VCU

Virginia Commonwealth University
VCU Scholars Compass

Electrical and Computer Engineering Publications

Dept. of Electrical and Computer Engineering

2007

Study of SiN_x and SiO₂ passivation of GaN surfaces

S. A. Chevtchenko

Virginia Commonwealth University, chevtchenkos@vcu.edu

M. A. Reshchikov

Virginia Commonwealth University, mreshchikov@vcu.edu

Q. Fan

Virginia Commonwealth University

See next page for additional authors

Follow this and additional works at: http://scholarscompass.vcu.edu/egre_pubs

Part of the [Electrical and Computer Engineering Commons](#)

Chevtchenko, S. A., Reshchikov, M. A., & Fan, Q., et al. Study of SiN_x and SiO₂ passivation of GaN surfaces. *Journal of Applied Physics*, 101, 113709 (2007). Copyright © 2007 American Institute of Physics.

Downloaded from

http://scholarscompass.vcu.edu/egre_pubs/142

This Article is brought to you for free and open access by the Dept. of Electrical and Computer Engineering at VCU Scholars Compass. It has been accepted for inclusion in Electrical and Computer Engineering Publications by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.

Authors

S. A. Chevtchenko, M. A. Reshchikov, Q. Fan, X. Ni, Y. T. Moon, A. A. Baski, and H. Morkoç

Study of SiN_x and SiO₂ passivation of GaN surfaces

S. A. Chevtchenko,^{a)} M. A. Reshchikov, Q. Fan, X. Ni, Y. T. Moon, A. A. Baski, and H. Morkoç

Department of Electrical and Computer Engineering and Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284

(Received 4 January 2007; accepted 12 April 2007; published online 13 June 2007)

The optical properties of GaN films have been found to be sensitive to SiN_x and SiO₂ surface passivation. The main effect of such passivation on photoluminescence (PL) data is an increase of the PL intensity for near-band-edge emission. This effect is attributed to the removal of oxygen from the surface of GaN and the subsequent formation of a protective layer during passivation. The increase in PL intensity is more pronounced for samples passivated with SiO₂, which demonstrate initially lower PL intensity and a lower equilibrium concentration of free electrons. A nearly constant band bending of approximately 1.0 eV at the surface has been observed for as-grown and passivated samples by scanning Kelvin probe microscopy (SKPM). This constant value is explained by pinning of the Fermi level at the surface. In addition, we have demonstrated that passivation of the GaN surface between the contacts of a Schottky diode leads to a reduction of the leakage current observed at reverse bias. It was found that the surface potential measured by SKPM increases as a function of distance from the Schottky contact much faster after SiN_x passivation. We suggest that the passivation reduces the total density of surface states and therefore reduces surface recombination. © 2007 American Institute of Physics. [DOI: 10.1063/1.2740324]

I. INTRODUCTION

Gallium nitride has attracted attention in recent years as part of an important class of electronic materials.¹ Achieving controllable GaN surfaces and interfaces is a critical step in the development of GaN-based electronic devices. The relatively high band bending observed on GaN surfaces and an incomplete understanding of the responsible mechanisms exacerbate this task. The polar and nonpolar surfaces of undoped and *n*-type GaN layers show upward band bending in the range from 0.4 to 1.4 eV, as reported by several groups.^{2–6} It should be noted that untreated GaN surfaces have band bending in the upper limit of the mentioned range. Upward band bending indicates negative charge at the surface. Charged acceptorlike surface states (due to dangling bonds, defects, adsorbates, etc.) and charges induced by spontaneous polarization may contribute to the observed band bending.

Experimentally, the effects of chemisorption of oxygen^{2,7} and fluorine,⁸ surface cleaning in aqueous NH₄OH,² HCl:HNO₃,^{5,6} and KOH,⁵ nitrogen ion sputtering,² etching,^{9,10} and annealing¹¹ have been studied. It was shown that the surface band bending depends on the bulk concentration of free carriers^{5,12} and surface polarity.^{5,13,14} The effect of band flattening under illumination with photon energies larger than the band gap, i.e., surface photovoltage, has also been studied. For GaN surfaces with an upward band bending on the order of 1 eV the photovoltage reached 0.2–0.3 eV and was saturated.¹⁵ The reduction of the initial band bending is explained by the spatial separation of electron-hole pairs in the depletion layer formed beneath the surface. This separation causes the capture of photogenerated holes

by negatively charged surface states and the subsequent reduction of net negative charge at the surface.

