

Cleaning of GaN Surfaces

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The work described in this paper is part of a systematic study of surface cleaning and ohmic contact strategies for GaN. The goal of this investigation was to determine the most effective methods of wet chemical and thermal desorption cleaning for the removal of oxygen (O) and carbon (C) prior to metallization. Hydrochloric (HCl) and hydrofluoric (HF) acid-based cleaning treatments were compared, and thermal desorption as a function of temperature was characterized by sequential heating under ultra high vacuum (UHV) conditions. Auger electron spectroscopy (AES) analysis was used to monitor the presence of surface O and C throughout the study. For the removal of surface oxide, HCl-based solutions were found to be most effective; under as-cleaned, air-exposed conditions, HCl:DI H₂O (1:1) solution resulted in the lowest levels of residual O and C. However, HF-based solutions resulted in more effective thermal desorption of C from the surfaces. In contrast to the results typically observed in the thermal desorption cleaning of GaAs, complete removal of oxygen and carbon from air-exposed GaN surfaces was not seen using vacuum heating alone, even to temperatures where GaN decomposition occurs (>800–900°C). The results of this study indicate that the presence of oxygen and carbon on the GaN surface is persistent even to high temperatures, and that further in-situ cleaning methods must be added to obtain spectroscopically clean GaN surfaces.

Key words: Auger electron spectroscopy (AES), gallium nitride, metallization, ohmic contacts, surface analysis, surface cleaning, thermal desorption

INTRODUCTION

The surfaces and interfaces between the various layers of semiconductor device structures are fundamental components of solid state architecture. As device size has diminished and the scale of integration has increased, the quality of these interfaces has become an increasingly important concern. In addition, the presence of parasitic resistances and capacitances, such as those existing at contact interfaces, becomes more detrimental at higher operating powers and higher oscillation frequencies. For many devices, the losses that occur at the contact interfaces account for a large fraction of the total losses, and as such are responsible for significant impact on device

performance. Over the course of the development of semiconductor device technology, surface cleaning procedures have been devised to

- degrease and remove gross contamination,
- remove particulates and metal atom contamination, and
- remove surface oxides to provide surfaces as atomically clean as possible.

In practice, surface cleaning is as much of an art form or craft as it is a science; understanding of the surface composition and structure often lags well behind the successful application of processing steps. Procedures are frequently derived empirically with little detailed investigation of the chemistry or physics involved. Often, the meaning of the word "clean" varies depending on the surface conditions required for success with different processing steps, though surface impurity

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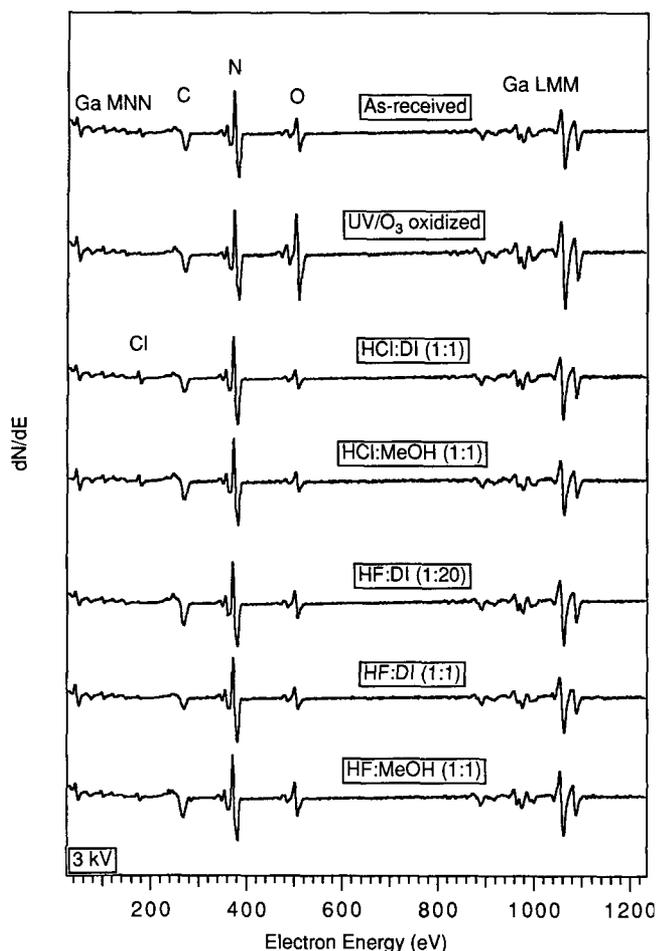


Fig. 1. AES survey spectra of GaN surfaces cleaned with different chemical treatments.

