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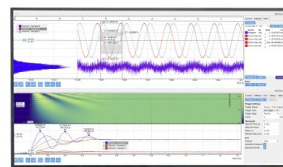
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GaN surface states investigated by electrochemical studies

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We present a systematic study of electrochemically active surface states on MOCVD-grown n-type GaN in aqueous electrolytes using cyclic voltammetry and impedance spectroscopy over a wide range of potentials and frequencies. In order to alter the surface states, the GaN samples are either etched or oxidized, and the influence of the surface treatment on the defect-mediated charge transfer to the electrolyte is investigated. Etching in HCl removes substoichiometric GaO_x, and leads to a pronounced density of electrochemically active surface states. Oxidation effectively removes these surface states. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4977947>]

Recently, group-III nitride materials have attracted considerable interest in fields such as photo-electrochemistry and photocatalysis due to the favorable energy position of their band edges with respect to the redox levels of relevant species in liquid electrolytes.^{1–6} The flexibility in doping III-nitrides in a controlled way enables the deterministic generation of either holes (for n-type doping) or electrons (for p-type doping) at the surface under illumination to selectively drive oxidation or reduction reactions, respectively. The presence of electronic defect states directly at or close to the semiconductor surface is known to influence charge transfer at semiconductor electrodes. Such electronically active surface defects, e.g., are responsible for surface band bending determining the separation of photo-excited charge carriers and laterally inhomogeneous charging of the surface due to local charge trapping. For a quantitative analysis of the influence of surface states on electrochemical processes and Schottky diodes, it is important to understand the mechanisms governing charge transfer across the GaN surface. In a previous work,⁷ we have combined the contact potential difference (CPD) and photoconductivity measurements to investigate electronic processes at or close to illuminated GaN surfaces. We could show that localized surface defect states play a crucial role in the kinetics of photo-generated charges. Sachsenhauser *et al.* have investigated the charge transfer across the n-type SiC/electrolyte interface.⁸ They performed cyclic voltammetry and impedance spectroscopy measurements over a wide range of potentials and frequencies. Adding the ferricyanide/ferrocyanide redox couple to the electrolyte made it possible to reveal the contribution of surface states to the charge transfer and determine the energy distribution of the surface states. In this work, we have investigated whether or not electrically active states located in the GaN band gap are also involved in the charge transfer to an electrolyte. To this end, we have systematically studied the n-type GaN grown by metal-organic chemical vapor deposition (MOCVD) in aqueous electrolytes using cyclic voltammetry and impedance spectroscopy. Different surface

treatments are applied in order to alter the surface states and investigate the influence of these on the details of defect-mediated charge transfer.

(0001) GaN layers grown by MOCVD n-type doped with a carrier concentration between $1.4 \times 10^{17} \text{ cm}^{-3}$ and $3.0 \times 10^{18} \text{ cm}^{-3}$ - in order to study the influence of the width of the space-charge region (SCR)—were purchased from Lumilog. Ohmic top contacts (Ti/Al/Ti/Au, 20/80/10/90 nm) were deposited by electron beam deposition and annealed in nitrogen for 5 min at 750 °C.

In order to alter the surface states prior to the electrochemical characterization, two different surface treatments are applied to the samples. First, all samples were cleaned in acetone and isopropanol in an ultrasonic bath. Next, the as-grown samples were etched in HCl for 5 min. For GaN it is known that oxygen is chemisorbed at the surface⁹ forming a thin substoichiometric GaO_x layer,^{10,11} which can be significantly reduced by etching in HCl or HF solutions.^{11–13} A stoichiometric and stable oxidation of the samples was achieved by treating them for 10 min in hot H₂SO₄:H₂O₂ followed by 5 min in oxygen plasma at 200 W. The samples will be referred to as “etched” and “oxidized,” respectively, in the following. The respective surface treatments were validated by X-ray photoelectron spectroscopy (XPS) measurements (see Table I).