The density of the surface states responsible for the observed band bending can be evaluated using the well-known model of barrier heights of metal-semiconductor systems.¹⁶ This model does not consider the case of bare semiconductor surfaces, but still works well for an approximate evaluation of the surface state density. The condition of electrical neutrality for the near-surface region in bare semiconductor surfaces leads to an effect known as Fermi-level pinning.¹⁷ This pinning effect has been discussed previously in connection with GaN surfaces and interfaces^{7,18}; however, no attempts have been made to account for Fermi-level pinning in quantitative terms for the observed band bending near GaN surfaces. In simulations the energy distribution of the surface states is important. Total-energy calculations in the framework of an *ab initio* multicenter tight-binding-like model show that the surface states within the band gap can be associated with dangling bonds of adatoms and the back bonds of first-layer atoms.¹⁹ X-ray photoemission spectroscopy (XPS) has been used to observe surface band structure and dispersion of surface states, but the results of these studies are controversial.^{20,21}

The detrimental effect of the surface on electrical and optical properties of a semiconductor material or device can be countered by its passivation with dielectric films. Among the variety of materials used for the passivation, SiO₂ and SiN_x are the most common passivators for semiconductors including GaN. The effect of passivation with SiO₂ and SiN_x on the performance of GaN Schottky diodes,^{22,23} GaN metal-insulator-semiconductor (MIS) structures,^{24,25} and AlGaIn/GaN heterostructure field-effect transistors (HFETs)^{26,27} can be found in the literature. Results obtained by XPS reveal that SiN_x passivation reduces GaN surface band bending,²⁸

^{a)}Electronic mail: chevtchenkos@vcu.edu

which indicates a decrease in the charged surface state density that is expected to vary for different types of passivation. This difference comes from the various chemical processes that take place at the GaN surface during the initial stages of SiO₂ and SiN_x deposition. It has been shown that an uncontrollable oxidation reaction during the initial stages of SiO₂ passivation leads to the formation of an interfacial oxide layer,²⁹ while passivation with SiN_x is presumably effective in suppression of the V_N -related surface defects.³⁰ In contrast to a large number of works where the SiO₂/GaN and SiN_x/GaN interfaces are analyzed in the context of fabricated devices, there are only a few reports where the physical properties of unprocessed passivated surfaces are discussed.

The effect of GaN surface passivation on photoluminescence (PL) results has also been studied. An increase of the room-temperature PL intensity in the excitonic region has been commonly observed after passivation with aqueous and alcoholic solutions of inorganic sulfides.^{31–34} There is significant dispersion, however, among reports for the factor by which the PL intensity increases after passivation. Our preliminary study of passivated GaN layers indicated similar effects for both SiN_x and SiO₂ passivation.³⁵ However, the mechanism responsible for the increase in PL intensity has not been yet sufficiently explained.

In the present work we have systematically studied the effect of SiN_x and SiO₂ passivation on the optical properties of both undoped and Si-doped GaN layers. We investigated the correlation of the passivation effects with the initial optical quality and carrier concentration in these samples. An analysis of the experimental observations is based on a surface band bending model that accounts for the Fermi-level pinning. Scanning Kelvin probe microscopy (SKPM) was used to determine band bending values for the bare and passivated GaN surfaces. The variation of the surface potential between the ohmic and Schottky contacts in fabricated diodes was also measured to delineate possible transport mechanisms in the near-surface region.

II. MODEL

In this study we follow the model of surface band bending suggested by Mönch.¹⁷ This model is based on the condition of charge neutrality for the near surface region which can be written as:

$$Q_1 + Q_2 = 0, \quad (1)$$

where Q_1 is the total charge at the surface per unit area due to charged surface states and Q_2 is the charge beneath the surface. The condition of charge neutrality in the near-surface region requires the formation of a space charge region to compensate the surface charge. The two values in (1) in the case of localized surface states can be expressed as¹⁷

$$Q_1 = \frac{-qN}{\exp\left[\frac{E_{ss} - E_F}{kT}\right] + 1}, \quad (2)$$

FIG. 1. Calculated dependence of the surface band bending on the total density of surface states for a bulk carrier concentration of 1.7×10^{16} and $1.2 \times 10^{18} \text{ cm}^{-3}$ and an acceptor level located 1.1 eV below the conduction band.

