# Surface states and surface oxide in GaN layers

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Surface photovoltage spectroscopy, photoluminescence, Auger electron spectroscopy and x-ray photoelectron spectroscopy were used to correlate the chemical changes induced by HCl etching of GaN surface to changes in the yellow luminescence related states, through their manifestation in surface photovoltage. The results show a correlation between a removal of the gallium oxide from the surface and a reduction of the yellow luminescence related transition in the surface photovoltage spectra. Based on this observation, it is suggested that the well known yellow luminescence is emitted from surface states associated with the gallium oxide that decorates the free surface and possibly also the substrate interface and internal grain boundaries. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1330553]

## I. INTRODUCTION

Despite the rapid development in GaN growth and device technologies, most of todays GaN is still grown on substrates to which it is both lattice and thermally mismatched, resulting in high concentrations of structural defects.[1] These grain boundaries, dislocations, and point defects are commonly observed in the form of a high density of electronic states in the forbidden gap. Thus, it is possible to obtain an indirect assessment of crystalline quality using deep level spectroscopies. Of the various spectroscopic methods used by GaN growers, photoluminescence has probably been the most common. A frequent finding is that when GaN films are exposed to super-band gap illumination, a characteristic yellow luminescence (YL) is emitted. This luminescence appears as a broad spectral peak, centered around $\sim560$ nm (photon energy of $\sim2.2$ eV).[2] Hence, under identical excitation conditions, the ratio of the band edge to YL peak intensities can be used as an informal figure of merit, indicating the film quality.[3,4]

Many studies have so far attempted to uncover the physical nature and the chemical source of the YL. The accumulated information illustrates the physical nature of the YL as an electronic transition taking place between a shallow donor and a deep acceptor widely distributed around $\sim2.2$ eV below the condition band minimum.[5] It has also been shown that the YL related states are not evenly distributed in the bulk but rather decorate grain boundaries,[6] of which the free surface is but a special case. Using surface photovoltage (SPV) spectroscopy, a surface sensitive deep-level spectros-

copy, it was shown that the YL related states possess a significant density at the free surface.[7]

Theoretical studies have shown that, based on its energy position, $V_{\text{Ga}}^{-3}$ is the most probable acceptor to cause the YL.[8] It has also been shown that $V_{\text{Ga}}^{-3}$ can form a stable complex with the nearest neighbor $O_N^+$. Considering the low formation energy of the complex $(V_{\text{Ga}}-O_N)^{-2}$ it was suggested that oxygen contaminants enhance the formation of Ga vacancies during growth.[8,9] The role of $V_{\text{Ga}}$ in the YL was later confirmed experimentally by positron annihilation,[10] while the presence of oxygen was shown to be correlated with the presence of several luminescence features, including the YL.[11] However, studies of the influence of oxygen on the electronic properties of GaN have suggested[12] or challenged[13] its role as a shallow donor but have not related directly to its possible role in the YL.

The purpose of this work was to examine experimentally whether oxygen is directly involved in the YL related transitions or only indirectly influences the formation of YL related states during the growth. We have previously attributed the observed YL-related transition in SPV conclusively to a discharge of YL-related *surface* acceptor states negatively charged in equilibrium.[7] The approach employed in this work was, therefore, to check the influence of oxygen removal from the free surface of GaN, as evidenced by x-ray photoelectron spectroscopy (XPS) and Auger Electron Spectroscopy (AES), on the SPV signature of the YL related states.

## II. EXPERIMENTAL DETAILS

The GaN films used in this work were grown using metalorganic vapor phase epitaxy on (0001) oriented $12\times12$ mm sapphire substrates.[7] The samples were $\sim2$ $\mu$m thick with an effective doping level of $n\sim4\times10^{17}$ cm$^{-3}$. After the

growth, each sample was cut. SPV spectra were then obtained from the center of each half. One half was kept as a reference while the other etched in an aqueous solution of 36% HCl for 20 s and then blown dry with $N_2$ gas. The two halves were then introduced into the XPS/AES vacuum chamber. After the XPS/AES measurements, the samples were removed from the vacuum and photoluminescence and SPV spectra were obtained. SPV spectra and XPS/AES measurements were repeated on the same samples after a few days. For references, XPS spectra on an oxidized Ga sample and sputter cleaned GaN and Ga samples were recorded.

