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Cleaning of AlN and GaN surfaces

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Successful *ex situ* and *in situ* cleaning procedures for AlN and GaN surfaces have been investigated and achieved. Exposure to HF and HCl solutions produced the lowest coverages of oxygen on AlN and GaN surfaces, respectively. However, significant amounts of residual F and Cl were detected. These halogens tie up dangling bonds at the nitride surfaces hindering reoxidation. The desorption of F required temperatures >850 °C. Remote H plasma exposure was effective for removing halogens and hydrocarbons from the surfaces of both nitrides at 450 °C, but was not efficient for oxide removal. Annealing GaN in NH_3 at 700–800 °C produced atomically clean as well as stoichiometric GaN surfaces. © 1998 American Institute of Physics. [S0021-8979(98)02821-7]

I. INTRODUCTION

Aluminium nitride (AlN), gallium nitride (GaN), and indium nitride (InN) are semiconductors with band gaps of 6.2, 3.5, and 1.9 eV, respectively.^{1–4} The recent demonstration of a blue laser based on an InGaN quantum well structure⁵ highlights many of the recent advances which have been made in this field. GaN, AlN, and their alloys are also of interest for high-power, high-frequency, and high-temperature device applications.^{1,2} The recent observation of a negative electron affinity for AlN⁶ and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ⁷ alloys also makes these candidate materials for field emitters in cold cathode electron devices.

Surface cleaning processes are the foundations on which most semiconductor device fabrication steps are built.^{8–10} Experience gained in silicon and gallium arsenide technology has shown that surface cleaning has a significant influence on epitaxial defects, metal contact resistance/stability, and overall device quality. Thus the criteria for surface cleanliness must consider the entire electrical, structural, and physical state of the surface. This includes removal of native oxides, organic contaminants, metallic impurities, particulate contaminants, adsorbed molecules, and residual species.^{11–14} Studies concerning the cleaning of Si and GaAs surfaces have investigated many *ex situ* and *in situ* processes including wet chemical (see, e.g., Refs. 8–10, 14–16), UV/O₃ oxidation,^{17–20} thermal desorption,²¹ and chemical beam,^{22,23} and atomic H cleaning.^{24,25} There have been fewer investigations of methods to obtain clean AlN^{26–31} and GaN^{32–52} surfaces.

In the first surface cleaning study of GaN, Hedman and Martensson³² used x-ray photoelectron spectroscopy (XPS) to examine single-crystal GaN films grown via halide vapor phase epitaxy (HVPE) which have been etched in H_3PO_4 at 100 °C and annealed *in situ* at 300 °C. The *in situ* anneal removed some oxygen and carbon contaminants; however, it was incomplete at this temperature. Subsequent investiga-

tions of surface cleaning processes for GaN have only recently been conducted on films grown via organometallic vapor phase epitaxy (OMVPE) on sapphire or 6H-SiC substrates.^{32–52}

Hunt *et al.*³³ investigated the efficacy of the combination of sputtering with Ar^+ , Xe^+ , or N_2^+ ions followed by thermal desorption/annealing as a cleaning procedure. Prior to processing, they observed monolayer coverages of oxygen and carbon contaminants by Auger electron spectroscopy (AES) with corresponding N/Ga ratios of 0.47–0.57 and a diffuse (1×1) hexagonal reflection high-energy electron diffraction (RHEED) pattern. Sputtering with 5 keV Ar^+ or Xe^+ ions resulted in an incomplete reduction of carbon and oxygen contaminants, and a simultaneous reduction in the nitrogen concentration to a N/Ga ratio of 0.25. When the sputtered surfaces were annealed in UHV at 500–600 °C, a minor increase in the nitrogen surface concentration (N/Ga=0.5) and a disordered RHEED pattern were observed. These results suggested that nitrogen was preferentially removed from the surface by the sputtering process. This was confirmed by Ma *et al.*³⁴ For GaN surfaces sputtered with 5 keV N^+ ions, however, the AES results of Hunt *et al.*³³ showed only a small decrease of the nitrogen content (N/Ga=0.43). After annealing at 500 °C, the N/Ga ratio increased to 0.8, and a well-defined hexagonal (1×1) RHEED pattern developed.

Khan *et al.*³⁵ obtained atomically clean metalorganic chemical vapor deposition (MOCVD) GaN(0001) surfaces in a molecular beam epitaxy (MBE) system via either annealing in an evaporated flux of Ga at 600–900 °C or by flashing off several monolayers of Ga at 900 °C which had been previously deposited at room temperature. *In situ* Auger electron spectroscopy (AES) analysis showed the O *KLL* peak intensity to be 2% of the N *KLL* signal while the O contamination was close to the AES sensitivity limit. Low-energy electron diffraction (LEED) of these surfaces displayed only unreconstructed (1×1) diffraction patterns. Kahn *et al.*³⁵ concluded, based on the AES ratios, that GaN samples prepared in this fashion were N terminated.

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The technique of Kahn has since been used by Bermudez *et al.* to prepare clean GaN surfaces to study the interfaces and interaction of GaN with Ni,³⁶ Al,³⁷ and O₂.³⁸ In the latter study, Bermudez observed via XPS that for clean GaN surfaces the valence band maximum (VBM) lies only ≈ 2.4 eV below the surface Fermi level indicating ≈ 0.9 eV of upward band bending for surfaces prepared in this fashion. This has been additionally observed by King *et al.*³⁹ for pristine high quality GaN surfaces grown and analyzed in an UHV environment. Bermudez could not identify the exact origin of the surface state responsible for pinning the surface Fermi level; however, he did show that exposure of the clean GaN surface to O₂ decreased the band bending by 0.15 eV. Bermudez also found that surfaces prepared only by wet chemical cleaning in 1:10 NH₄OH:H₂O showed only a 0.4 ± 0.2 eV upward band bending. A recent study by Prabhakaran *et al.*⁴⁰ has indicated that this etch predominantly removes gallium oxides (Ga₂O₃) from the GaN surface.

Bermudez³⁸ additionally investigated the combination of N₂⁺ sputtering followed by *in situ* annealing at 900 °C. This technique was determined to be equivalent to the Ga flux technique. Surfaces prepared by N₂⁺ sputtering showed both the same sharp (1×1) LEED patterns and the ≈ 0.9 eV of upward surface band bending as the surface cleaned in the Ga flux. The latter is in sharp contrast with the results of Hunt *et al.*³³ which showed essentially no band bending for N₂⁺ sputtered surfaces. Bermudez has also studied the interaction of XeF₂ with nitrogen ion sputter cleaned GaN surfaces.⁴¹ He observed that XeF₂ exposure resulted in an almost complete relaxation of the band bending in comparison to the slight 0.15 eV reduction for O₂ exposed surfaces.

Nitrogen ion sputtering has also been used by Sung *et al.*⁴² to examine the polarity of GaN films grown on sapphire. Their time of flight scattering and recoiling spectrometry (TOF-SARS) and classical ion trajectory simulations indicate that (0001) GaN/Al₂O₃ surfaces prepared in this fashion are nitrogen terminated with Ga atoms comprising the second layer. Their results also indicated that the surface is bulk terminated with no detectable reconstruction or relaxation within the uncertainty of their measurements and that the bulk termination is stabilized by $\approx 3/4$ ML of hydrogen atoms which terminate the outermost N atoms. This conclusion is in agreement with recent theoretical calculations by Rapcewicz *et al.*⁴³ which have indicated that a (1×1) bulk surface termination with $3/4$ monolayer (ML) hydrogen is energetically more stable than any of the several (2×2) reconstructions that they examined. This is in contrast to the fact that (2×2) reconstructions are consistently observed using RHEED during MBE growth of high quality GaN films; whereas (1×1) reconstructions are typically associated with poor growth conditions.^{44–46} The findings of Sung *et al.*⁴² are also contrary to those of both Ponce *et al.*⁴⁷ and Daudin *et al.*⁴⁸ whose convergent beam electron diffraction (CBED) and ion channeling diffraction techniques showed that smooth MOCVD GaN films grown on sapphire are Ga terminated, whereas rough/pyramidal GaN films are N terminated.