$$Q_2 = \sqrt{2\varepsilon_b \varepsilon_0 n k T \left[\exp\left(\frac{-|\Phi|}{kT}\right) + \left(\frac{|\Phi|}{kT}\right) - 1 \right]} \approx \sqrt{2\varepsilon_b \varepsilon_0 n k T \left(\frac{|\Phi|}{kT}\right)}, \quad (3)$$

where N is the concentration of surface acceptors per unit area, E_{ss} and E_F are the energy levels of the surface acceptor and the Fermi level measured from the conduction band, respectively, ε_b is the bulk dielectric constant, n is the concentration of uncompensated donors (assumed to be equal to the bulk electron concentration for simplicity), and Φ is the surface band bending. The approximation is justified as $|\Phi|/kT \gg 1$ and $\exp(-|\Phi|/kT) \approx 0$.

An upward band bending at the surface of n -type GaN corresponds to the presence of negatively charged surface acceptors and the formation of a positive space-charge region as required by the neutrality condition (1). In equilibrium, the space charge in the depletion layer below the surface compensates the charged surface states. The width of the layer depleted from free electrons is given by

$$W = \frac{N^-}{n}, \quad (4)$$

where N^- is the concentration of charged surface acceptors per unit area. According to Eq. (4), for a set of samples having the same density of charged surface states, the depletion region width is larger in those samples with a lower electron concentration.

To illustrate the effects of electron concentration and surface acceptor state density on band bending, we show the results from Eqs. (1)–(3) for two bulk electron concentrations corresponding to the extreme values in our experiments (see Fig. 1). The energy of the surface acceptor, E_{ss} , is assumed to be 1.1 eV below the conduction band minimum, which is consistent with the typical value of $\Phi \approx 1$ eV commonly observed in experiments.⁵ Note that only *charged* surface states contribute to band bending as can be seen from Eqs. (1)–(3). The effect of the surface band bending satura-

tion with increasing density of surface states is commonly known as *pinning of the Fermi level*. For this pinning condition, the position of the Fermi level at the surface remains almost unchanged with a further increase in the total density of surface states, because the concentration of charged surface states remains nearly unchanged. It follows from the calculations that the effect of carrier concentration on band bending is significant only in those samples with a relatively low density of surface states when the Fermi level is unpinned. For example, when the density of acceptorlike surface states is $2 \times 10^{12} \text{ cm}^{-2}$, the upward band bending changes from 1.00 to 0.32 eV with an increase in bulk electron concentration from 1.7×10^{16} to $1.2 \times 10^{18} \text{ cm}^{-3}$. In contrast, for a surface state density of $3.5 \times 10^{12} \text{ cm}^{-2}$, the band bending varies only from 1.02 to 0.91 eV for the same range of electron concentrations. In reality, a number of both acceptor- and donor-type surface states may be present, and their distribution in the band gap may be complicated. Nevertheless, the qualitative picture described here would remain the same.

III. EXPERIMENTAL DETAILS

The undoped and Si-doped GaN layers used in this study were grown on *c*-plane sapphire substrates by low-pressure organometallic vapor phase epitaxy (OMVPE) using trimethylgallium and ammonia for the Ga and N sources, respectively. Details of the growth conditions can be found elsewhere.³⁶ The GaN layers had a thickness of $\sim 2 \mu\text{m}$ and an electron concentration in the range from 1.7×10^{16} to $1.2 \times 10^{18} \text{ cm}^{-3}$ at room temperature as determined from Hall effect measurements. Several samples were cut from each layer for a comparative study of the passivation effects of SiO_2 and SiN_x with an untreated air-exposed sample left as the control. The passivation procedure started with degreasing and reduction of the natural oxide by chemical etching in boiling $\text{HNO}_3\text{:HCl}$. Immediately after etching and rinsing, samples were loaded into a remote enhanced plasma-chemical vapor deposition (REPCVD) chamber for passivant deposition. The deposition of SiO_2 and SiN_x films was performed at 300°C by using SiH_4 , He, and O_2 or N_2 gases, respectively. The passivation process was similar to that reported in the literature with a small variation of substrate temperature.^{29,37} The thickness of the deposited films was approximately 10 nm.