XPS and AES measurements were carried out in an ultrahigh vacuum ($3 \times 10^{-10}$ Torr) using a 5600 Multitechnique System (PHI, USA) with a spherical capacitance analyzer and monochromatized Al $K_\alpha$ radiation ($h\nu = 1486.6$ eV) source at a pass energy of 117 eV and an energy interval of 0.125 eV step. Photoelectron spectra were acquired over a 400 $\mu$m diameter spot. The acquisition time was kept constant for all the measurements. $4f_{7/2}$ Au peak energy, obtained from a sputter cleaned Au sample, was used as reference.

Photoluminescence was excited using a HeCd laser (325 nm, 10 mW). The emitted luminescence was monochromatized, filtered, and sensed using a GaAs photomultiplier tube.

SPV spectroscopy measurements were conducted inside a dark Faraday cage in nitrogen atmosphere. The SPV was measured by monitoring changes in the surface work function. These changes were monitored using the Kelvin probe technique. The latter measures the contact potential difference (CPD), i.e., the difference in work function, between the semiconductor free surface and a vibrating reference probe.[14,15] The photovoltage is defined as the difference between the CPD values in the dark and under illumination. A commercial Kelvin probe (Besocke Delta Phi, Germany), with a sensitivity of ~1 mV, was used in all measurements. To provide a common background for the probe and the sample an Ohmic ''back contact'' ''of indium was soldered on the periphery of the sample surface, while the Kelvin probe was brought to a distance of about 1 mm from the sample over the free part of the surface. We emphasize that as the back contact was not illuminated, the results given as follows were not influenced by either defects at the metal GaN interface or the exact resistance characteristics of the contact.[14]

## III. RESULTS

### A. SPV spectroscopy

Figure 1 shows CPD spectra of the same sample, as-grown and after etching in HCl. In both spectra, a transition is observed around photon energy of 3.4 eV indicating *n*-type conductivity. Another transition is observed between 1.6 and 2.9 eV. This transition correlates with the range of the well known YL that was also observed in our samples. This correlation occurs because this technique senses the ''yellow absorption'', an inverse transition to the ''yellow emission'' observed in photoluminescence.[7,16]

A key observation is that the CPD values on the left edge of the curves (marked by arrows, labeled ''dark'') were
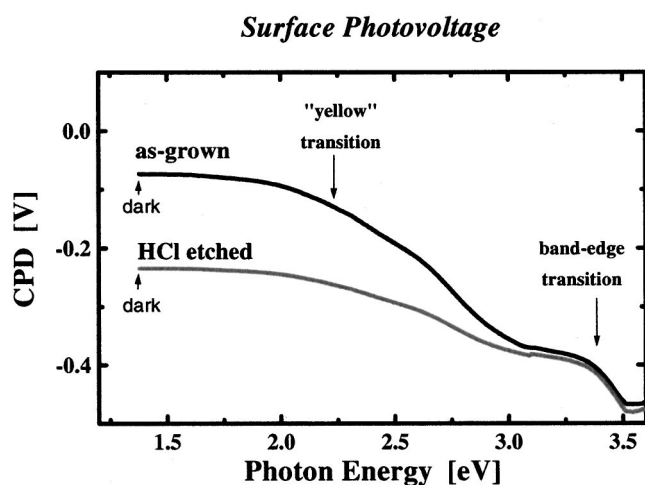


FIG. 1. CPD spectra obtained before and after HCl etching from the same GaN film.

obtained *in the dark* (with subsequent illumination scanned from low to high photon energies). The dark CPD value is reduced significantly, by as much as ~0.16 eV after the etching. However, beyond the photon energy range of the yellow absorption the two curves practically overlap. Therefore, the two curves differ in the dark CPD values and the size of the transition in the yellow absorption photon energy range. Both of these values become smaller after the etching. Most of the SPV signal was restored within two days after the etching. The same procedure applied to samples with rough surfaces, densely covered with hexagonal pits, resulted in consistently higher differences, presumably due to the relatively larger surface areas of these samples.