Nitrogen ion sputtering and 900 °C annealing has also been used by Dhesi *et al.*⁴⁹ to examine the bulk and surface

valence band electronic structure of GaN surfaces using angle-resolved photoemission spectroscopy (ARP). Their studies of this surface showed ≈ 0.9 eV of upward band bending and the existence of a nondispersive feature near the VBM which they attributed to a surface state. A similar nondispersive state has also been reported from the theoretical calculations of Rapcewicz and appears to be related to a filled dangling bond state for a nitrogen surface atom which is not bonded to an adsorbed hydrogen atom.⁴³

A more practical approach to surface cleaning was taken by Ishikawa *et al.*⁵⁰ They investigated the influence of wet chemical treatments with HF solutions, N⁺/Ar⁺ ion sputtering and annealing on the electrical properties of *p*-type GaN/metal interfaces. Though their XPS studies showed that a wet chemical treatment with buffered (HF₂NH₄) HF reduced the O 1s intensity by 60% for the GaN surface, their electrical measurements showed only a slight improvement in current injection for Ni/GaN contacts. Their XPS studies showed a large reduction of C and O contaminants following the sputter cleaning (no annealing), but *I/V* measurements showed only decreased current densities for the same contacts. This was attributed to the generation of a large number of surface defects by the sputtering process. Improved contact resistances were obtained by annealing BHF cleaned GaN/Ni interfaces at 400–500 °C. High-resolution transmission electron microscopy (HRTEM) studies of the GaN/Ni interfaces with no BHF treatment or annealing showed the presence of a ≈ 2 nm amorphous layer between the Ni and GaN which was attributed to a contamination layer. HRTEM of GaN/Ni interfaces prepared after annealing of the GaN at 400 °C did not show this layer.

Smith *et al.*⁵¹ investigated cleaning of GaN surfaces using HF and HCl wet chemical processes followed by *in situ* thermal desorption. It was found that HCl:DI wet chemical processes produced the lowest coverages of oxygen and carbon contaminants, but HF wet chemistries combined with methanol resulted in GaN surfaces which were more efficient for *in situ* thermal desorption of carbon and oxygen.⁵¹ However, complete thermal desorption of all contaminants was not achieved at temperatures below 900 °C. Recent scanning tunneling microscope (STM) images obtained by Packard *et al.*⁵² from GaN surfaces prepared by annealing at 900 °C showed that these surfaces are highly defective exhibiting numerous arrangements of ordered N-surface vacancies. The observation of a large amount of nitrogen surface vacancies also indicates that some type of activated nitrogen must also be involved to prohibit loss of nitrogen from the surface. These results clearly indicate that thermal desorption alone is not capable of producing electronic grade atomically clean surfaces and that more elaborate means must be used.

In this study, we have investigated both *ex situ* and *in situ* cleaning of AlN and GaN surfaces using AES, XPS, UPS, LEED, and temperature programmed desorption (TPD). Oxidation via UV/O₃ process for *ex situ* carbon contamination removal and a variety of standard wet chemistries and *ex situ* chemical vapor exposures for oxide removal were investigated. Wet chemistries based on H₂SO₄ and H₃PO₄ solutions common in GaAs technology for chemical oxide growth were also investigated.^{14–16} The *in situ* cleaning pro-

cesses examined included thermal desorption, exposure to hydrogen plasmas and annealing in fluxes of Al, Ga, NH₃, and SiH₄. The use of GaN and In as a passivating/protective layer for AlN surfaces was additionally investigated.

II. EXPERIMENT

The AlN samples were derived from (i) films epitaxially grown on 6H-SiC (0001)Si by (a) OMVPE⁵³ or (b) gas source-molecular beam epitaxy (GSMBE),⁵⁴ or deposited via reactive ion sputtering on Si(111) and (ii) hot pressed polycrystalline AlN wafers. The GaN films were epitaxially deposited on AlN buffer layers grown on 6H-SiC (0001) by OMVPE⁵³ and GSMBE.⁵⁴

All *in situ* studies were conducted in an integrated surface analysis and growth system previously described in Ref. 55. The GSMBE system consisted of a UHV chamber having a base pressure of 3×10^{-10} Torr, a residual gas analyzer (RGA) and several gas dosers and Knudsen cells. The RGA was housed in a separate, differentially pumped cylindrical chamber which had a 0.5 cm diameter orifice at the head of the RGA for TPD experiments. Heating profiles to 1100 °C were achieved using a tungsten filament positioned near the back of the sample and mounted on a boron nitride disk. A thermocouple was employed to measure the temperature of the backside of the wafer. The actual surface/sample temperatures reported below were determined using an infrared pyrometer. The accuracy of the latter was ± 25 °C. Source materials in the GSMBE included Al (99.9999%), Ga (99.9999%), SiH₄ (99.995%), and NH₃ (99.9995% as-received and further purified via an in line metalorganic resin purifier).

CMOS grade acids and bases and high resistivity (18.4 M Ω) de-ionized water were used in all *ex situ* wet chemical cleaning processes. The wet chemical cleans investigated included various mixtures of the following acids and bases: HCl, HF, NH₄F, HNO₃, H₂SO₄, H₃PO₄, H₂O₂, NH₄OH, NaOH, KOH, RCA SC1 and SC2 (1:1:5 NH₃OH:H₂O₂:H₂O @85 °C and 1:1:5 HCl:H₂O₂:H₂O @85 °C). Unless otherwise noted, AlN and GaN samples were rinsed in DI water and blown dry with N₂ after all wet chemical processes. The samples were subsequently mounted on a molybdenum sample holder for loading into the UHV system.

The XPS and UPS experiments were performed *in situ*, without breaking vacuum, in a separate UHV chamber (base pressure= 2×10^{-10} Torr) equipped with a dual anode (Mg/Al) x-ray source, a He I UV lamp, and a 100 mm hemispherical electron energy analyzer (VG CLAM II). All XPS measurements on AlN were obtained using Al K α radiation ($h\nu = 1486.6$ eV); related spectra for GaN were acquired using Mg K α radiation ($h\nu = 1253.6$ eV). Calibration of the binding energy was achieved by periodically taking scans of Au 4f_{7/2} and Cu 2p_{3/2} from standard samples and corrected to 83.98 and 932.67 eV, respectively.²⁸ Sample charging was observed only in the case of polycrystalline bulk AlN wafers. This effect was corrected by assigning the C 1s peak to a value of 285.7 eV; all other core levels (O 1s, Al 2p, N 1s, F 1s) were shifted accordingly. The value of 285.7 eV was

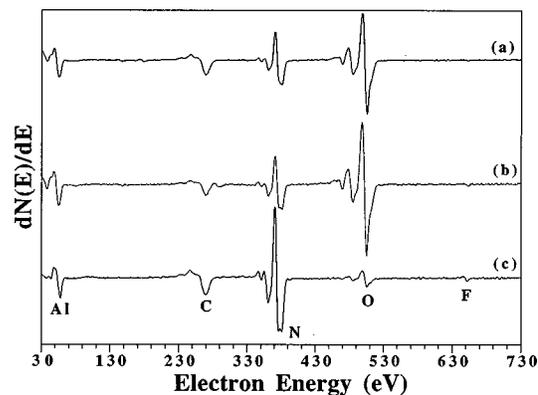


FIG. 1. AES survey spectra of OMVPE AlN (a) as-received, (b) solvent cleaned and 20 min UV/O₃ exposure, and (c) 3 min dip in 10:1 buffered HF.

based on the observation that adventitious carbon on thin AlN surfaces (≈ 30 Å) occurred at this energy. A combination of Gaussian and Lorentzian curve shapes with a linear background was used to fit the obtained data.

The AES spectra were obtained using a beam energy of 3 keV, collected in the undifferentiated mode and numerically differentiated. LEED pictures were obtained using an 80 eV, 1 mA beam.

The rf excited (13.56 MHz) remote plasma cleaning system, which was connected to the same UHV transfer line, had a base pressure of 4×10^{-9} Torr. The process gases flowed through a quartz tube mounted at the top of the chamber. The samples were located 40 cm below the center of the rf coil. An in-line purifier and filter was used for the purification of hydrogen and silane. Sample heating in the plasma system was achieved using a heater similar that one previously described in the GSMBE system.

The experimental system employed for *ex situ* UV/O₃ exposures used to remove carbon contamination from AlN and GaN surfaces employed a high intensity Hg lamp positioned ≈ 1 cm from the samples. In some cases the UV/O₃ box was purged with 1 L/s O₂ to increase the concentration of generated O₃. Further details of this process have been described in Refs. 56–59.

III. RESULTS

A. *Ex situ* cleaning of AlN

Figure 1(a) shows an AES spectrum of the surface of an as-received OMVPE AlN sample. Oxidation via UV/O₃ exposure was investigated initially for C removal. Both AES and XPS were used to examine an OMVPE film which had been previously cleaned in trichloroethylene, acetone, and methanol for 5 min in each solvent and then exposed to UV/O₃ for 10 min at room temperature. This treatment reduced the intensity of the C KLL peak by $\approx 50\%$, as shown in Fig. 1(b). A similar decrease in the intensity of the C 1s core level was observed in XPS. Longer UV/O₃ exposures of 30 min–1 h with or without a solvent preclean did not further appreciably decrease the surface C coverage. Figure 1(b) also shows that the AlN surface was further oxidized by the UV/O₃ treatment. The XPS spectrum of the O 1s core level

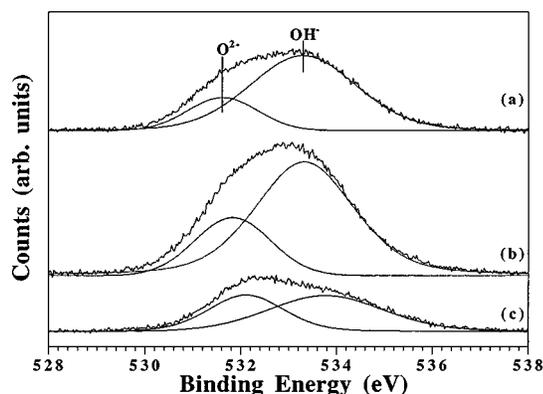


FIG. 2. XPS of the O 1s core level obtained from bulk AlN (a) as-received, (b) solvent cleaned and 20 min UV/O₃ exposure, and (c) 3 min dip in 10:1 buffered HF.

showed a broad peak which was deconvoluted into two peaks at 531.3 and 533.0 eV, as shown in Figs. 2(a) and 2(b).