Aqueous electrolytes were prepared from ultrapure water, containing 50 mM Tris and 100 mM NaCl as the supporting electrolyte. The buffer was adjusted to pH 7.3. Prior to the measurements, the electrolyte was degassed with a vacuum pump for 30 min, followed by thorough purging with nitrogen for 30 min. To minimize oxygen contamination, a constant flow of nitrogen was maintained over the electrolyte during the measurements.

For the electrochemical measurements, a homemade PEEK holder was used, which exposed a circular active electrode area of 0.28 cm² and shielded the contacts as well as the electrical wiring from the electrolyte. In order to minimize the native oxidation in air, the etched samples were measured immediately after the surface treatment within a few minutes. The electrolyte volume was fixed at 300 ml. All

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TABLE I. Relative contribution of the Ga3d core level components obtained from XPS measurements for GaN electrodes for the different applied surface treatments. For this purpose, a standard procedure is used, where the XPS spectra are fitted with a certain number of peaks using the program CasaXPS and the contents are determined as the ratio of the areas of different peaks.

Sample	Ga3d core level components		
	Ga – N [%]	Ga – O _x [%]	Ga ₂ O ₃ [%]
As-grown	65	35	–
Etched	63	37	–
Oxidized	38	30	32

measurements were performed at room temperature using a VoltaLab PGZ301 potentiostat in a three-electrode configuration^{14,15} with an Ag/AgCl reference electrode and a platinum wire as counter electrode. The measurements were performed in a Faraday cage to guarantee electrical shielding. All cyclic voltammograms (CVs) were obtained at a scan rate of 250 mV/s. Impedance spectra were recorded at different DC bias (between -1.2 V and 0.8 V vs. Ag/AgCl) in single-sine mode in a frequency range between 0.1 Hz and 50 kHz, with the AC modulation amplitude set to 50 mV. ZSimpWin software¹⁶ was used to analyse the measured impedance data.

A schematic view of the electronic structure near the surface of the n-type GaN is shown in Fig. 1(a). In the dark, an upward band bending of approximately 1 eV is expected due to electrons captured by surface states.^{9,17–19} Applying a bias in the dark between the GaN sample and a surface contact (electrolytic or metallic) leads to changes of charge density in the SCR and at the surface which results in a change of the band bending. The charge exchange between the SCR and the surface involves hopping of electrons via localized states in the shallow defect band. Figure 1(b) shows a comparison of the current-voltage (I-U)-characteristics of Pt/GaN Schottky diodes processed on oxidized and etched GaN surfaces to illustrate the general importance of surface states for GaN devices. Immediately after the respective surface treatment 15 nm of Pt were deposited by electron beam deposition on the GaN samples with a carrier concentration of $1.4 \times 10^{17} \text{ cm}^{-3}$. The I-U-characteristics is significantly affected by the surface treatment. A Schottky diode like behavior with an on-off-ratio of about three orders of magnitude is observed for the etched sample. However, the oxidized sample shows a predominantly ohmic behavior. The observed differences in the electrical characteristics of the diode strongly suggest a change in the surface states due to the applied surface treatment. The existence of a Schottky barrier in the etched sample can be explained by a higher density of defects causing a stronger pinning of the Fermi level by surface defects. On the other hand, the observed ohmic behavior for the oxidized sample indicates a low density of defects. We want to point out that we have to distinguish between two types of defect states - deep and shallow ones. According to our understanding, the surface defects are deep and strongly localized defect states which are responsible for the band bending and formation of a Schottky barrier.