### B. Photoluminescence

Figure 2 shows photoluminescence spectra before and after the etching. Both spectra show the YL peak, a wide peak centered at ~2.2 eV, and a narrow band edge peak at ~3.4 eV. After the etching, the intensity of the band edge
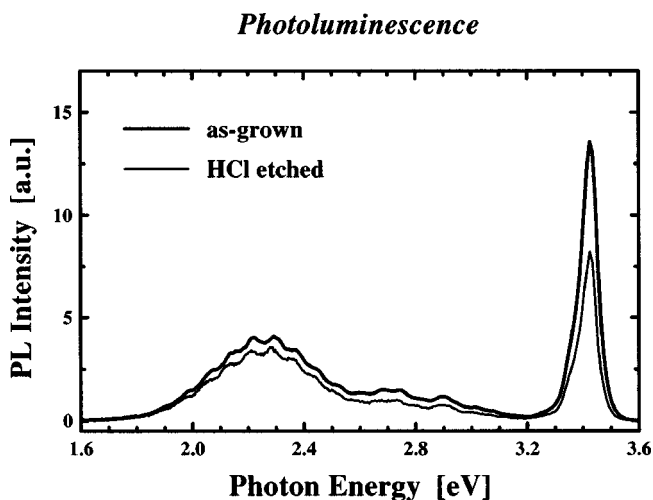


FIG. 2. Photoluminescence spectra obtained before and after HCl etching from the same GaN film.
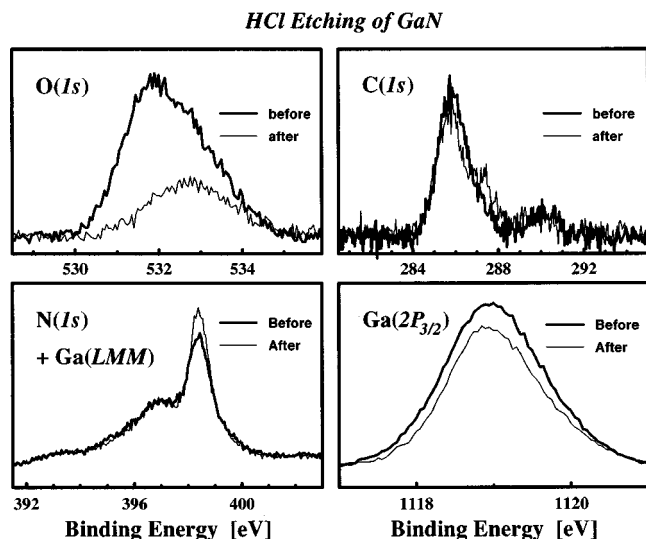
**HCl Etching of GaN**



FIG. 3. O($1s$), C($1s$), Ga($2p_{3/2}$), and N($1s$)+Ga($LMM$) photoemission peaks obtained before and after HCl etching from the same GaN film.

**O($1s$) Peak on GaN Surface**



FIG. 4. Gaussian fit of O($1s$) photoemission peak of Fig. 3.

peak decreases to 68% of its as-grown value, while that of the YL peak decreases to 84% of its as-grown value. Since the absorption coefficient is considerably higher for band edge photons as compared to sub-band gap photons,[17] the band edge peak is likely to be much more sensitive to changes at the surface as compared to the YL peak. The relative weights of the bulk and surface luminescence components may thus reverse the picture in cases where changes take place only at the surface.

