was found to be 3.0±0.1 eV. This value is in better agreement with the value expected from calculation, 3.3 eV. However, the measured value is still slightly lower than the calculated value, indicating that band bending is present even on the cleaned surface.

The Ga face GaN(0001) is a polar surface, and spontaneous polarization will lead to a negative bound charge at the Ga-face film surface and a positive bound charge at the N face. These effects can lead to band bending. For an n-type sample, the negative surface bound charge is compensated for by surface states and screened by ionized donors whereas the positive bound charge at the substrate interface is screened by free electrons in the conduction band. The polarization bound charge screened by the ionized donors would lead to upward band bending at the GaN surface. As shown in Fig. 7(a) our results are at least consistent with the prediction.

Based upon the polarity of the crystal structure, p-type GaN(0001) films should exhibit the same negative bound charge as n-type films. The negative bound charge would be screened by free holes in the valence band, and upward band bending would also be expected. However, in the present work, as well as in the work of Wu and Kahn,[12] downward band bending was observed in p-type GaN films. In the present work, the UPS determined VBM was 1.1±0.1 eV below the Fermi level. As shown on the right side in Fig. 7(b), 0.8±0.1 eV downward band bending is seen. This value is in good agreement with the value of 0.75±0.1 eV reported by Wu and Kahn[12] for p-type GaN(0001), but is lower than the value of 1.4±0.1 eV reported by Hartlieb *et al.*[32] The downward band bending indicates electron transfer to surface states or to the formation of positive bound surface charge. The origin of this downward band bending is not known at this time.

It is also important to consider the possible effects of surface photovoltage (SPV) when working with semiconductor materials. Work done by Alonso *et al.*[36] showed the effects of SPV on metal–GaP interfaces, and in work by Eyckeler *et al.*[37] and by Long and Bermudez[38] SPV on GaN surfaces was investigated. In the former work,[37] a Kelvin probe and UPS were used to measure the properties of n- and p-type GaN surfaces which had been cleaned by Ga deposition and desorption at 800 °C. The measurements were performed at 150 K. Band bending was found to be 0.4 eV upward for n-type surfaces and 2.9 eV downward for p-type surfaces. In their work, Long and Bermudez[38] used UPS and XPS to study the band bending dependence on the temperature. In their nitrogen ion sputter and anneal cleaned samples, they found that a SPV effect persisted up to ~150 °C, and was more significant on p-type GaN surfaces. Those authors reported that the position of the Fermi level in the dark should be 2.55 eV above the VBM, independent of the type of doping. This is somewhat lower than the results of Eyckeler *et al.*[37] who found the Fermi level to VBM energy to be 3.1±0.35 eV at 150 K. Based on the work of these authors, the band bending reported in this work may be influenced by surface photovoltage effects. However, the magnitude of these effects at the surface seems to be independent of UPS or XPS excitation, based on a comparison of UPS measurements with the XPS core level positions. This is contrary to the work of Long and Bermudez[38] who found the intensity of the light source influenced the magnitude of SPV.

Reported VBM values for n-type GaN range between 3.5 (Ref. 10) and 2.4 eV (Ref. 14) relative to the Fermi level. The former value was determined for GaN cleaned by electron beam heating. The latter value was deduced by Bermudez[14] after the removal of surface states from a GaN surface cleaned using sputtering and annealing. In a study of XeF_2 adsorption, Bermudez[27] reported a VBM of ~2.7 eV on the clean GaN surface. While Bermudez reported band bending of 0.9 (Ref. 14) and 0.6 eV (Ref. 27) on the cleaned GaN surface, Hunt *et al.*[8] reported no band bending on similarly cleaned GaN surfaces. The reason for this difference in measured value for identical processing of the surface is not known. The VBM position of 3.0±0.1 eV and the associated 0.3 eV band bending observed on the clean GaN surfaces are within the range of values reported for other cleaning techniques.

The aforementioned and companion UPS studies by Bermudez and his colleagues[14,24–27] of adsorbates on sputtered and annealed GaN have detected surface states at the VBM. To ensure that the VBM results reported in the present work were not influenced by these surface states, a secondary method was used to verify the position of the VBM.