An unintentionally doped GaN film ($5.0 \times 10^{16} \text{ cm}^{-3}$) was used for the fabrication of Schottky diodes. The contacts had a circular geometry with an inner Schottky contact (250 μm diam) surrounded by an outer, annular ohmic contact with a distance between the electrodes of approximately 25 μm . The ohmic contact was formed by evaporation of a Ti/Al/Ti/Au (30/100/30/50 nm) metal stack and annealed in a nitrogen ambient at 800°C for 1 min. The Schottky contact was a Ni/Au (30/30 nm) metal stack. Two samples cut from the same GaN film were used for the fabrication. Immediately after the final stage of the fabrication procedure, one of the samples was loaded into a RECVD chamber for passivation with SiN_x . The thickness of the deposited film was 10–12 nm. We used dilute HF acid to remove SiN_x and form

patterned windows on the contacts. The window diameter on the Schottky contact was 200 μm and therefore the edges remained passivated. All further studies were performed on passivated and unpassivated samples.

With regard to characterization techniques, the *I*-*V* characteristics were measured using a Keithley parameter analyzer with a minimum detectable current of 10 pA. Steady-state PL was excited with the 325 nm line of a He-Cd laser, dispersed with a 0.5 m SPEX grating monochromator, and detected with a Hamamatsu photomultiplier tube R955P. The PL was measured at 15 and 300 K in a closed-cycle optical cryostat. We also investigated the effect of air ambient on PL by comparing room-temperature PL spectra measured in vacuum and air ambient. SKPM was used to measure the contact potential difference (V_{cp}) between the GaN surface and a gold-coated tip. The surface band bending, Φ , was calculated using the formula

$$\Phi = \phi_M - qV_{\text{cp}} - \Phi_{\text{off}} - \chi + E_F, \quad (5)$$

where ϕ_M is the tip metal work function ($\phi_M = 5.1 \text{ eV}$ for Au), χ is the electron affinity [$\chi = 3.2 \text{ eV}$ for GaN (Ref. 2)], and Φ_{off} is the measured offset determined by measuring V_{cp} on a gold film. A more detailed description of the method can be found in our previous works.^{9,15}

IV. EXPERIMENTAL RESULTS

A. Effect of passivation on optical properties

In this section we compare the effect of passivation on PL intensity at room temperature (RT) for a set of GaN samples with different electron concentrations. In these samples the RT PL spectrum showed near-band-edge emission at approximately 3.4 eV, which is presumably the recombination of free excitons, and a yellow luminescence (YL) band peaking at 2.2 eV, which is commonly attributed to unidentified deep-level acceptors.³⁸ Since the origin of the YL band and even the question whether defects responsible for this band are uniformly distributed in bulk or predominantly located at the surface remain uncertain,^{38–40} in this work we will focus on the effect of passivation on the near-band-edge emission intensity only. The changes of this intensity due to passivation are summarized for several samples in Fig. 2 and Table I. An increase of the PL intensity due to passivation is larger for the samples with a lower concentration of free electrons, however, the correlation between the passivation effect and the carrier concentration is not strong. On the other hand, a clear correlation can be observed for the PL intensity before passivation and its increased value after passivation (see Fig. 2). The intensity after passivation increases by a factor of approximately 5 for the samples with the lowest initial intensity values before passivation.

The RT PL spectra from three pieces of one sample (air-exposed, SiO_2 , and SiN_x passivated) are shown in Fig. 3. Note that the variation of the YL band intensity upon passivation does not correlate with changes of the near-band-edge emission. In particular, passivation with SiN_x sometimes slightly reduced the YL band intensity (Fig. 3) but sometimes slightly enhanced it (not shown) in the samples with the same concentration of free electrons. It is possible that de-

FIG. 2. Dependence of the factor by which the initial intensity of the near-band-edge region in PL changed after passivation. The data are given for seven GaN layers (from Table I) and include results obtained from different samples of the same layer passivated in different runs in order to confirm reproducibility of the effect observed in this study.

fects responsible for the YL band are created or partially eliminated near the GaN-passivant interface. A more detailed analysis of the effect of passivation on the YL band is beyond the scope of this work. All samples had room- and low-temperature PL spectra typical for GaN of relatively high quality. The low-temperature spectrum contains the donor-bound exciton line at 3.484 eV, the ultraviolet luminescence (UWL) band with its main peak at 3.27 eV, and the YL band peaking at ~ 2.2 eV.³⁸ We did not observe any significant difference in intensity for the low-temperature PL of unpassivated (control) and passivated samples.