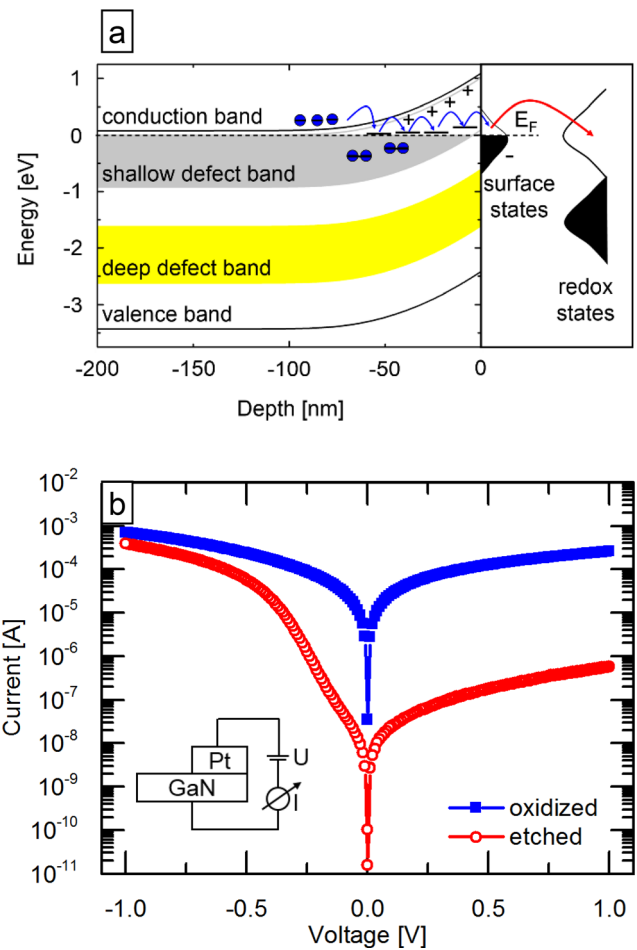


FIG. 1. (a) Schematic view of the electronic structure near the GaN/electrolyte interface. The possible hopping processes are illustrated with blue arrows. (b) Comparison of the I-U-characteristics of Schottky diodes processed on an oxidized (filled blue squares) and etched (empty red circles) GaN surface.

In contrast, shallow defects are delocalized and are needed to achieve good ohmic contacts.

Changing the contact from metallic to electrolytic (and using GaN samples with a carrier concentration of $3.0 \times 10^{18} \text{ cm}^{-3}$), cyclic voltammograms (CVs) and electrochemical impedance spectra have been recorded to investigate the influence of surface states on the charge transfer to the electrolyte. Figure 2(a) shows CV curves of oxidized and etched GaN electrodes. As expected for n-type semiconductor electrodes, no Faradaic currents are observed at positive potentials: therefore, the experimental data is only shown in the cathodic regime. For the oxidized sample, for potentials more negative than -1.0 V vs. Ag/AgCl, a cathodic current tentatively assigned to hydrogen evolution is observed. Assuming that charge transfer only involves the conduction band and redox states in solution (see Fig. 1(a)), this behavior is expected. However, for the etched sample, a cathodic current is already observed for potentials close to -0.5 V vs. Ag/AgCl, for which no direct charge transfer between the conduction band and redox levels in the electrolyte is expected. Thus, surface states with energy levels located in the band gap could be responsible for the charge transfer at this bias regime. Whether the surface states are also involved in the charge transfer across the GaN/electrolyte interface,