The reported binding energies of the O 1s core level from various forms of aluminum oxide have range from 530.7 to 532.5 eV,^{60–65} the reported binding energies for the O 1s core level from various nitrate compounds range from 532.7 to 533.6 eV.⁶⁵ It is tempting to assign the O 1s peak at 531.3 eV to Al–O bonding and the O 1s peak at 533.0 eV to N–O bonding, but the second peak at 533.0 eV could alternatively be due to aluminum hydroxides.^{60–64} The XPS studies of various aluminum oxides and hydroxides (sapphire, gibbsite, bayerite, bauxite, boehmite, and diasporite) by Tsuchida and Takahashi,⁶² have shown that the binding energy of the O 1s core level of OH[−] species (hydroxides) is typically 532.0–532.3 eV while for O^{2−} species it is typically 530.7–531.5 eV. Tsuchida and Takahashi⁶² were successful in deconvoluting the broad O 1s spectrum from boehmite [AlO(OH)] and diasporite [AlO(OH)] into two separate peaks located at 530.7 and 532.2 eV, respectively, which they attributed to O^{2−} and OH[−] species. Additionally, the binding energy of the O 1s core level for H₂O has been reported to be 533.3 eV.⁶⁵ It seems, therefore, more likely that the native oxide and UV/O₃ generated oxides on AlN surfaces may be composed primarily of both Al–O and AlO–OH states. The issue of N–O bonding versus AlO–OH bonding could be resolved more easily by the detection of chemically shifted Al 2p and N 1s core levels, but no chemical shifts were observed in the XPS spectra.

The AlN surface is reasonably inert and oxidation in a typical laboratory ambient was not observed to proceed rapidly. Therefore, UV/O₃ exposures were used to repeatedly grow a thin oxide layer with which to assess the efficacy of wet chemical removal of this oxide. The 1:1 HCl:DI, 1:1 NH₄OH:H₂O₂, RCA SC1 and SC2 solutions were observed to significantly reduce the surface oxide. A comparison of the AES peak-to-peak height (pph) ratios for the various wet chemical cleans is provided in Table I. A 10:1 buffered HF (7:1 NH₄F:HF) process was observed to be most effective at removing the surface oxide, as shown in Fig. 1(c). Close examination of this figure reveals that the Al LVV line shape changed from that typical of aluminum oxide to that of AlN after the 10:1 BHF clean.⁵¹ Figure 2(c) also shows that the

TABLE I. O KLL/N KLL, C KLL/N KLL, and Al LLV/N KLL AES pph ratios from OMVPE AlN surfaces given various wet chemical treatments following a UV/O₃ oxidation (uncorrected for differences in sensitivity).

| | C/N | O/N | Al/N |
|--|------|------|------|
| UV/O ₃ | 0.27 | 2.57 | 0.66 |
| 10:1 BHF | 0.22 | 0.12 | 0.24 |
| 1:1 HCl:DI | 0.29 | 0.36 | 0.27 |
| 1:1 NH ₄ OH:H ₂ O ₂ | 0.32 | 0.58 | 0.27 |
| RCA SC1 | 0.20 | 0.21 | 0.30 |
| RCA SC2 | 0.33 | 0.21 | 0.30 |

10:1 BHF treatment reduced the integrated intensity of the higher binding energy (OH[−]) O 1s core level to about equal to that of the lower binding energy (O^{2−}) O 1s core level. This suggests that BHF primarily attacks hydroxide (OH[−]) species on AlN surfaces. Similar results were also obtained with both 10:1 HF and 40% NH₄F experiments.

Further examination of Table I shows that the BHF treatment produced AlN surfaces with the lowest carbon coverages for the wet chemistries examined. The RCA SC1 clean produced surfaces with essentially the same carbon coverages as the BHF treatment but with correspondingly higher oxygen coverage. In contrast the RCA SC2 clean produced surfaces with essentially the same oxygen coverage as the SC1 clean but with higher carbon coverages.

A small concentration of fluorine was also detected in the AES spectra after the BHF clean, as shown in Fig. 1(c). The presence of fluorine is better illustrated in the XPS spectrum of the F 1s region from a 30 Å GSMBE AlN film after dipping in 10:1 buffered HF (BHF) for 10 min, as shown in Fig. 3(a). This broad peak was deconvoluted into two lines at 686.8 and 688.5 eV. These lines were assigned to Al–F and N–F bonding based on previous reports of XPS from AlF₃–H₂O and NF₃.^{65–67} The carbon contamination on the AlN surface was also studied by XPS. After an HF dip, most of the surface carbon was located at a binding energy of 285.8 eV [full width at half maximum (FWHM)=2.3 eV], which is typical of adventitious carbon and is indicative of a mixture of C–O and C–H bonding⁶⁵ [see Fig. 4(a)].

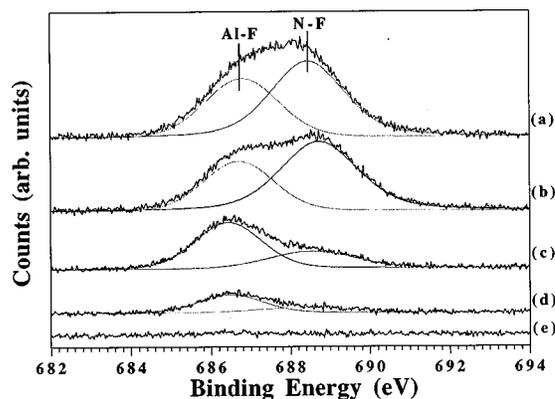


FIG. 3. XPS of the F 1s core level from a 30 Å AlN GSMBE film on (0001) 6H-SiC after (a) dipping in 10:1 BHF, and annealing for 15 min at (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 950 °C.

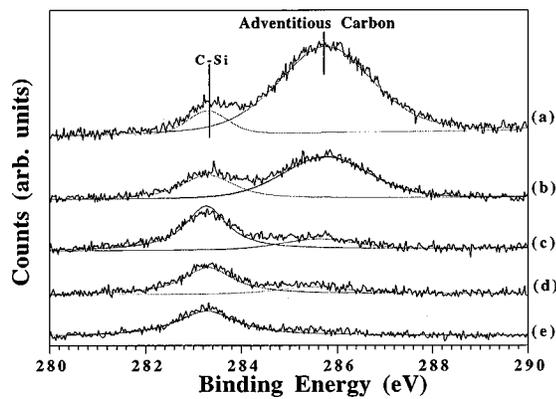


FIG. 4. XPS of the C 1s core level from a 30 Å AlN GSMBE film on (0001) 6H-SiC after (a) dipping in 10:1 BHF, and annealing for 15 min at (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 950 °C.

Other wet chemistries based on H_2SO_4 , H_3PO_4 , and NaOH, etc. were also investigated. Treatments in concentrated H_2SO_4 and H_3PO_4 were observed to leave residual sulfate and phosphate on the surface which was related to difficulties in rinsing these viscous chemicals from the AlN surface. The $\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4$ (Piranha) etch was observed to remove gross carbon contamination from AlN surfaces. Exposure to NaOH left traces of Na on the surface which were removed below the detection limits of XPS with an RCA clean. More dilute levels of H_3PO_4 were moderately successful for oxide removal at room temperature; however, it was observed that when etching AlN in H_3PO_4 at higher temperatures of 100–150 °C, the surface roughness (rms) increased from as low as 20 Å to as high as 200 Å.

B. *In situ* processing of AlN

The chemistry and thermal desorption of F, C, and O contaminants on AlN surfaces after HF processing was further examined using AES, XPS, and TPD. Figures 3(b)–3(e) show the F 1s core level spectra of the HF-etched AlN surface after subsequent *in situ* annealing at different temperatures. The two F 1s peaks became more distinguishable after annealing at 400 °C (positions: 686.7 and 688.7 eV). The intensity of the higher binding energy line was reduced after annealing at 600 °C and almost disappeared after annealing at 800 °C. Complete elimination of the low and high binding energy peak was not achieved until 950 °C. The C 1s and O 1s core levels were also monitored. Figure 4 shows the C 1s core level spectra as a function of annealing temperature. A gradual decrease in intensity for the C 1s core level was observed over the temperature range investigated with complete removal of the adventitious carbon again occurring only after annealing at a temperature of 950 °C. This is similar to the dependence observed for fluorine. The intensity of the O 1s peak initially decreased slightly after the 400 and 600 °C anneals, presumably due to desorption of water and CO. However, the O 1s intensity almost doubled after the 950 °C anneal. We attribute this to the reaction of the AlN surface with water desorbing from the chamber during the heating.