It was also found that SiN_x passivation is less effective in increasing the PL intensity as compared to SiO₂. All of the samples passivated with SiO₂ demonstrated an increase in the PL intensity, whereas those passivated with SiN_x did not. The PL intensity even slightly decreased in some SiN_x-passivated samples with a high electron concentration. The observed increase of PL intensity in the passivated samples can be explained by either (i) a decrease of the density of charged surface states and subsequent decrease of band bending and depletion region width or (ii) a decrease of the total density of surface states, resulting in a reduced surface recombination velocity. The roles of these mechanisms will be discussed below.

TABLE I. Summary of the SiO₂ and SiN_x passivation effect on the intensity of near-band-edge PL emission ($\uparrow$ =increased by factor of; $\downarrow$ =decreased by factor of), where average factors are presented from different experiments.

Sample No.	Carrier concentration (cm ⁻³)	Initial intensity (arb. units)	SiO ₂	SiN _x
1	1.7×10^{16}	$\sim 9 \times 10^4$	$\uparrow 6.8$	$\uparrow 3.0$
2	3.0×10^{16}	$\sim 5 \times 10^5$	$\uparrow 3.3$	$\uparrow 2.7$
3	1.0×10^{17}	$\sim 1 \times 10^5$	$\uparrow 7.5$	$\uparrow 2.7$
4	3.7×10^{17}	$\sim 2 \times 10^7$	$\uparrow 1.4$	$\downarrow 1.3$
5	4.6×10^{17}	$\sim 1 \times 10^7$	$\uparrow 1.3$	$\downarrow 1.3$
6	5.5×10^{17}	$\sim 1 \times 10^7$	$\uparrow 1.6$	$\uparrow 1.1$
7	1.2×10^{18}	$\sim 8 \times 10^6$	$\uparrow 1.9$	$\downarrow 1.5$

FIG. 3. Example PL spectra at 300 K of GaN samples that are unpassivated (air-exposed control) or passivated (SiO₂ or SiN_x). The excitation power density is 0.3 W/cm².

We also investigated the effect of the air ambient on PL intensity by repeating the RT measurements in vacuum. The near-band-edge PL intensity of the unpassivated sample increased in vacuum, and as a result the difference in PL intensity between unpassivated and passivated samples almost completely vanished. The process of oxygen desorption in vacuum under UV illumination is plausibly responsible for this observed effect.^{39,40} Interestingly, the passivated samples demonstrated no detectable difference in PL between air and vacuum conditions. These observations suggest that surface states induced by adsorbed oxygen dominate the behavior of these samples, and not surface states due to dangling bonds, defects, impurities, etc. It should be noted that our earlier results indicating similar low-temperature PL intensities for unpassivated and passivated samples (in contrast to RT measurements) are consistent with these vacuum measurements, since low-temperature PL is measured under conditions that create a high vacuum.

B. SKPM measurements of surface band bending

In the previous section we suggested that the increased intensity of the near-band-edge PL emission after passivation may be caused by a reduction of the total surface state density. If the density of *charged* surface states also decreases, then the upward band bending and surface potential observed at the GaN surface must decrease. Using SKPM, we found that the surface potential for unpassivated layers was uniform and yielded surface band bending values in the range from 0.9 ± 0.1 to 1.0 ± 0.1 eV (see Fig. 4). Surprisingly, the measured surface potential values showed no significant change after passivation with either SiO₂ or SiN_x. The surface band bending values for both types of passivation on all samples are therefore in the same range (Fig. 4). This result indicates that to within experimental error passivation does not change the surface band bending, and therefore the density of charged surface states remains relatively unchanged.

FIG. 4. Upward band bending measured by SKPM as a function of bulk carrier concentration for GaN samples that are unpassivated (air-exposed control) or passivated (SiO_2 or SiN_x).