Table I. Relative Auger Peak Intensities from GaN Surfaces Cleaned with Different Wet Chemical Treatments

Treatment	O/N	C/N
As-received	0.39	0.28
UV/ozone oxidized	0.98	0.31
HCl:DI (1:1)	0.21	0.24
HCl:MeOH (1:1)	0.24	0.32
HF:DI (1:20)	0.33	0.38
HF:DI (1:1)	0.26	0.18
HF:MeOH (1:1)	0.33	0.41

concentrations may vary by orders of magnitude. Given that the sensitivity of surface analytical techniques for detection of submonolayer coverage is limited, there are inherent limits on the ability to show conclusively that a surface is truly atomically clean.¹

The goal of the surface cleaning study described in this paper is to determine the most effective choices of wet chemical cleaning and thermal desorption cleaning to use prior to metallization. In other areas of semiconductor device processing, the importance of interfacial cleanliness is already well established. The deleterious effects of residual contaminants, in-

cluding carbon and oxygen, on epitaxial film growth have been noted.²⁻⁴ There is increasing evidence in the literature that the cleanliness and preparation of the semiconductor surface prior to metal contact deposition play significant roles in the electrical performance of the contact interface as well.⁵⁻⁸ Thorough oxide removal is especially important, though it may well prove to be as persistent a challenge with Al-containing nitrides as has been the case with other Al-containing compound semiconductors.

Hydrochloric (HCl) and hydrofluoric (HF) acids as cleaning agents are compared in this study; the effects of aqueous vs methanol-based solutions are compared as well. Both HCl and HF solutions are known to remove oxides from Ga-based semiconductors.^{1,5,9,10} However, there is evidence that HF solutions are more effective for the electrical and chemical passivation of semiconductor surfaces, by "tying up" exposed dangling bonds with atomic hydrogen.^{1-3,11} The use of low-molecular weight organic compounds to passivate surfaces has also been investigated.¹ Methanol solutions have been used in this study and have been compared to aqueous solutions to observe any differences in thermal desorption behavior due to differences in the bonding of oxygen and carbon residues to the GaN surface.

EXPERIMENTAL

The GaN films used in this study were grown on (0001) 6H-SiC substrates by means of ECR plasma-enhanced molecular beam epitaxy (MBE); film thickness was approximately 300 nm. To allow efficient radiant heating of the samples for thermal desorption by means of a hot filament, a layer of tungsten was sputter-deposited on the back sides of the specimens. All samples had been exposed to air after removal from the growth chamber and had been stored in a desiccator for at least one week prior to each cleaning and analysis step. The UV/ozone apparatus used in this study consisted of a Hg lamp in room air. The sample surfaces were placed within 2-3 mm of the lamp surface; a typical UV exposure was 20 min. Except for the as-received and UV/ozone oxidized condition, the samples were solvent-cleaned with successive treatments of trichloroethylene (TCE), acetone, and methanol (MeOH) and immersed in each acid-cleaning solution for 3 min. All chemical reagents used in this study were high-purity electronic grade; no final water rinse was used. After each wet chemical cleaning, the specimens were immediately blown dry with N₂, affixed to the sample holder, and inserted into the vacuum system (base pressure 5×10^{-9} Torr and below) as quickly as possible to minimize exposure to room air. Each specimen received an unavoidable exposure to air for approximately 10 min during the time required to secure it to the sample block. For thermal desorption, the samples were heated under (UHV) conditions (base pressure of chamber $<5 \times 10^{-9}$ Torr) using a hot filament behind the sample block; samples were heated at a rate of approximately 75°C per min and held at the desired

temperature for 15 min before cooling down for analysis.