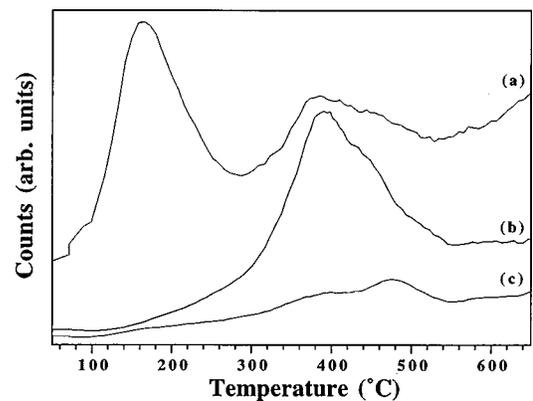


FIG. 5. Temperature programmed desorption (TPD) of m/e^- (a) 18, (b) 20, and (c) 38 from a 10:1 BHF dipped AlN (ramp: 20 °C/min).

Temperature-dependent desorption (TPD) studies were performed on a polycrystalline AlN film reactively sputtered on Si(111) which had been subsequently dipped in 10:1 BHF. Figure 5 shows a strong desorption peak for m/e^- 16 (O) and 18 (H_2O) at temperatures of <200 °C. This is in agreement with the observed decrease in O 1s intensity in XPS. Another large TPD peak was detected for desorption of fluorine at m/e^- 19 and 20 (F and HF) at 400 °C, while a small peak for m/e^- 38 (F_2) was detected at 500 °C. This is also in agreement with the XPS data. Desorption features at 400–500 °C for m/e^- 2, 12, and 28 were also detected and are related to desorption of H_2 , C, and N_2 or CO.

Complete thermal desorption of O, C, and F contaminants occurred only at elevated temperatures. As such *in situ* exposure to various different activated chemical species was investigated as a means of lowering the temperature to produce atomically clean AlN surfaces. In a previous study,⁶⁸ we investigated remote H plasma cleaning of AlN. This technique was extremely efficient for removing C and F at temperatures as low as 400 °C, however, only slight removal of oxygen was observed. Annealing in separate fluxes of Al (0.1 ML/s), Ga (0.1 ML/s), and NH_3 (1–10 sccm) was effective for removing fluorine and carbon at temperatures <800 °C. None of these processes were effective in further removing oxygen. Exposure to silane (0.1–1 sccm) at 1000 °C was the only *in situ* process which removed appreciable oxygen from the AlN surfaces. However, the loss of oxygen was at the expense of some deposition of silicon onto the surface.

A thin (<1 Å) In passivation has been successfully used to protect GaAs surfaces in air. It was subsequently thermally desorbed in vacuum.⁶⁹ As such, In was deposited on OMVPE and GSMBE AlN films *in situ* immediately after growth. The In films balled up instead of wetting the AlN surface.

By contrast, complete surface coverage of the AlN with 20 nm films of GaN was achieved. Thermal desorption of the GaN occurred at \approx 950 °C and resulted in an essentially oxygen and carbon free surface, as shown in Figs. 6 and 7. Complete desorption of the GaN film did not occur at this temperature as AES and XPS detected a persistent trace of

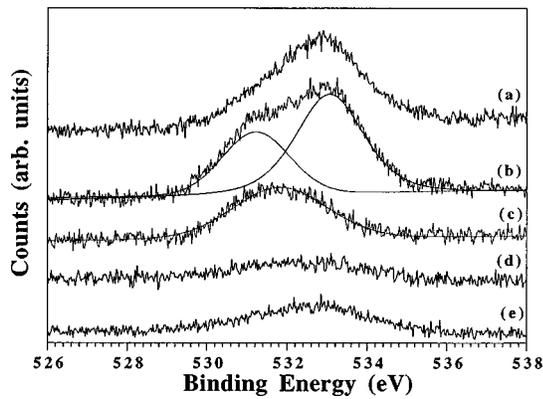


FIG. 6. XPS of O 1s core level from 200 Å GaN capping layer on (0001) AlN buffer layer, (a) as-received, (b) after annealing at 500 °C, (c) 750 °C, (d) 950 °C, and (e) >1000 °C.

Ga on the surface even after extended annealing at >1000 °C, as shown in Fig. 8.

C. Ex situ cleaning of GaN

Figure 9 displays XPS spectra of the C 1s core level from an OMVPE GaN surface after (a) solvent cleaning (trichloroethylene, acetone, and methanol) followed by (b) UV/O₃ exposure. Only partial removal of the carbon contaminants from the GaN surface by the UV/O₃ exposure was achieved, similar to that for the AlN surfaces. As-received GaN and AlN surfaces had comparable levels of carbon contaminants. The data of Fig. 9 also show that the UV/O₃ exposure shifts the peak energy of the C 1s core level to a higher binding energy (285.3–285.8 eV) which is consistent with oxidation of the carbon surface species.

To determine if carbon removal could be enhanced by increased oxidation of the GaN surface, the UV/O₃ box was purged with 1 L/s of oxygen. It is anticipated that this procedure will increase the concentration of ozone. A further decrease in the surface carbon coverage was achieved; however, complete carbon removal was not realized. The oxygen purge did enhance the oxidation rate of the GaN surface. This was observed by an almost complete disappearance of the N KLL and N 1s peaks. The Ga 3d and N 1s core levels

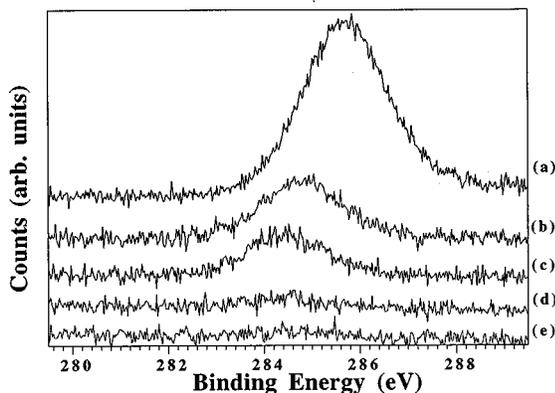


FIG. 7. XPS of C 1s core level from 200 Å GaN capping layer on (0001) AlN buffer layer, (a) as-received, (b) after annealing at 500 °C, (c) 750 °C, (d) 950 °C, and (e) >1000 °C.

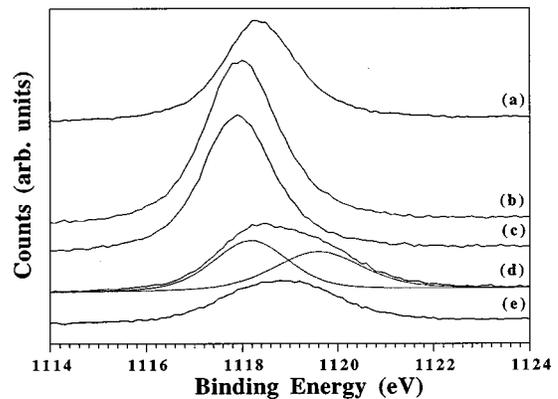


FIG. 8. XPS of Ga 2p_{3/2} core level from 200 Å GaN capping layer on (0001) AlN buffer layer, (a) as-received, (b) after annealing at 500 °C, (c) 750 °C, (d) 950 °C, and (e) >1000 °C.

were also observed to broaden and shift to the higher binding energies of 20.8 and 398.2 eV, respectively. Binding energies of 19.6–21.0 eV⁶⁵ have been reported for the Ga 3d core level from Ga₂O₃. The reported Ga 3d core levels for GaN are 19.2–20.3 eV.^{37,65} The chemical shifts for the N 1s core level for N–Ga (397.2 eV⁶⁵) and N–O_x (400–405 eV⁶⁵) bonding are much larger. A large chemically shifted N 1s core level at ~405 eV has been also observed for oxidized InN which was attributed to NO and NO₂ species.⁷⁰ Since such a large shift of the N 1s core level was not observed in our XPS data, it appears that the oxide is composed mostly of Ga bonded to oxygen (Ga–O). No diffraction patterns were detected from this surface using LEED, which indicates that the O₃ generated oxide is likely to be amorphous.

As shown in Fig. 10(a), only a single broad O 1s core level (FWHM=3.1 eV) centered at 532.4–532.7 eV could be detected from GaN surfaces after solvent cleaning and prior to the UV/O₃ exposure. However, after a 24 h UV/O₃ exposure, the O 1s core level spectrum showed the development of a second O 1s peak at 531.5 eV, possibly due to the formation of stoichiometric Ga₂O₃ (O 1s=530.8 eV).⁶⁵ Thus, the oxides formed on UV/O₃ treated GaN surfaces are also very likely composed mostly of O²⁻ and OH⁻ species. This result is similar to that for AlN surfaces (Sec. III A).