C. Effect of SiN_x passivation on a Schottky diode

A comparative study of the current-voltage (I - V) characteristics for both passivated and unpassivated Schottky diodes have shown a significant performance improvement for SiN_x -passivated diodes in terms of leakage current at reverse bias. At 7 V reverse bias, unpassivated diodes had leakage currents of 0.5–2 μA , whereas passivated diodes had significantly lower currents of 3–24 nA. The passivated diodes show a reduction of reverse current by one to two orders of magnitude. Typical I - V characteristics for devices with and without passivation are shown in Fig. 5. Using a linear fit to the forward bias characteristics (log scale), we obtained barrier heights of 0.77 and 0.83 eV at zero bias for unpassivated and passivated diodes, respectively. These values are in the range of reported barrier heights for Ni/GaN contacts.⁴¹

In order to determine the surface potential profile between the two contacts, SKPM scans were taken from the Schottky contact edge to just before the ohmic contact (distance of $\sim 29 \mu\text{m}$). Variations of the surface potential as a

FIG. 5. Typical current-voltage (I - V) characteristics of Schottky diodes fabricated both with and without SiN_x passivation. A schematic of the diode structure is shown as an inset.

FIG. 6. AFM topography and corresponding SKPM surface potential profiles for unpassivated (solid lines) and passivated (dotted lines) Schottky diodes under a reverse bias of 6 V. The edge of the Schottky contact is shown at the left.

function of distance from the Schottky contact at 6 V reverse bias are shown on Fig. 6. The surface potential at the Schottky contact equals -4.3 V for both passivated and unpassivated diodes, and at the edge of the contact equals -3.6 V (passivated) and -4.2 V (unpassivated). This difference in potential for the two diodes increases with increasing distance from the Schottky contact, e.g., at $10 \mu\text{m}$ from the contact edge the surface potential equals -0.2 V (passivated) and -1.4 V (unpassivated). In the case of forward bias, there is no detectable difference of the surface potential at the Schottky contact and along its edge, but at a distance of $10 \mu\text{m}$ from the edge the surface potential equals 2.5 V (passivated) and 1.5 V (unpassivated). These results are consistent with the lower forward-bias current observed for unpassivated diodes as shown in Fig. 5.

V. DISCUSSION

As it was pointed out in Sec. IV A, the effect of passivation on PL is more pronounced in the samples with lower carrier concentration, although the correlation is not strong. This result apparently has something in common with previously reported reductions of charge trapping processes in GaN-based FET structures caused by Si doping,^{42–44} where the physics of the effect was not clarified. The situation may be complicated by the fact that doping with Si not only reduces the depletion region width but also can change density of the surface states.¹² Below we will try to explain our experimental results within two simple models, namely (i) the reduction of depletion width due to reduction of negative charge at the surface caused by passivation and (ii) reduction of total density of the surface states upon passivation resulting in reduction of the surface recombination velocity.

A different carrier concentration in bulk results in a change of the depletion width at the surface. Accounting for a possible error in the calculated values of band bending (estimated as $\pm 0.1 \text{ eV}$), we attempted to explain the changes in PL intensity by a small, experimentally undetectable (within 0.1 eV) decrease of the band bending, which would result in a small increase of the depletion region width upon passivation. It was assumed that the electric field in the depletion region is so strong that all photogenerated electrons and holes are quickly separated, i.e., electrons are swept away to the bulk region, while all holes generated in the depletion region reach the surface and recombine at sur-

face states with bulk electrons that have overcome the barrier. Even if excitons were formed, they would be ionized in an electric field of about 10^5 V/cm.⁴⁵ Then, only PL occurring in the bulk region beyond the depletion region would contribute to the PL signal. Given an absorption coefficient for GaN at 325 nm of 1.2×10^5 cm⁻¹,⁴⁶ we estimated that the samples with the smallest electron concentration would have a decrease of band bending from 1.0 to 0.9 eV and an increase of PL intensity by only a factor of 1.3, in contrast to the experimentally observed factor of up to 8. For the samples with a higher electron concentration, the PL intensity would have an even smaller increase. Thus, we were unable to explain the significant increase of PL intensity upon passivation due to only a variation in band bending, indicating the role of other mechanisms.