The position of a core level, such as Ga 3d, relative to the VBM is a constant of the element and may be independent of any band bending or charging effects.[39] Waldrop and Grant,[40] measured the value of $E_V - E_{\mathrm{Ga}\,3d}$ to be 17.76±0.03 eV. Subtracting this value from the XPS measured position of the Ga 3d core level provides an alternate method by

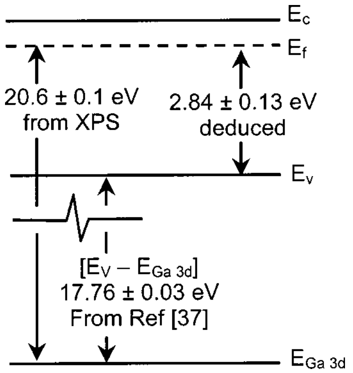

FIG. 8. Diagram of the level of energy, showing calculation of the VBM based on $E_V - E_{Ga\ 3d}$ reported by Waldrop and Grant (Ref. 40) and $E_{Ga\ 3d}$ measured in this study. The energy levels are not to scale.

which to calculate the VBM position. This method is outlined in Fig. 8, and the result obtained for the *n*-type sample is 2.84±0.13 eV. This is within experimental error of the value of 3.0±0.1 eV determined by fitting the UPS spectra. Applying this technique to the *p*-type CVC spectra, the calculated VBM position was 1.14±0.13 eV, also in agreement with the UPS derived value of 1.1±0.1 eV. This indicates that the present UPS measurements of the CVC surfaces were not affected by the surface states reported by Bermudez.

When the as-loaded surfaces were examined in this manner, the *n*-type VBM was calculated to be 3.24±0.13 eV; this value is markedly different from that of the UPS turn on of 3.9±0.1 eV. In a similar way, the *p*-type VBM was calculated from the Ga 3*d* core level to be 1.84±0.13 eV, compared to 3.0±0.1 eV extrapolated from the UPS spectrum. The contamination of the as-loaded surface apparently causes the difference between these calculations for the VBM position. Here it indicates that the surface band gap of this layer is greater than that of GaN.

The electron affinity (χ) can be determined from the UPS spectra via the following equation:

$$\chi = h\upsilon - W - E_g, \tag{1}$$

where $h\upsilon$ is the energy of incident photons, W is the spectrum width and E_g is the band gap of the material. For the present work He I radiation was used with $h\upsilon = 21.2$ eV; the room temperature value of E_g is 3.4 eV. The width of the spectrum can be determined by taking the difference between the VBM and the low energy cutoff features of the CVC samples. However, the VBM region of the UPS spectrum for the as-loaded surface shows that the oxygen and carbon contamination greatly affect the properties of this surface. The band gap of the surface could be influenced by contamination, and the position of the VBM is questionable for the as-loaded surfaces; thus, it is difficult to use Eq. (1) to calculate the electron affinity of a dirty surface. Due to the uncertainties introduced by contamination, we do not report the electron affinity of the as-loaded surfaces in this study.

For the clean GaN surface the low energy cutoff was determined from spectrum (ii) in Fig. 4(a) to be 18.0±0.1 eV from the Fermi level. Subtracting the VBM value of 3.0±0.1 eV obtained from spectrum (ii) in Fig. 4(b) gives a value of $W = 15.0 \pm 0.2$ eV. The electron affinity of the CVC surface was calculated to be 2.8±0.2 eV.

Similar calculations based on the spectral features of a CVC *p*-type GaN film surface showed the VBM to be 1.1 ±0.1 eV below the Fermi level, the cutoff at 16.3±0.1 eV, and an electron affinity of 2.6±0.2 eV. The range of values reported[12,27,41,42] for the electron affinity of *n*-type GaN(0001) subjected to cleaning techniques of varying effectiveness was 3.5–3.2 eV, somewhat higher than that reported here. While the band bending could have been affected by SPV, the electron affinity would not be. A decrease in electron affinity could be caused by a surface dipole layer with the positive pointing outward from the surface. Since ammonia is a polar molecule, it is possible that the surface dipole layer is made up of adsorbed ammonia or ammonia fragments, NH_x. Based on the ammonia adsorption work of Bermudez,[25] it is possible that some form of ammonia remains adsorbed on the surface after the CVC process.