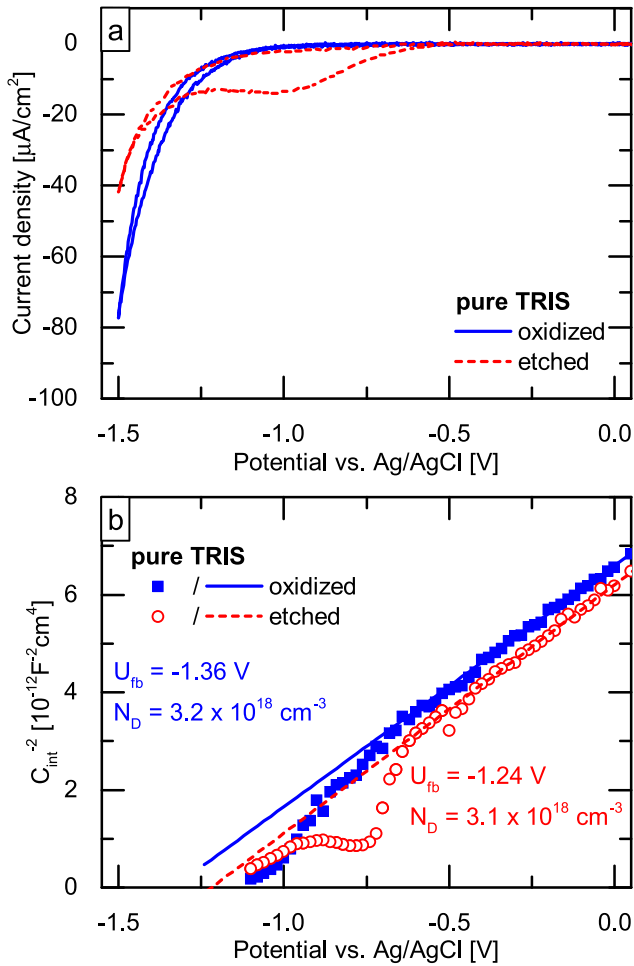


FIG. 2. (a) CVs of an oxidized (solid blue line) and an etched (dashed red line) GaN electrode, recorded at 250 mV/s in pure TRIS buffer. (b) Mott-Schottky plots resulting from impedance measurements. The experimental data is represented by symbols, and the lines show fits according to the Mott-Schottky equation.

like it is observed for SiC electrodes,⁸ depends on their energetic position with respect to the redox levels in the electrolyte. The observed difference between the two investigated surface treatments is attributed to a different distribution of surface states. As can also be seen in Fig. 2(a), the expected onset of hydrogen evolution at sufficiently negative potentials occurs earlier for the oxidized sample than for the etched sample. This is also indicative of less Fermi level pinning in the oxidized sample due to the reduced density of surface states.

For a more quantitative analysis, Fig. 2(b) shows the inverse square of the interfacial capacitance C_{int}^{-2} resulting from impedance measurements as a function of the applied bias potential U_{bias} , known as Mott-Schottky plot. The experimental data is fitted using the equivalent circuit models presented in previous work on SiC by Sachsenhauser *et al.*⁸ A detailed analysis of the impedance data is beyond the scope of this work and will be reported elsewhere. The experimental data deduced from impedance analysis is represented by symbols and the lines show fits according to the Mott-Schottky equation. A linear dependence between the inverse square of the interfacial capacitance, C_{int}^{-2} , and the applied bias potential U_{bias} is expected for an ideally polarizable

semiconductor electrode, as observed in Fig. 2(b) for potentials less negative than -0.5 V vs. Ag/AgCl. Fitting the experimental data in this bias regime, the Mott-Schottky equation was used to determine the values of the flat band potential U_{fb} and the donor density N_{D} , which are given for the oxidized and etched sample in Fig. 2(b). The donor density is in good agreement with the value obtained from Hall measurements. A difference of about 0.1 V in the value for the flat band potential is determined for the applied surface treatments. For potentials more negative than -0.7 V vs. Ag/AgCl and for potentials more negative than -0.6 V vs. Ag/AgCl for the oxidized and the etched sample, respectively, a significant deviation from the ideal Mott-Schottky behavior is observed. As the observed onset of the cathodic current and the observed deviations from the Mott-Schottky equation start for potentials more positive than the flat band potential, we conclude that surface states with energy levels located in the band gap cause the observed charge transfer.

Sachsenhauser *et al.*⁸ have demonstrated for SiC that the energy distribution of the surface states can be determined using the potential dependence of the interface capacitance C_{int} . To account for the pseudo-capacitive contribution of the surface states, a constant phase element (CPE), with an impedance $Z_{\text{CPE}} = \frac{1}{Q(j\omega)^\alpha}$, is used. As the CPE exponent α is always larger than 0.9, the CPE parameter Q can be interpreted as an approximate value for the interface capacitance C_{int} .²⁰ When the GaN Fermi level is aligned with the electronic levels of the surface states, charge transfer can take place and, thus, an effective surface states capacitance C_{SS}^* has to be considered in parallel with the capacitance C_{SC} of the semiconductor SCR. Therefore, we can calculate C_{SS}^* as the difference between the experimentally determined interface capacitance C_{int} and the theoretically predicted space-charge capacitance C_{SC} .^{21,22} Figure 3 shows the effective surface state capacitance for an oxidized and an etched GaN sample. In agreement with the CV curves, we do not observe a peak in the effective surface state capacitance of the oxidized GaN electrode. However, a peak at -0.8 V vs. Ag/AgCl appears in the effective surface state capacitance for the etched GaN electrode. Assuming a voltage of $\approx 1 \text{ V}$,