## C. X-ray photoelectron spectroscopy

### 1. Gallium nitride

Figure 3 compares O($1s$), C($1s$), N($1s$) +Ga($LMM$), and Ga($2p_{3/2}$) photoemission peaks obtained from the surface of GaN sample as-grown and immediately after etching in HCl (as etched). The main C($1s$) peak on the surface of the as-grown GaN was centered at 285.7 eV, typical of hydrocarbon contaminants on GaN.[18] Additionally, a small peak is observed at a binding energy of 289.9 eV. After etching, there is no significant change of the overall peak area, however a small peak is superimposed on the high energy ''shoulder'' of the C($1s$) peak at 287.8 eV. The N($1s$) peak becomes more intense after the etching, while changes in the Ga($LMM$) are below the resolution of the measurement. The Ga($2p_{3/2}$) peak is centered at 1119 eV in the as-grown sample and is made less intense after the etching with its peak centered at a binding energy of 1118.4 eV.

The most significant change is observed in the O($1s$) peak, where both a major shift of the binding energy and a significant drop of the intensity are observed after the etching. To investigate the details of the change, the O($1s$) peaks are redrawn and fitted with Gaussians in Fig. 4. The O($1s$) peak of the as-grown sample decomposes into two Gaussian peaks, one centered at 531.6 eV, whereas the other is centered at 532.75 eV. The former is completely removed after the etching, while the latter is only decreased in intensity.
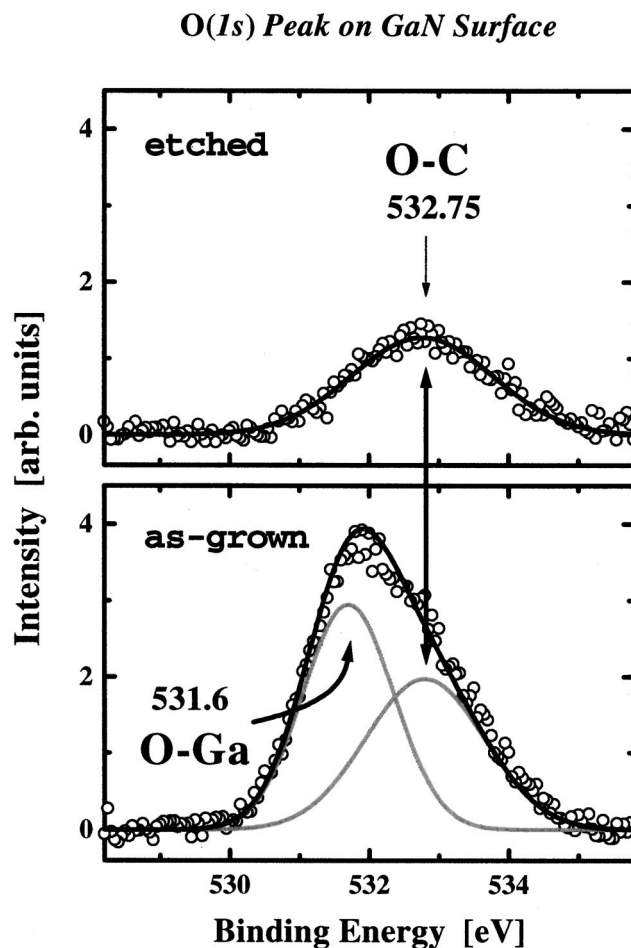
The spectra measured on the as-grown sample are almost fully restored in the etched sample after storage of ten days in air.

### 2. Oxidized gallium

The spectra of Ga($2p_{3/2}$), C($1s$), and O($1s$) were also obtained before and after sputtering of an oxidized Ga reference sample. Figure 5 compares these peaks before and after sputtering steps of 30 and 300 s. Before the sputtering, the O($1s$) peak is very similar to the one obtained from as-grown GaN. It is composed of two Gaussian components: one centered at a binding energy of 531.6 eV, and another centered at a binding energy of 532.7 eV (the fit is omitted to avoid cluttering Fig. 5). The latter is removed after 30 s of sputtering and both are removed after 300 s of sputtering.