In the above discussion, we neglected the change in the velocity of nonradiative surface recombination caused by passivation, which is often suggested as an explanation for the effect of surface treatment on PL intensity.^{47–49} Previously, an increase of PL intensity for GaAs of up to 2800 times has been observed after passivation with Na₂S-9H₂O for samples having low free electron concentrations.⁵⁰ The necessary condition for nonradiative surface recombination to produce a significant effect on PL is the possibility for electrons and holes to reach the surface. In the case of upward band bending, an electron diffusion length should be sufficiently large for electrons to overcome the depletion region and reach the surface, and the capture cross section of the surface states should be large enough for electrons to explain small decrease of band bending [about 0.3 eV (Ref. 15)] upon illumination. The experimentally determined diffusion length of electrons in GaN along the *c* direction [about 950 nm (Ref. 51)] is indeed larger than the depletion region widths in our samples. Although the value of the near-surface barrier of about 0.7 eV is much larger than *kT* at room temperature, the diffusion of electrons from the bulk region to the surface over the barrier appears to be the dominant mechanism of electron transfer. Indeed, photogenerated electrons would be swept from the depletion region with an electric field of about 10^5 V/cm in a time of about 10^{-12} s at room temperature, which is about two orders of magnitude faster than the lifetime of photogenerated electrons in the conduction band and holes in the valence band in GaN.³⁸ Recombination between electrons trapped at defect levels in the depletion region and holes captured by the surface states can also be ignored due to relatively strong localization and negligible overlap of their wave functions. Thus, we assume that nearly all holes created by light in the depletion region are captured by the surface states and eventually recombine with bulk electrons passing over the barrier. The variation of the surface nonradiative recombination velocity due to a significant variation of the surface state density can qualitatively explain the observed changes of PL intensity. In this case, the rate of recombination occurring at surface states decreases in passivated samples due to a large decrease of the *total* density of surface states, even though the density of charged states remains nearly unchanged. If the surface states are induced by oxygen species, a strong variation of PL in passivated samples may indicate that either the oxygen

surface layer is removed, or that electrons are unable to pass through the passivation layer to be trapped by surface states.

With regard to our Schottky device results, the trapping of electrons tunneling from metal contacts by surface states has been previously observed for FETs and Schottky diodes.^{52–54} In our experiments, the surface potential measured by SKPM is a superposition of the applied potential and the potential at the GaN surface between the Schottky and ohmic contacts. The difference in surface potential measured for the passivated and unpassivated devices indicates different contributions of the GaN surface potential, i.e., different concentrations of charged surface states. Since the fabrication procedure is the same for both devices, the observed difference should be associated with the passivation layer. This layer reduces the total concentration of surface states available for charging due to an applied bias, and therefore reduces the surface recombination rate. This reduction of negatively charged surface states under bias results in a higher surface potential as measured by SKPM for the passivated devices (see Fig. 6). In unpassivated devices, the capture of electrons tunneling from the Schottky contact by surface states and their subsequent release into the bulk results in additional leakage. Therefore, the reduction of leakage current in passivated diodes is due to the reduction of surface states participating in the conductance of electrons tunneling from the Schottky contact.

VI. CONCLUSIONS

In summary, we have investigated the effects of SiN_x and SiO₂ surface passivation on the optical and electrical properties of GaN layers with different carrier concentrations. The main effect of such passivation on the PL spectra is an increase of the near-band-edge emission intensity. We observed that this increase is significantly more pronounced for samples with a lower initial PL intensity and lower carrier concentration. The increase of the PL intensity as a result of passivation occurs mainly due to the removal of oxygen species from the surface, which leads to a reduction of the surface state density. In this case, the dielectric layer serves as a protective layer against adsorption of oxygen on the GaN surface. The effect of passivation on optical properties was significantly more pronounced for SiO₂ as compared to SiN_x. SKPM measurements indicate surface band bending values from 0.9 ± 0.1 to 1.0 ± 0.1 eV for unpassivated samples with different electron concentrations, where passivation did not change these values to within experimental error. These results were explained by Fermi-level pinning at the GaN surface. It appears that passivation decreases the total density of surface states, but does not significantly change the density of charged surface states. We suggest that PL in passivated GaN increases mostly due to reduction of the surface recombination velocity rather than due to change in the depletion region width. We also demonstrate that passivation of the GaN surface between the contacts of a Schottky diode leads to a reduced density of charged surface states at reverse bias, and thereby a reduction in the device leakage current.