C. Surface structure and microstructure

Unlike the spread of values obtained for the photoemission results, the reconstruction observed for atomically clean GaN is independent of the cleaning technique and sample growth technique.[4,9,12,14,20,42] The LEED images of the CVC surfaces acquired in the present research show a (1×1) pattern, in good agreement with the results of the majority of prior studies of both MBE and MOVPE grown films. It is important to note that a comparison of the images acquired from the as-loaded and the CVC surfaces indicates that the ammonia CVC cleaning process does not change surface reconstruction on either *n*- or *p*-type GaN. Furthermore, the LEED images show no indication of faceting when higher beam energies are used. Based on the theoretical work of Smith *et al.*[18] and of Feenstra *et al.*,[19] (1×1) reconstruction is unstable for GaN(0001). Since the films are not stabilized by faceting, it is again possible that an adsorbate layer remains on the surface and provides the stability required to show (1×1) reconstruction. As mentioned earlier, the adsorbates would likely be ammonia fragments or perhaps hydrogen atoms that remain on the surface, thus providing stability to the (1×1) LEED pattern.

The AFM images of the GaN(0001) surfaces of the *n*- and *p*-type samples before and after CVC revealed very similar terraces and rms roughness values of ~0.6 nm. These values are in agreement with the rms value of 0.8 nm obtained by Wolter *et al.*[43] on GaN films rinsed in HCl. The scans of as-loaded and cleaned surfaces also appeared very similar to those of as-grown samples reported by several other groups.[44,45] The LEED and AFM results show that the *in situ* CVC process does not alter the microstructure of the surface from that of the as-grown condition.

V. SUMMARY

The XPS, UPS, LEED and AFM characteristics of *n*- and *p*-type GaN(0001) thin film surfaces immersed *ex situ* in HCl and chemically vapor cleaned *in situ* in flowing ammonia under optimized conditions of 860 °C and 10^{-4} Torr pressure were investigated. A contamination layer of hydrocarbons and oxygen, the latter contained in a hydroxide, remained on the HCl-treated surfaces. In contrast, the ammonia-based CVC produced surfaces that were free of these contaminants within the limits of XPS and UPS detection. Shifts in the Ga 3d and the N 1s core level positions from the as-loaded to the CVC surfaces on n-type films were from 21.0±0.1 to 20.6±0.1 eV and from 398.3±0.1 to 398.0 ±0.1 eV, respectively. On p-type films, the core levels positions shifts were from 19.6±0.1 to 18.9±0.1 eV for the Ga 3d level and from 397.1±0.1 to 396.3±0.1 eV for the N 1s core level. The gallium-to-nitrogen core level XPS ratio of 1.3 on the n-type and of 1.2 on the p-type as-loaded surfaces decreased to 1.0 in each case after CVC. Both sets of data indicate that the hydrocarbons and the hydroxide/oxygen are removed by chemisorption of N from the ammonia or ammonia fragments. The VBM of the as-loaded and the CVC of n-type GaN were determined via UPS and XPS measurements to be 3.24±0.13 and 3.0±0.1 eV below the Fermi level; the latter value indicates a clean surface and associated upward band bending of ~0.3 eV. The VBM of p-type GaN as-loaded and CVC were similarly determined to be 1.84±0.13 and 1.1±0.1 eV below the Fermi level, respectively. The latter value indicates downward band bending of ~0.8 eV. The calculated band bending values may contain surface photovoltage effects, but the magnitude is not a function of the photoexcitation source. Electron affinities of 2.8 ±0.2 and 2.6±0.2 eV were determined from the UPS data of clean n-type and p-type surfaces, respectively. LEED and AFM studies revealed that the (1×1), terraced (0001) surfaces and the rms roughness value of 0.6 nm of the as-loaded samples did not change during the CVC process. While electron affinity and LEED patterns may indicate the presence of adsorbates remaining on the surface, the oxygen and carbon contamination was successfully removed from the GaN surface, and the resulting surface was well characterized. In subsequent research the efficacy of the CVC approach for cleaning of GaN substrates in a chemical vapor deposition environment will be investigated.

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