The as-mounted C($1s$) peak is composed of two peaks. The main peak is centered at 285.7 eV, likely associated with hydrocarbons, and another peak is centered at 289.9 eV, typical of carboxylic group bonding.[19] Both peaks diminish after 30 s of sputtering, correlating the removal of the O($1s$) 532.7 eV component.

As mounted, the Ga sample shows a Ga($2p_{3/2}$) peak composed of two Gaussian components: the larger of the two is centered at binding energy of 1119.1 eV, typical of Ga$_2$O$_3$
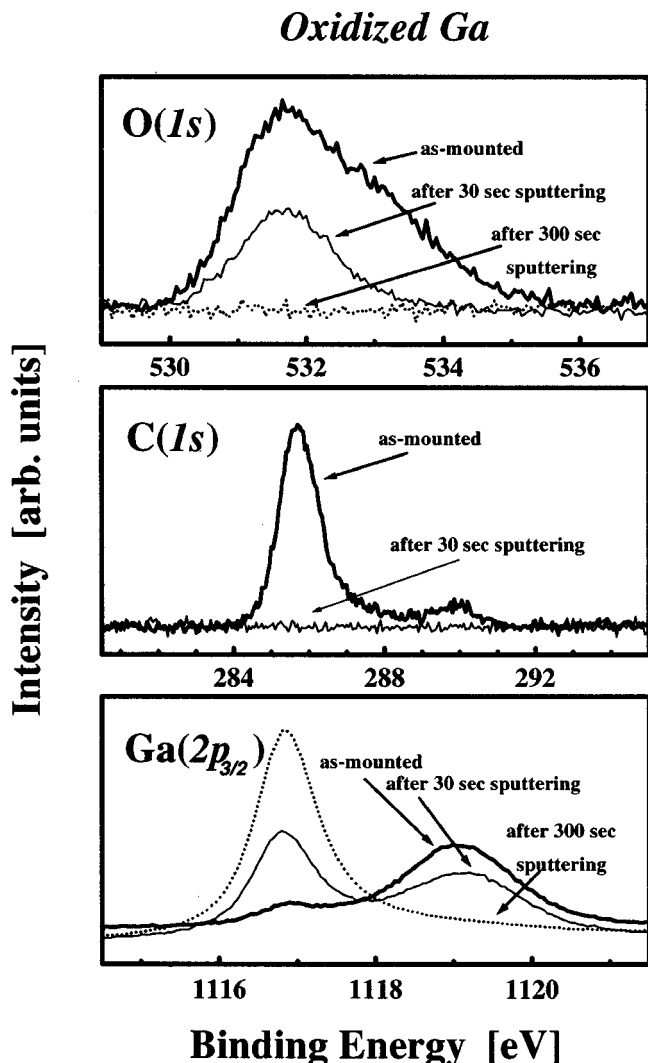
## Oxidized Ga



FIG. 5. O(1s), C(1s), and Ga(2p_{3/2}) photoemission peaks obtained before and after sputtering of oxidized Ga.

(Ref. 20), and the smaller is centered at 1116.85 eV, typical of Ga.[21] The former subsides with the sputtering while the latter is made more intense.

### D. Auger electron spectroscopy

Since the N(1s) peak coincides with the Ga(*LMM*) peak, assessment of changes in atomic concentrations by the XPS technique is difficult. To avoid that, AES was used. Figure 6 compares the atomic concentrations of Ga, N, C, and O at the surface of the as-grown sample and the etched sample both as etched and after storage. The main change induced by the HCl etching is observed in the concentration of oxygen, which decreased from 25% to 8%. After storage, the concentration of oxygen was mostly restored and increased to 21%. Residual Cl concentration of 6% observed in the as-etched sample reduced to 0.2% after the storage.