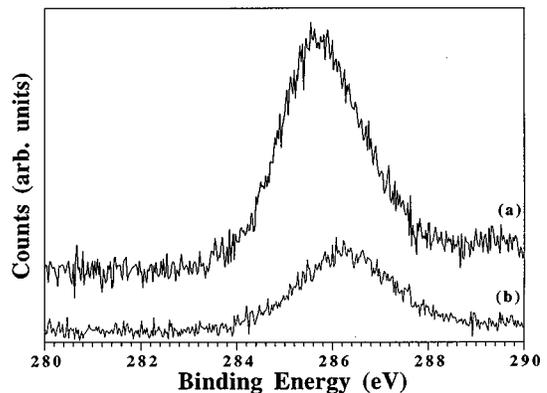


FIG. 9. XPS of C 1s core level from (0001) OMVPE GaN after (a) ultrasonication in trichloroethylene, acetone, and methanol, and (b) UV/O₃ exposure.

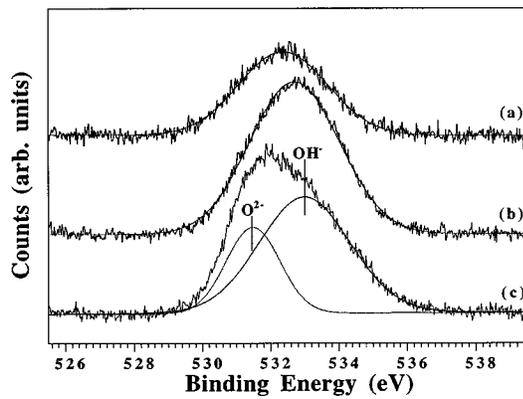


FIG. 10. XPS of O $1s$ core level from (0001) OMVPE GaN (a) after solvent cleaning, (b) after UV/O₃ oxidation for 25 min, and (c) after UV/O₃ oxidation for 24 h with 1 L/s flowing O₂.

The combination of UV/O₃ oxidation and exposure to acids and bases was also used to determine the best chemical method for removing oxides from GaN surfaces. Solutions of HCl, NH₄OH, and HF were very effective for oxide removal. Table II summarizes the AES O *KLL*/N *KLL* and C *KLL*/N *KLL* pph ratios obtained from GaN surfaces undergoing UV/O₃ oxidation followed by numerous wet chemical treatments. A 1:1 HCl:DI solution was found to produce the lowest C *KLL*/N *KLL* ratio; however, significant coverage of Cl was observed. Slightly higher O *KLL*/N *KLL* ratios were obtained with 10:1 HF and 10:1 BHF solutions, but unlike AlN fluorine was not detected either by AES or XPS. Similar to AlN, the lowest C *KLL*/N *KLL* ratios were obtained with these HF based solutions. For HCl treatments, the oxygen surface coverage was inversely related to the amount of Cl detected on the surface (i.e., higher Cl coverage leads to lower oxygen coverage). A similar relation was also observed between carbon and oxygen. All GaN surfaces treated in HCl:DI, HF, BHF, or NH₄OH:H₂O₂ displayed (1 × 1) LEED patterns indicating removal of the UV/O₃ oxide.

Other wet chemistries including RCA SC1 and RCA SC2, 1:1:7 H₂SO₄:H₂O₂:DI, H₃PO₄, and acetic acid were also investigated. RCA SC1 and SC2 reduced the UV/O₃ oxide on GaN surfaces, but the SC2 clean was left more

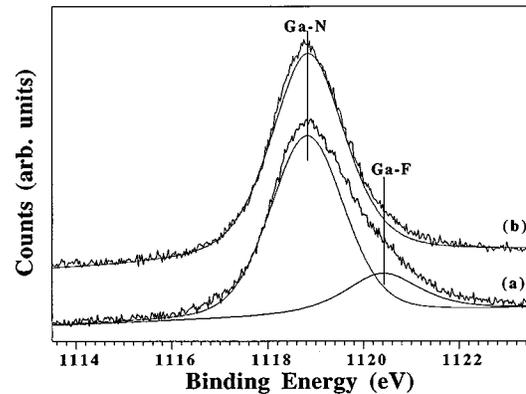


FIG. 11. XPS of Ga $2p$ core level from (0001) OMVPE GaN after UV/O₃ oxidation and (a) BHF vapor clean and (b) DI rinse and NH₄OH:H₂O₂ clean.

carbon on the surface relative to the SC1 clean, similar to AlN surfaces. H₂SO₄ and H₃PO₄ left residual sulfates and phosphates on the GaN surfaces with accordingly higher oxygen levels.

An *ex situ* exposure to the equilibrium vapor from a BHF solution was also useful for UV/O₃ oxide removal from (0001)Si 6H-SiC surfaces.⁵⁴ As shown in Table II, the oxygen surface coverages on the treated GaN surfaces were not lower than those for typical wet chemical approaches. One significant difference was the detection of large amounts of fluorine as compared to the BHF wet chemical cleans where no fluorine was detected. XPS of this surfaces showed a broad F $1s$ peak which could be deconvoluted into two separate peaks at 686.6 and 688.2 eV. Shifted Ga $2p$ [Fig. 11(a)] and N $1s$ [Fig. 12(a)] core level lines at 1120.5 and 403.8 eV were detected. This together with the two F $1s$ lines indicate the formation of both GaF₃ and NF₃ on the surface. Both Ga-F and N-F lines were completely removed by cleaning in 1:1 NH₄OH:H₂O₂, as shown in Figs. 11 and 12(b).

Finally, AFM examinations revealed that all of the above wet chemical treatments, except H₃PO₄, did not increase the rms surface roughness beyond the initial value of ≈ 10 Å.

TABLE II. AES pph ratios of UV/O₃ and wet chemical processed OMVPE GaN surfaces.

| Treatment | O <i>KLL</i> / N <i>KLL</i> | C <i>KLL</i> / N <i>KLL</i> | Ga <i>LMM</i> / N <i>KLL</i> |
|---|-----------------------------|-----------------------------|------------------------------|
| 3 h in air | 0.22 | 0.07 | |
| As-received | 0.15 | 0.21 | 0.59 |
| Solvents | 0.20 | 0.24 | 0.61 |
| UV/O ₃ | 0.85 | 0.19 | 0.81 |
| HCl:DI | 0.12 | 0.23 | 0.62 |
| NH ₄ OH:H ₂ O ₂ | 0.29 | 0.22 | 0.73 |
| 10:1 HF | 0.15 | 0.10 | 0.69 |
| 40% NH ₄ F | 0.23 | 0.14 | 0.77 |
| 10:1 BHF | 0.23 | 0.20 | |
| 1:1:7 H ₂ SO ₄ :H ₂ O ₂ :DI | 0.33 | 0.22 | 0.63 |
| 85% H ₃ PO ₄ @ 125 °C | 0.27 | 0.15 | 0.76 |
| RCA SC1 | 0.25 | 0.24 | 0.60 |
| RCA SC2 | 0.16 | 0.35 | 0.62 |
| BHF vapor | 0.43 | 0.35 | 0.77 |

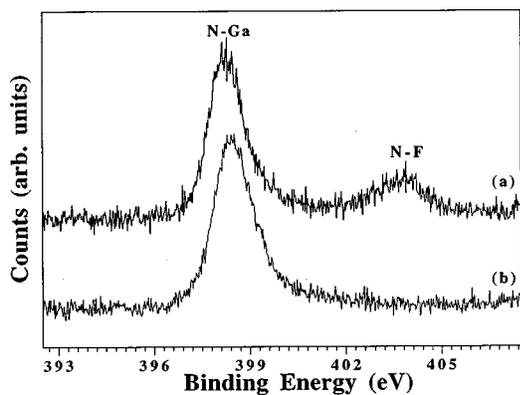


FIG. 12. XPS of N 1s core level from (0001) OMVPE GaN after UV/O₃ oxidation and (a) BHF vapor clean and (b) DI rinse and NH₄OH:H₂O₂ clean.

D. In situ processing of GaN

In a previous study, AES was used to examine the thermal desorption of O, C, and Cl contaminants on GaN surfaces after various DI:HCl:HF:MeOH wet chemical processes.⁵¹ Annealing at 800 °C resulted in incomplete desorption of carbon and oxygen contaminants; while complete desorption was achieved after annealing at 950 °C. In this present study, desorption of carbon and oxygen contaminants was more closely examined using XPS. The data in Figs. 6–8 are representative of our findings. Figures 6 and 7 show that both oxygen and carbon remained on the surface after vacuum annealing at 800 °C and that complete removal these species was only achieved after annealing at 950 °C. Following the latter anneal, the Al 2p core level from the AlN surface appeared and the Ga 2p core level decreased in intensity and split into two lines [see Fig. 8(d)] indicating decomposition/sublimation had occurred at this temperature. This is supported by a separate TPD experiment, where an exponential increase of the mass 69 (Ga) with temperature was observed at $T_{\text{sub}} > \approx 800$ °C (see Fig. 13). This shows that the oxygen and carbon contaminants were likely removed from the GaN surface through sublimation of the GaN film.