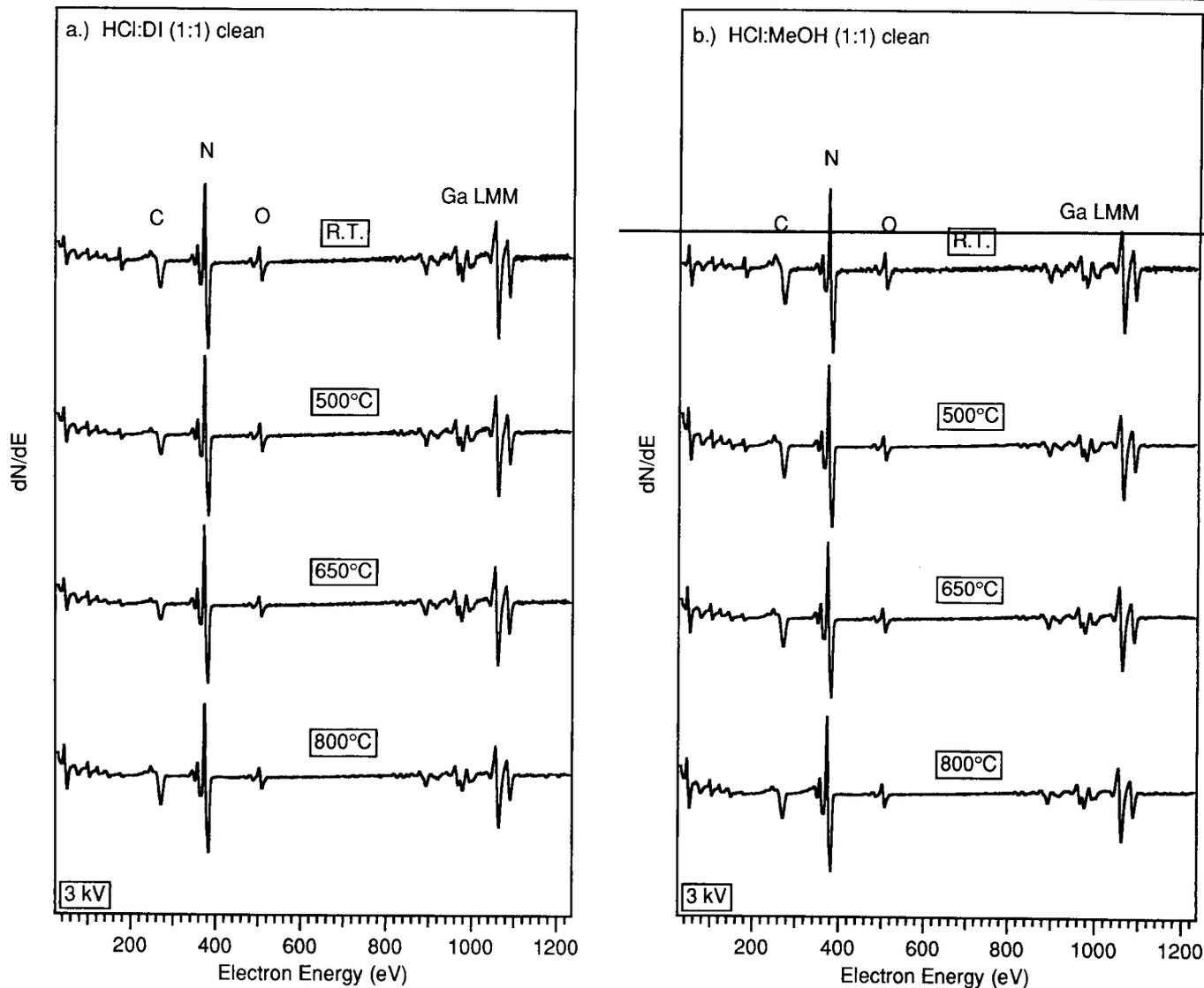
Auger electron spectroscopy (AES) was used to characterize the presence of chemical impurities on the cleaned and thermally desorbed GaN surfaces. This technique allows the detection of atoms in the first few atomic layers of a surface (1–5 nm), to a sensitivity of approximately 0.5–1%. This sensitivity corresponds under most conditions to submonolayer coverage, and thus is usefully applied to studying the contamination of surfaces by oxide and hydrocarbon deposition. Auger electron spectroscopy was performed at the North Carolina State University (NCSSU) Surface Science Laboratory, using a Perkin-Elmer PHI AES analysis system. Incident beam energy was 3 kV with a spot size of 1 μm . Spectra were acquired over the energy range 30–1230 eV, with an energy resolution of 1 eV/step. The thermal desorption procedures were performed in a chamber adjacent to the AES analysis chamber, and the desorption samples were transferred and kept under UHV conditions through-