### IV. DISCUSSION

The XPS chemical analysis shows that the surface of our as-grown GaN is contaminated with carbon and oxygen phases. The C(1s) peak consists mainly of two components
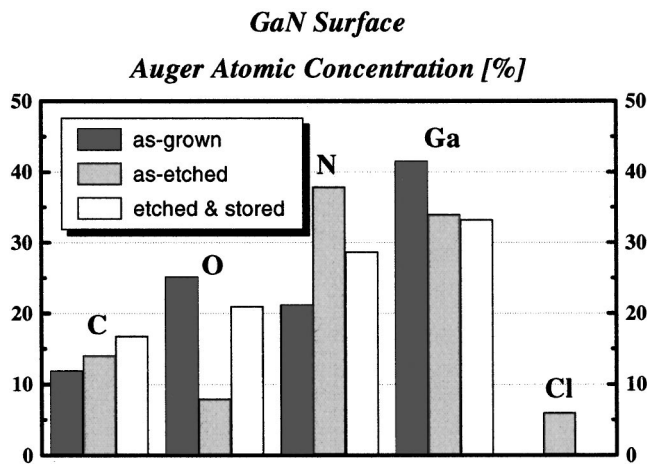


FIG. 6. AES atomic concentrations of Ga, N, C, and O on the surface of as-grown, as-etched, and for the etched GaN sample after storage in air.

(Fig. 2). The main one, centered at a binding energy of 285.7 eV, is commonly attributed to the presence of hydrocarbon species.[18] The other component appears at a higher binding energy (289.9 eV) and is attributed to the presence of the carboxylic group (COOH).[19] After etching in HCl, a new peak at about 287.7 eV forms and is assigned to C–Cl bonds formed with the residual Cl (a binding energy of 287.8 eV was reported for $CH_2Cl_2$).[21] The relative part of carbon in the atomic concentration calculated from AES increases from a value of 12% as grown to a value of 14% as etched. However, the total area under the C(1s) peak remained nearly unchanged after etching. Hence, this increase seems to manifest a reduction in the concentration of the other species at the surface rather than an increase of the carbon concentration.

As opposed to carbon, oxygen shows a major change after etching. The atomic concentration of oxygen in as-grown GaN sample is 25%. This concentration decreases to 8% after the etching. The as-grown O(1s) peak (Fig. 4) decomposes into two Gaussian components. One, centered at a binding energy of 531.6 eV, seems to be removed by the HCl etch, while the other, centered at 532.7 eV is only slightly reduced. These same two components are also identified at the surface of the oxidized Ga sample (Fig. 5). Sputtering of this sample for 30 s removes the 532.7 eV peak concurrently with a removal of the C(1s) peak. This correlates the presence of the oxygen peak at 532.7 eV with the presence of C–O bonding. The same correlation is evident in the GaN sample, where the 532.7 eV component of the O(1s) peak is the only one that remains after etching, while the C(1s) peak is mainly unchanged. After 30 s of sputtering, only oxygen and Ga are observed on the surface of the oxidized Ga sample. The O(1s) peak is composed of a single Gaussian component centered at 531.7 eV. Therefore, we conclude that this binding energy represents an oxide of Ga. Indeed, this value is also in good agreement with reported values for $Ga_2O_3$.[22] Hence, we infer that HCl efficiently etches Ga oxide, but has only minor effect on carbon contamination species.

Before etching the GaN, the Ga concentration (42%) exceeds that of N (28%). After the removal of the Ga oxide, the concentration difference decreases and reverses to 34% and 37%, respectively. Clearly, the as-grown GaN sample is covered with Ga oxide, which increases the concentration of Ga within the Auger electron escape depth, while after the etching, most of this depth seems to be occupied by GaN.