The position of C 1s core level from carbon on the GaN surface also shifted with increasing annealing temperature

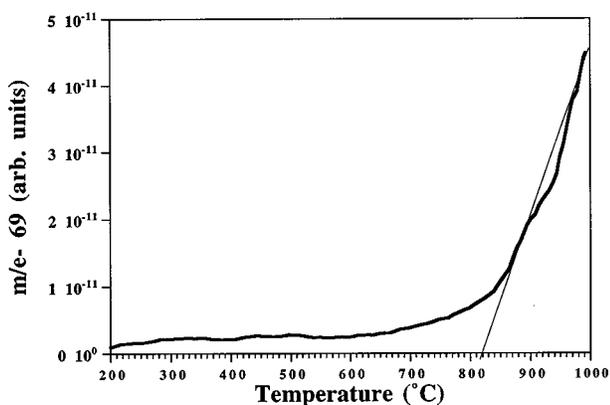


FIG. 13. TPD m/e^- 69 (Ga) signal from GSMBE GaN as a function of surface temperature.

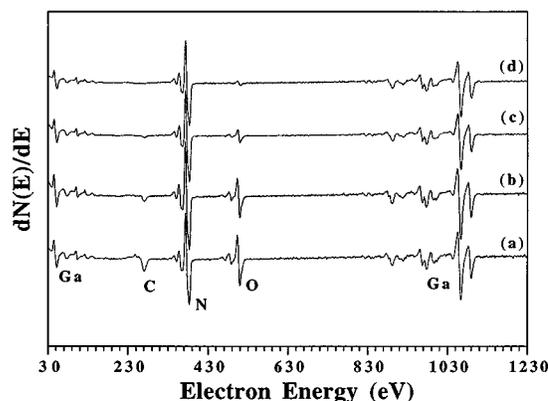


FIG. 14. AES survey spectra from GSMBE GaN (a) exposed to UV/O₃, and after annealing in: (b) UHV at 650 °C, 20 min, (c) NH₃ (5×10^{-6} Torr) at 650 °C, 20 min, and (d) NH₃ (5×10^{-6} Torr) at 800 °C, 25 min (spectra normalized to N KLL).

from 285.7 to 284.5 eV. This indicates that primarily C–O bonded carbon desorbs from GaN surfaces at temperatures of 400–600 °C with only primarily C–H bonded carbon remaining at higher temperatures of 600–950 °C. Similarly, the higher energy O 1s core level was also observed to disappear in the temperature range of 400–600 °C suggesting that OH⁻ species desorb at lower temperatures leaving only O²⁻ species at higher temperatures.

The removal of native and UV/O₃ oxides from GaN via annealing in fluxes of Ga and NH₃ was conducted. Both procedures resulted in a reduction in the amount of oxygen and carbon, as shown in Fig. 14. However, complete removal of oxygen could not be observed due to electron beam oxidation of the GaN surface during the AES analysis. Figure 15 shows a series of AES spectra taken sequentially for differing periods of time from an as-grown GSMBE GaN surface. The intensity of the O KLL peak increased with time of the measurements. Essentially no oxygen could be detected after one scan. Therefore, we conclude that atomically clean GaN surfaces were obtained by annealing in NH₃ at 800 °C. Furthermore, (2×2) reconstructions were observed in LEED from both OMVPE and GSMBE GaN films.

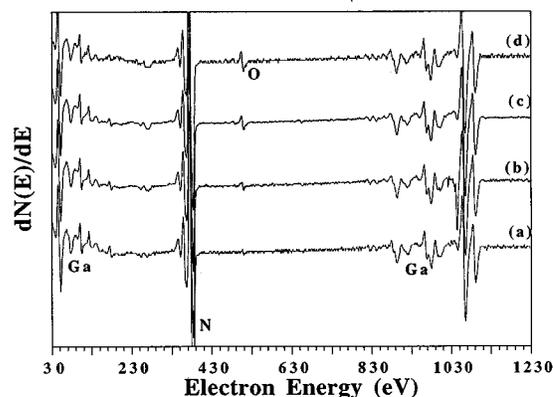


FIG. 15. AES survey spectra from GSMBE GaN after various sequential scans (a) 1, (b) 3, (c) 8, and (d) 9 scans (spectra normalized to N KLL).

IV. DISCUSSION

A. Air exposed and UV/O₃ treated AlN and GaN surfaces

In our XPS analysis of the O 1s core level from as-received and UV/O₃ treated AlN and GaN surfaces, the presence of oxygen in two different chemical states was attributed to oxygen bonded to Al or Ga in both O²⁻ and OH⁻ chemical states. This was primarily based on the inability to observe a chemically shifted N 1s core level (at ~401–402 eV), and this conclusion is supported by previously reported observations of hydroxides on aluminum, aluminum oxide and aluminum nitride surfaces.^{60–64} Our inability to detect chemical shifts for either the N or Al core levels is likely related to the comparable magnitude of the chemical shift for Al–O and Al–N bonding and the lack of surface sensitivity for the N 1s core level. However, the N KLL and N 1s signal in both AES and XPS decreased with increasing UV/O₃ exposure and, accordingly, the intensity of both the O 1s core levels increased in tandem with a broadening of the Al/Ga core levels. This argues against the formation or inclusion of oxynitride phases in the UV/O₃ generated oxide. One would expect that the more volatile N–O species is removed from the surface during the UV/O₃ treatment. This may be the limiting factor in growing an oxide by this technique. Finally, a decrease in intensity on the low binding energy side of the N 1s core level was not observed after etching by HCl, HF, or NH₄OH. We conclude that the higher binding energy O 1s peak is not due to N–O bonding. However, this does not exclude the possibility that during initial oxidation of AlN or GaN surfaces, NO_x species are formed and gradually removed from the surface allowing the formation of aluminum or gallium oxides and hydroxides. These conclusions are supported by recent XPS and glancing angle x-ray diffraction (XRD) studies by Wolter *et al.*⁷¹ of GaN films thermally oxidized in dry air at 900 °C. Their studies showed minimal oxidation of the GaN surface at temperatures of 450–750 °C for >25 h, but at 900 °C growth of purely monoclinic Ga₂O₃ was observed.

Prabhakaran *et al.*⁴⁰ have examined the native oxide formed on GaN via XPS and observed two O 1s core levels located at 531.3 and 532.7 eV, which is in agreement with our results. They assigned the lower binding energy peak to Ga₂O₃ based on the observation that this peak was removed during etching in NH₄OH, which is known to dissolve Ga₂O₃. They did not explain the origin of the higher binding energy O 1s core level but did observe a decrease in intensity on the lower binding energy side of the Ga 2p and N 1s core levels after etching in NH₄OH, which they attributed to removal of an oxynitride phase. Bermudez³⁸ has recently used XPS with Zr Mξ radiation ($h\nu=151.6$ eV) to study the interaction of O₂ with atomically clean GaN surfaces. He identified the satellite on the Ga 3d core level as due to oxygen exposure which indicates the formation of Ga–O bonds.

The XPS C 1s core level was generally located at 285.2–285.8 eV with a broad FWHM of 2.2–3.0 eV on both AlN and GaN surfaces after ambient exposure or wet chemical processing. Prabhakaran *et al.*⁴⁰ has made similar observations for GaN surfaces and concluded that this adventi-

tious carbon is mostly composed of C–H bonding. However, we conclude that the surface carbon is a mixture of C–H and C–O bonding. This is based on the work of Miyauchi *et al.*⁷² which showed that the C 1s core level for CH₂, C–O, and O–C=O bonded carbon on silicon surfaces are located at 284.6, 286.3, and 288.4 eV, respectively. This is also supported by our AES/XPS data which showed a decrease in intensity and shift to lower binding energy for the C 1s after annealing at 500 °C and our TPD data which showed desorption of C–O in the same temperature range.