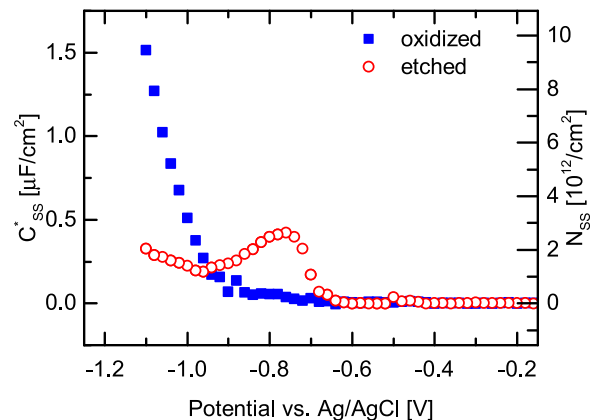


FIG. 3. Effective surface state capacitance C_{SS}^* (left y-axis) calculated as the difference between the interface capacitance C_{int} and the space-charge capacitance C_{SC} for an oxidized (filled blue squares), an etched (empty red circles) GaN electrode and the corresponding surface state density N_{SS} (right y-axis).

the surface state density can be estimated as the effective surface state capacitance divided by the electron charge, the resulting values are shown in Fig. 3 on the right y-axis. This suggests that by etching the sample, we have generated the surface states with a density of $2.6 \times 10^{12} \text{ cm}^{-2}$, whereas the surface states are to a large extent passivated after oxidation.

For GaN, it is known that there is an upward band bending of approximately 1 eV due to electrons captured by surface states.^{9,17–19} The origin of these electron acceptor surface states is still not well understood. These states may be related to intrinsic defects such as dangling bonds, impurities, surface reconstruction, or random stress, as it is also discussed for other semiconductors.^{23–26} They may also originate from extrinsic sources such as atoms or molecules absorbed on the surface or defects in the surface oxide layer. Recently, Eller *et al.* have investigated the influence of polarization of GaN and AlGaIn on the surface band bending and the electronic surface states.²⁷ They suggest nitrogen vacancies or gallium dangling bonds as the surface states responsible for the observed Fermi level pinning.

Our experimental data shows a similar flat band potential—corresponding to a similar surface band bending—both for the etched and oxidized GaN electrode, which is in good agreement with the value of 1 eV reported in the literature.^{9,17–19} The effective surface state capacitance depends on the applied surface treatment. Our observation that the surface defect states are passivated to a large extent upon oxidation is in agreement with Eller *et al.*, who suggested gallium dangling bonds as the origin of surface states.²⁷

In summary, we have investigated the electrochemical properties of MOCVD grown n-type GaN in aqueous electrolyte. Cyclic voltammetry and impedance spectroscopy measurements were performed over a wide range of potentials and frequencies. Two different surface treatments were applied to alter the surface states and investigate the influence of these on the defect-mediated charge transfer. We find that these surface states not only induce a significant surface band bending and play crucial role in the charge exchange between the SCR and the surface as well as in the charge exchange between GaN and a metal contact, but also dominate the electron transfer reactions between GaN and an aqueous electrolyte. We can modify the surface states by the applied surface treatment. Etching the GaN sample in HCl generates surface states, whereas the oxidation passivates them to a large extent. For the etched sample, a value of $2.6 \times 10^{12} \text{ cm}^{-2}$ for the surface state density can be estimated assuming a voltage of ≈ 1 V. This is relevant for electronic processes at the GaN surface as it is known that surface state

densities of 10^{13} cm^{-2} are sufficient to cause complete Fermi level pinning.^{28,29}

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