While the XPS and AES spectra were obtained in vacuum, the SPV measurements were done in nitrogen atmosphere, after exposure to air. Therefore, considerable re-oxidation is likely to have taken place prior to the measurement. Nevertheless, a decrease in the magnitude of the ''yellow'' SPV transition is still clearly observed. The amount of decrease is not uniform in wavelength and is larger at the YL range and below, suggesting a decrease in the density of the related surface states. Combining this observation with the identification of the etched oxide as Ga–oxide suggests that the surface states responsible for the yellow transition in SPV are present in the Ga-oxide covering the free surfaces of GaN layers and/or at the interfaces of this oxide with GaN. The SPV yellow transition has already been shown to relate to the ubiquitous YL. However, while SPV senses YL-related states at the surface, the YL is highly likely to originate in large part from surfaces other than the free surface.[16] These include internal surfaces such as the interface with the sapphire substrate or intergrain interfaces.[6] Internal surfaces can neither be attacked by the etching nor can they be sensed by the SPV setup employed in this experiment (surface ''back contact''). Hence, the overall small decrease of the YL peak (16%) observed after the etching is in line with our interpretation. To account for the stronger decrease of the band edge luminescence peak, we refer to differences in absorption coefficients between band edge and sub-band gap luminescence.[17] Both of these components of the spectra may form anywhere within the volume penetrated by the exciting laser beam. However, photons generated within the semiconductor still have to traverse the material on their way out to reach the detector. During this journey, there is a chance that they are reabsorbed. For the yellow photons, this probability is small because their energy is well within the forbidden gap (the material is transparent to these photons). For band edge photons, the probability is relatively high. As a result, the probability to detect band edge photons generated near the surface is higher as compared to band edge photons created deeper inside the material. This makes the band edge emission more surface sensitive as compared to the yellow emission. Hence, surface changes that cannot be detected by optical spectroscopies, e.g., etching induced nonradiative surface recombination,[23] may have a stronger effect on band edge luminescence as compared to their effect on the YL, and may thus account for at least part of the 16% difference. Another possible mechanism could be a decrease of the absorbed intensity of the excitation light. Since the yellow emission intensity saturates already at low excitation intensities,[24] one may expect *any* decrease in the absorbed intensity to have a stronger affect on the band edge peak as compared to the yellow one. The precise mechanism, however, remains a subject for further research.

Elsner *et al.* have used a density-functional approach to examine theoretically the influence of oxygen on the growth of GaN.[25] They found that oxygen tends to segregate to (1010) surfaces. They suggest that during a Stranski–Krastanov growth, this segregation of oxygen inhibits the complete coalescence of islands leaving interisland spaces, whose walls are decorated with complexes of $V_{Ga}$ and oxygen. These complexes were previously shown by Neugebauer and Van de Walle to be associated with the YL related states.[8] Indeed, cathodoluminescence results show that the YL is mainly emitted from grain boundaries.[6] In this work, we show that the removal of surface oxide correlates with a reduction in the yellow SPV signal attributed to the surface component of the YL related states. This adds to the accumulated knowledge in showing that the YL originates from grain boundaries and is correlated to the presence of oxide therein, whereas the free surface is but a special case of a grain boundary. This assignment of YL to grain boundary and surface defects has already been used successfully to describe transport-related phenomena in GaN films.[16] Furthermore, the observations reported herein suggest that oxygen may be involved in the YL more directly than just enhancing the formation of the related states during the growth, as suggested by theoretical studies.

## V. CONCLUSION

HCl etching of GaN films is shown to remove Ga oxide from the surface while reducing the SPV signature of the YL related states. These results support the assignment of YL to grain boundaries. It is suggested that oxygen, present at the free surface and also decorating other grain boundaries, is involved in producing this luminescence. Also, its role may not be limited to the growth phase in stabilizing Ga vacancies, but rather is more direct and takes an active part in establishing the related states.

## ACKNOWLEDGMENTS

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