The UV/O₃ exposure always reduced the level of carbon for contaminated AlN and GaN surfaces. The C 1s line was always shifted to higher binding energy indicating some oxidation of the surface carbon (i.e., formation of C–O bonds). However, complete carbon removal was never achieved. Baunack and Zehe²⁰ and Fominski *et al.*⁵⁹ have also reported incomplete removal of carbon from silicon surfaces using UV/O₃ oxidation, and we have also observed this for 6H-SiC surfaces.⁵⁴ The inability to achieve complete removal of carbon from nitride surfaces via UV/O₃ oxidation may be related to this primary factors: (i) the extreme chemical inertness of GaN and AlN as well as their resistance to oxidation which prevents carbon reaccumulation during sample mounting and transfer, and (ii) the wide band gap of these materials. The UV light from the Hg lamp may create electron hole pairs at the surface which assist in the oxidation of surface carbon via transfer of electrons/hole pairs in the low band gap materials. Due to the larger band gap, fewer electron/hole pairs are generated at the surface of GaN and none for the surface of AlN. (iii) Finally, the bonding in GaN and AlN is much more ionic than in the case of GaAs and Si and therefore adventitious carbon may be more strongly bonded or attracted to the nitride surfaces. In summary, the UV/O₃ oxidation treatment was found most useful for the removal of gross carbon contamination left from photoresist or excessive handling.

B. Wet chemical etching and HF vapor processing

Ex situ wet chemical cleaning of GaN and AlN surfaces with HCl and HF based solutions produced surfaces with the lowest levels of oxygen, but significant concentrations of Cl and F were observed. Fluorine was detected exclusively on AlN surfaces; Cl was detected only on GaN surfaces. This indicates that F and Cl are mainly bonded to Al and Ga atoms, respectively. This is supported by the fact that the bond strengths of Al–F and Ga–Cl are much larger than those for N–Cl and N–F.⁷³ However, the formation of N–F bonds on the AlN surface cannot be excluded, as the F 1s peaks had two contributions positioned at ≈686.5 and 688.5 eV in the case of BHF-treated AlN. The F 1s peak at ≈688.5 eV may also be due to physisorbed HF. TPD analysis of BHF-treated surfaces showed a desorption peak for both m/e^- 20 and 38 within the 400–500 °C range which corresponds with the observed decrease of the 688.5 eV F 1s peak. This line did not completely disappear until 950 °C. Therefore, the possibility exists that N–F and H–F bonded fluorine is present on BHF processed AlN surfaces.

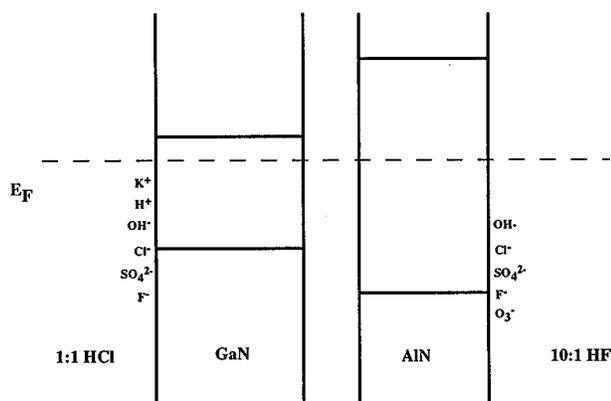


FIG. 16. Schematic illustrating alignment of Cl and F ions with VBM of GaN and AlN in 1:1 HCl:DI and 10:1 HF, respectively.

The possible formation of N–F bonds on HF wet chemically processed AlN surfaces raises the question of whether some N–Cl bonding is also present on HCl wet chemically treated GaN surfaces. Chemically shifted Ga or N peaks were not detected, and Cl was extremely difficult to detect with XPS due to the weak sensitivity. Hence, no conclusions can be drawn concerning the bonding state of Cl on GaN surfaces except those which are based on our previous bond strength arguments. The bond strength of N–Cl is ≈ 150 kJ/mol and larger than the N–F bond strength, therefore N–Cl bonding on GaN may be likely.

The specificity of F adsorption on AlN surfaces and Cl adsorption on GaN surfaces may be alternatively related to the differences in band gap. Ohmi¹⁰ has shown that the ability of HF to terminate silicon surfaces with hydrogen is based on the excellent alignment of the H^+ ion energy with the valence band maximum of silicon in HF solutions. This close alignment allows efficient electron transfer and the formation of covalent bonds. This investigator has also stated that the energy position of an ion in an aqueous solution is a direct function of the electronegativity. As fluorine is more electronegative than chlorine, the ion of the former should lie at a lower energy. The band gap of AlN is much larger than GaN and the VBM of AlN lies below that of GaN with respect to the Fermi level. Accordingly, interaction of F^- with the VBM of AlN would be expected; whereas the Cl^- ion would be expected to more strongly interact with the VBM of GaN. This is schematically shown in Fig. 16. One important aspect regarding the scenario illustrated in Fig. 16 is that the termination of GaN and AlN in aqueous solutions may be dependent on the doping type and level (i.e., the position of the Fermi level). The termination of GaN surfaces by H^+ or OH^- ions may be more favored for p -type material leading to less chlorine termination. In contrast, increased Cl and F termination of GaN and AlN surfaces could be alternatively achieved by adjustment and optimization of the pH level of HCl and HF solutions.

Complete Cl and F termination of GaN and AlN surfaces is desirable, because these contaminants desorb at much lower temperatures than both carbon and oxygen. As the bond strengths of N, Ga, and Al with Cl and F are strong, tying up dangling bonds at nitride surfaces with Cl and F

should stabilize and inhibit reoxidation of the surface in air. We have observed an inverse correlation between the halogen surface coverage after wet chemical processing and the carbon and oxygen surface coverage. Typically, the larger the halogen coverage, the lower are the oxygen and carbon coverages and vice versa. This is in agreement with observations of Ingrey¹⁴ for III–V arsenide and phosphide surfaces. Saturation of sites with one particular specie hinders the adsorption or contamination by other species.

Putting the scenario in Fig. 16 aside, we note that HF processes generally resulted in surfaces with fewer carbon contaminants relative to HCl processes. This may be related to the fact that HCl and other processes were conducted in glass beakers; whereas HF processes were conducted in Teflon beakers. However, the RCA SC1 clean which was also conducted in glass left a similar level of carbon to HF processed GaN and AlN surfaces. The RCA SC2 clean always left a higher carbon coverage relative to SC1. This suggests that the chemical state of the carbon species in HF is different from that in HCl. The C $1s$ peak on HF-treated GaN surfaces was typically 0.2–0.4 eV higher in binding energy than that for HCl-treated GaN surfaces. This, in turn, implies that the HF processes may leave more C–O bonded carbon; whereas HCl processes leave more C–H bonded carbon. This is important, because we observed in our TPD experiments that C–O bonded carbon desorbs at a lower temperature compared to C–H bonded carbon.

Removal of the UV/ O_3 oxide from AlN surfaces using HF was initially surprising given the known chemical inertness of sapphire.⁷⁴ However, our XPS results show that HF attacks primarily the oxide associated with the higher binding energy O $1s$ core level which we have attributed to oxygen in a OH^- chemical state (see Fig. 2). On the other hand, oxide removal from GaN surfaces using HCl, HF, and NH_4OH was achieved. Solutions of 1:1:7 $H_2SO_4:H_2O_2:DI$ are also used to clean GaAs surfaces, but do so via formation of a thin passivating oxide layer.^{15,16} In our case, exposure to $H_2SO_4:H_2O_2$ removed carbon from the GaN surface but did result in an oxide layer. This shows again the chemical inertness of GaN compared to GaAs.

The BHF vapor treatment does not appear to be very effective for removal of oxides from AlN and GaN surfaces relative to other wet chemical processes. Higher temperature processing may be necessary to force desorption of GaF_x and NF_x species which will allow continued etching of the surface oxides.

C. Thermal desorption and capping layers

We have previously examined the thermal desorption of oxygen and carbon from GaN surfaces after wet chemical cleaning using the following solutions in HCl:methanol(MeOH), HCl:DI, HF:DI, and HF:MeOH.⁵¹ Complete removal of these contaminants was not achieved even after annealing at 800 °C. The carbon desorption from the HF:MeOH-treated GaN surfaces was observed to be the most complete of the wet chemical treatments investigated.⁵¹ These observations suggested that the chemical state of the carbon contaminants left on GaN surfaces after HCl and HF

wet chemical processing were different. In fact, we observed in this study that the binding energy of the C 1s peak on GaN surfaces is typically ≈ 0.4 eV higher in binding energy for HF processed surfaces compared to HCl processed surfaces. This difference in binding energy suggests that HF wet chemical processes leave more C–O bonded carbon on the surfaces, whereas HCl processes leave more C–H_x bonded carbon. This is consistent with the observation that the C 1s core level is located at ≈ 285 – 286 eV after wet chemical processing and shifts to 284 – 285 eV after annealing at 500 – 600 °C. Ignoring the possibility of band bending effects, this indicates that most of the C–O bonded carbon desorbs at temperatures ≤ 500 – 600 °C leaving behind only C–H bonded carbon which apparently desorbs at much higher temperatures. As HF processes and MeOH cleans tend to leave more C–O bonded carbon contaminants, the thermal desorption of carbon contaminants at 800 °C from these surfaces should be more complete.