out the analytical series.

RESULTS AND DISCUSSION

Ex-situ cleaning

Acquired AES spectra from GaN surfaces cleaned in a variety of wet chemical solutions are shown in Fig. 1, along with spectra for the typical air-exposed condition and from the UV/ozone oxidized surface. The label "DI" refers to deionized water; the term "solvent cleaning" refers to the conventional sequence trichloroethylene (TCE), acetone, and methanol (MeOH). For the purpose of graphing these data, the nitrogen peak-to-peak heights were all set to the same value so that the relative concentrations of oxygen and carbon could be compared. The associated data of peak height ratios are listed in Table I. The peak-to-peak heights of the oxygen and carbon signals are related to the peak-to-peak height of the nitrogen signal and indicate the relative abundance of oxygen-based and carbon-based surface coverages. The ratios



a b
 Fig. 2. AES survey spectra of HCl-cleaned GaN surfaces as a function of temperature.

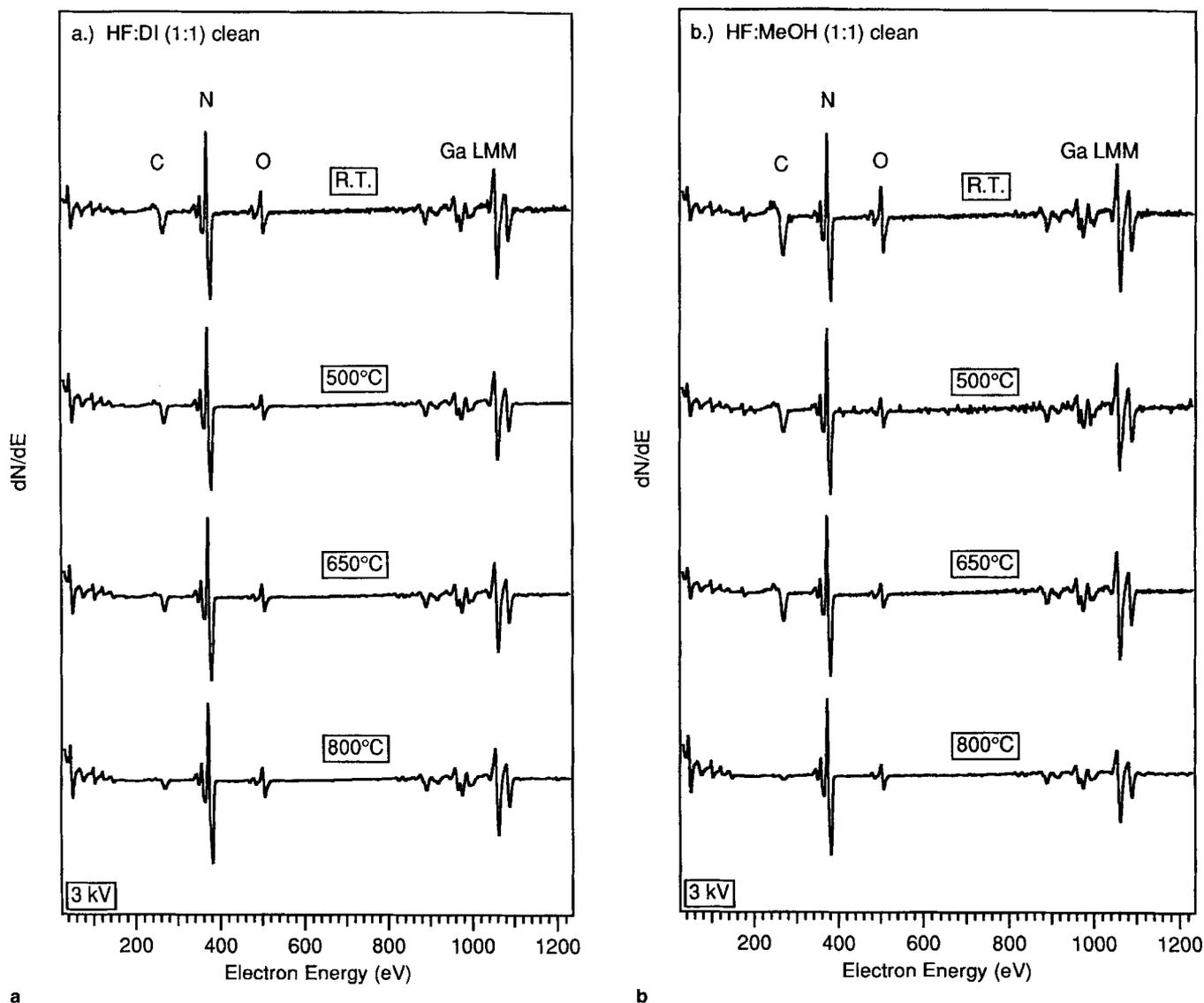


Fig. 3. AES survey spectra of HF-cleaned GaN surfaces as a function of temperature.

of peak heights have been used because, though the total number of counts in a given peak may vary from run to run, the *relative* peak intensities remain the same for a given surface.

The use of UV/ozone oxidation on the as-received surface resulted, not surprisingly, in a very large increase in O and a slight increase in C coverage. Of all the wet chemical cleaning methods compared here, the HCl:DI (1:1) solution yielded the lowest relative concentration of oxygen. A substantial decrease in O coverage after HCl- and HF-based cleaning treatments has been observed for both simple air-exposed and UV/ozone oxidized GaN surfaces, indicating the actual removal of surface oxides. The use of methanol to dilute the HCl solution resulted in an increase of both O and C, presumably due to the physisorption of methanol, though both HCl-based cleaning solutions resulted in lower O/N ratios than did any other surface condition examined. All of the remaining cleaning treatments showed larger relative concentrations of both O and C, with the excep-

tion of HF:DI, which produced an as-cleaned C/N ratio of 0.18. Of all the HF cleaning treatments examined, the HF:DI (1:1) treatment gave the lowest O and C concentrations. The highest concentrations of O and C observed were found on the HF:MeOH-treated surface, slightly higher than those on the as-received surface. Again, the adsorption of methanol is presumably contributing to the higher peak intensities for O and C, but for HF:MeOH these intensities are noticeably higher than the same peak intensities from the HCl:MeOH sample. The presence of measurable amounts of O and C on all of the air-exposed surfaces is not surprising, given the fact that at atmospheric pressure, the time required to adsorb one monolayer is less than 10^{-9} s.

Thermal Desorption

The effects of heating GaN surfaces on the presence of O and C are shown in Fig. 2 and Fig. 3. The associated data of peak height ratios are listed in Table II. The following HCl-based and HF-based

Table II. Relative AES Peak Intensities for GaN Surfaces as a Function of Temperature and Surface Treatment

Desorption Temperature	HCl:DI (1:1)		HCl:MeOH (1:1)		HF:DI (1:1)		HF:MeOH (1:1)	
	O/N	C/N	O/N	C/N	O/N	C/N	O/N	C/N
As-cleaned	0.21	0.24	0.23	0.31	0.26	0.18	0.41	0.33
500°C	0.18	0.17	0.16	0.27	0.16	0.16	0.18	0.32
650°C	0.14	0.14	0.16	0.25	0.17	0.13	0.16	0.24
800°C	0.15	0.26	0.15	0.21	0.19	0.08	0.16	0.05