Consideration of the above results reveals that no wet chemical treatments exhibited a significant effect on the desorption of oxides from GaN and AlN surfaces. Thermal desorption of the surface oxide for GaN surfaces was not observed to start at temperatures of 900 – 950 °C where decomposition of the GaN film was initiated (see Fig. 13). The Ga $2p_{3/2}$ XPS spectra from this surface displayed two core levels indicating the preferential loss of nitrogen (see Fig. 8). In contrast thermal desorption of the surface oxide on GaAs is observed at 650 °C. The discrepancy between oxide desorption from GaAs and GaN surfaces can be explained by considering that the oxides from GaAs and probably from GaN leave the surface as either Ga–O, As–O, or N–O species instead of O₂. Therefore, Ga–As or Ga–N bonds must be broken in this procedure. Higher temperatures will be required to break the much stronger Ga–N bond. Annealing GaN in fluxes of atomic N or Ga are then necessary to maintain a stoichiometric surface during the thermal desorption process of the surface oxide (annealing GaN in fluxes of Ga and NH₃ will be discussed in the following section). This also explains the inability to thermally desorb the oxide from AlN surfaces. The Al–N bond is significantly stronger than the Ga–N bond, and even higher temperatures than investigated in this research are necessary.

The two O 1s core levels after annealing AlN and GaN to temperatures of ≈ 800 °C and attributed to oxygen in the O²⁻ and OH⁻ chemical states merge into one peak having a smaller FWHM. Analysis of the thermal decomposition of aluminum hydroxides [Al(OH)₃] using thermogravimetric analysis (TGA) has shown that these materials decompose into aluminum oxides at temperatures of ≈ 500 °C.⁷⁵ This is 300 °C lower than the oxygen desorption temperature, and suggests that the higher binding energy O 1s peak is due to oxygen bonded to aluminum in some other chemical state than OH⁻. For example, it could be related to the nonbridging versus bridging oxygen state seen in silicon oxide films.⁷⁶

The high temperature stability of F and Cl on AlN and GaN surfaces is not surprising, given that both AlF₃ and GaCl₃ sublime at 1300 and 800 °C, respectively.^{73,77} Complete thermal desorption of fluorine from AlN was not ob-

served until 950 °C. However, both TPD and XPS experiments revealed the loss of fluorine from AlN surfaces at the relatively low temperatures of ~ 500 °C. This effect was correlated with the desorption of either physisorbed HF or the desorption of fluorine from nitrogen sites. Desorption of fluorine from AlN at $T > 500$ °C was correlated primarily with desorption of F bonded to Al sites. For Cl on GaN, a significant decrease in intensity in AES was likewise observed at temperatures of ~ 450 °C with complete desorption of Cl from GaN occurring at ~ 700 – 800 °C. Desorption of Cl from GaN in this temperature range is consistent with the results obtained by Bermudez⁴¹ for the desorption of F from GaN. This study showed that complete desorption of F adsorbed on GaN (via decomposition of XeF₂) occurred at ~ 550 – 750 °C and primarily from Ga sites.⁴¹

Our results on capping layers for AlN indicate that the success of this idea is dependent on finding a layer which (i) uniformly covers/wets the surface, (ii) can be desorbed at $T < 800$ °C, and (iii) can be deposited *in situ* directly after film growth. As shown above, GaN does not fulfill the second criterion and complete coverage with In and other groups III (Ga, Th), IV (Sn, Pb), and V (As, Sb, Bi) elements is a problem in terms of surface wetting. Group III- As and P compounds, however, are likely to exhibit both the lower temperature stability and coverage needed. Unfortunately, most OMVPE and MBE systems do not have the capability of depositing both nitride and phosphide or arsenide compounds. InN may be the best alternative. InN has been reported to decompose in UHV at ≈ 600 °C⁷⁸ and should cover the AlN surface, but growth of pure InN is difficult and has not been frequently reported.

D. Chemical vapor cleaning and H plasma processes

Annealing GaN surfaces in a flux of Ga or atomic N to maintain stoichiometry is a more appropriate method for removal of oxides as opposed to simple thermal desorption where decomposition of the GaN film occurs. Annealing GaN surfaces in fluxes of reactive gas or vapor species such as Ga, N₂⁺, and NH₃ is also beneficial in the removal of carbon and oxygen via the formation of volatile species which desorb at lower temperatures. Kahn *et al.*³⁵ and Bermudez^{36–38} have demonstrated cleaning of GaN surfaces via annealing in a flux of Ga, but our results have shown that annealing in an NH₃ flux also results in atomically clean GaN surfaces. This approach is more similar to reactive cleaning of other III–V compounds where it is necessary to anneal in a flux of the group V component to counteract the incongruent sublimation of this component.²³

The results presented in Fig. 14 show that NH₃ is effective for the removal of carbon at temperatures below 600 °C. Ammonia has been previously reported to be an excellent scavenger of hydrocarbons.⁷⁹ It is also shown in Fig. 15 that annealing GaN in 5×10^{-6} Torr NH₃ at 800 °C completely removes carbon and leaves only $\approx 1/10$ th ML coverage of oxygen. The NH₃ cleaned GaN surfaces displayed (2×2) reconstructions in LEED, which has only been previously observed from as-grown rf and ECR MBE samples.^{45,80}

Our plasma cleaning results indicate that an H plasma is very efficient for *in situ* removal of halogen and carbon species at temperatures of 450 °C, which is 300–400 °C lower than the temperature required to desorb these contaminants in UHV or annealing in a flux of NH₃ or Ga. Halogen removal from silicon surfaces using atomic H has been shown to be via an Ely-Rideal mechanism.⁸¹ In this mechanism, atomic H is able to extract halogens from silicon without being thermally accommodated at the surface due to its 220 kJ/mol of excess potential energy.

Nakamura *et al.*⁸² reported that annealing *p*-type GaN in ammonia led to high resistivity material due to compensation of the *p*-type dopants with hydrogen. It is therefore likely that cleaning GaN surfaces via annealing in NH₃ or a H plasma will lead to compensation of *p*-type dopants by forming acceptor-H complexes. A much lower flux of ammonia was used in our experiments and hence hydrogen incorporation and *p*-type dopant compensation could be much less. Kim *et al.*⁸³ have recently achieved the growth of *p*-type GaN via NH₃ GSMBE without post-growth annealing. The NH₃ flux and temperature employed in this case were equivalent to the NH₃ flux and temperature used to clean the GaN surface in our study. By contrast, Pearton *et al.*^{84,85} have intentionally used an ECR H plasma at 250–400 °C to implant H into GaN, AlN, and InN. They observed significant compensation of both *n*- and *p*-type material.

V. CONCLUSIONS

The surfaces oxides remaining on as-received and UV/O₃ and wet chemically treated AlN and GaN surfaces are composed of oxygen bonded primarily to Al and Ga in both O²⁻ and OH⁻ states. The presence of some oxynitride/N–O bonding at the surface cannot be ruled out.

UV/O₃ oxidation was effective for removing carbon from GaN and AlN surfaces; however, complete removal of the carbon was never achieved. This is attributed to the inability of this technique to grow a complete passivating oxide layer due to the resistance to continued oxidation of these materials. XPS showed that the oxides formed on AlN and GaN via UV/O₃ were aluminum and gallium oxides.

Removal of surface oxides from AlN using HCl, NH₄OH, and HF mixtures occurs primarily through attack of the OH⁻ species on the surface.

The lowest oxygen coverages on AlN and GaN surfaces was achieved using HF and HCl. However, residual F and Cl remain on the AlN and GaN surfaces, respectively. The fluorine is believed to be bonded to both Al and N with the presence of some physisorbed HF also being a possibility. For GaN, the Cl is believed to be bonded primarily to Ga based on bond strength considerations.

Thermal desorption of carbon contaminants from both AlN and GaN surfaces was not observed to be complete until temperatures of >900 °C. For GaN, this was observed to coincide with some sublimation of the GaN film. XPS analysis showed that C–O bonded carbon desorbed from the surface in the temperature range of 400–600 °C resulting in primarily C–H bonded carbon which is stable to higher temperatures (600–950 °C).

Complete thermal desorption of oxygen from AlN was not observed even at temperatures >1100 °C. Some desorption was observed to occur at lower temperatures (400–600 °C) presumably due to desorption of hydroxide species. Complete thermal desorption of oxygen, like carbon, from GaN was observed to occur only at temperatures where some sublimation of the film occurred. Complete thermal desorption of fluorine from AlN occurred at 950 °C. Complete thermal desorption of Cl from GaN occurred at ~600 °C.

Remote H plasma process were found to be extremely efficient for removing carbon and halogen species from AlN and GaN surfaces at temperatures as low as 400 °C. However, it was not possible to remove oxide from AlN and only moderate success was achieved with GaN using this technique.

Annealing AlN in fluxes of SiH₄ was the only chemical beam technique of the many investigated which was successful in removing oxides from AlN surfaces. However, this was at the expense of some deposition of silicon. In and GaN were found to be moderately successful capping layers for AlN. Atomically clean and (2×2) reconstructed GaN surfaces were produced by annealing in NH₃ at 800 °C.

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