cleaning methods were compared: HCl:DI (1:1), HCl:MeOH (1:1), HF:DI (1:1), and HF:MeOH (1:1). All of the desorption series show a gradual decrease in the presence of O and C through 800°C. However, small but detectable amounts of O and C were still present on the GaN surfaces even after heating to 800°C. During the 800°C heating steps, residual gas analysis in the ultra high vacuum heating chamber revealed the presence of small amounts of gas-phase Ga released by the samples, indicating the beginnings of GaN decomposition. The relative proportions of O and C that remained on each surface after the desorption series were different for the HCl-cleaned and HF-cleaned samples: after the 800°C desorption step, the HCl-cleaned surfaces showed the lowest O levels, while the HF-cleaned surfaces showed the lowest C levels.

Though the acid:MeOH-treated surfaces naturally exhibited higher C peak intensities before the thermal desorption, both the HCl:MeOH- and HF:MeOH-treated samples showed lower C peak intensities than the HCl:DI and HF:DI-treated samples after the 800°C heating step. This observation is consistent with the expectation that the methanol is primarily physisorbed, and its occupation of many available surface sites protects the surface from coverage with more strongly bound C-containing species. This effect is much more pronounced with the HF cleaning than with HCl; for both the HF:DI and the HF:MeOH-cleaned surfaces, the C/N peak height ratios had diminished drastically after the 800°C heating step. This substantial difference in thermal desorption behavior supports the expectation that HF is more effective than HCl at passivating active sites on the surface, or at least active sites with respect to carbon bonding. On all of the samples heated to 800°C, a certain amount of the initial oxide coverage stubbornly refused to desorb. Approximately similar O/N signal intensities remained after the 800°C desorption, with the HF:DI-treated samples retaining somewhat more oxygen than the others.

The results of other recent thermal desorption experiments at NCSU performed in vacuum on similar GaN films have so far shown that O and C do not completely disappear, even to temperatures where GaN decomposition occurs (>800–900°C). These observations are in contrast to the well-established and usually straightforward thermal behavior of the GaAs surface oxide.^{12,13} However, Ingrey et al. have also reported difficulty in the complete thermal removal of

oxygen from InGaAs surfaces.¹⁴ The presence of active species to assist in surface removal (e.g., hydrogen plasma, ion bombardment, etc.) and heating in a NH₃ flux to inhibit GaN decomposition are expected to produce substantially cleaner surfaces than simple thermal desorption in vacuum. An important consideration in this regard is the current concern with the role of H and its compensation of acceptor impurities. The search for a method of obtaining surfaces as atomically “pristine” as possible must necessarily include the characterization of any surface damage or other property degradation that may occur in connection with surface cleaning procedures. The use of ionized, accelerated gas-phase species in cleaning methods is likely to cause some surface damage, depending on the kinetic energy and mass of the ionized species. It is also possible that some surface damage can be caused by the wet chemical cleaning steps as well; there are indications that even short-term exposure to aqueous acid cleaning solutions can cause microroughening of GaAs surfaces, which increases with time of exposure.¹⁵

CONCLUSIONS

The results of surface cleaning experiments conducted in this study suggest that the choice of cleaning solution to use for GaN surfaces depends upon whether thermal desorption in vacuum is to be performed prior to subsequent processing steps. Of the wet chemical cleaning methods examined here, the HCl:DI (1:1) solution resulted in the lowest levels of residual oxygen and carbon on the as-cleaned, air-exposed surfaces. All of the cleaning methods examined that involved HF were found to leave more O and C on the surface initially. By contrast, it was found that HF-based cleaning treatments resulted in more effective desorption of C from the surfaces. In contrast to the results typically observed in the thermal desorption cleaning of GaAs, complete removal of O and C from air-exposed GaN surfaces was not seen using vacuum heating alone, even to temperatures where GaN decomposition began to occur (>800–900°C). Upon heating to 800°C, the HF-cleaned surfaces, especially the HF:MeOH sample, experienced substantial removal of C; however, the residual oxygen coverage did not drop below the levels seen on the HCl-cleaned surfaces. Further in-situ processing beyond simple wet chemical cleaning and thermal desorption is necessary to achieve spectroscopically clean GaN surfaces.

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