ACKNOWLEDGMENTS

This work was funded by grants from the National Science Foundation (V. Hess) and the Air Force Office of Scientific Research (K. Reinhardt). The authors would like to thank Dr. V. Avrutin for informative discussions.

- ¹H. Morkoç, *Handbook of GaN Materials and Devices* (Springer, Berlin, 2007).
- ²V. M. Bermudez, J. Appl. Phys. **80**, 1190 (1996).
- ³C. I. Wu, A. Kahn, N. Taskar, D. Dorman, and D. Gallagher, J. Appl. Phys. **83**, 4249 (1998).
- ⁴C. I. Wu and A. Kahn, J. Vac. Sci. Technol. B **16**, 2218 (1998).
- ⁵S. Sabuktagin, M. A. Reshchikov, D. K. Johnstone, and H. Morkoç, Mater. Res. Soc. Symp. Proc. **798**, Y5.39 (2004).
- ⁶S. Chevtchenko, X. Ni, Q. Fan, A. A. Baski, and H. Morkoç, Appl. Phys. Lett. **88**, 122104 (2006).
- ⁷J. P. Long and V. M. Bermudez, Phys. Rev. B **66**, 121308 (2002).
- ⁸V. M. Bermudez, Appl. Surf. Sci. **119**, 147 (1997).
- ⁹S.-J. Cho, S. Dogan, S. Sabuktagin, M. A. Reshchikov, D. K. Johnstone, and H. Morkoç, Appl. Phys. Lett. **84**, 3070 (2004).
- ¹⁰Q. Fan, S. Chevtchenko, X. Ni, S.-J. Cho, F. Yun, and H. Morkoç, J. Vac. Sci. Technol. B **24**, 1197 (2006).
- ¹¹S. Chevtchenko, Q. Fan, C. W. Litton, A. A. Baski, and H. Morkoç, Mater. Sci. Forum **527–529**, 1529 (2006).
- ¹²K. A. Bulashevich and S. Yu. Karpov, Phys. Status Solidi C **3**, 2356 (2006).
- ¹³K. M. Jones, P. Visconti, F. Yun, A. A. Baski, and H. Morkoc, Appl. Phys. Lett. **78**, 2497 (2001).
- ¹⁴B. J. Rodriguez, W.-C. Yang, R. J. Nemanich, and A. Gruverman, Appl. Phys. Lett. **86**, 112115 (2005).
- ¹⁵M. A. Reshchikov, S. Sabuktagin, D. K. Johnstone, and H. Morkoç, J. Appl. Phys. **96**, 2556 (2004).
- ¹⁶S. M. Sze, *Physics of Semiconductor Devices* (Wiley, Hoboken, NJ, 2004).
- ¹⁷W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer, Berlin, 1993).
- ¹⁸H. Hasegawa and T. Hashizume, Mater. Res. Soc. Symp. Proc. **743**, L2.6 (2003).
- ¹⁹J. Fritsch, O. F. Sankey, K. E. Schmidt, and J. B. Page, Phys. Rev. B **57**, 15360 (1998).
- ²⁰S. S. Dhesi, C. B. Stagarescu, K. E. Smith, D. Doppalapudi, R. Singh, and T. D. Moustakas, Phys. Rev. B **56**, 10271 (1997).
- ²¹V. M. Bermudez, T. M. Jung, K. Doverspike, and A. E. Wickenden, J. Appl. Phys. **79**, 110 (1996).
- ²²O. Cojocari, V. Popa, V. V. Ursaki, I. M. Tiginyanu, H. L. Hartnagel, and I. Daumiller, Semicond. Sci. Technol. **19**, 1273 (2004).
- ²³V. Adivarahan, G. Simin, J. W. Yang, A. Lunev, M. Asif Khan, N. Pala, M. Shur, and R. Gaska, Appl. Phys. Lett. **77**, 863 (2000).
- ²⁴C. Bae and G. Lucovsky, Surf. Sci. **566–568**, 356 (2004).
- ²⁵C. Bae, C. Krug, G. Lucovsky, A. Chakraborty, and U. Mishra, J. Appl. Phys. **96**, 2674 (2004).
- ²⁶B. M. Green, K. K. Chu, E. M. Chumbes, J. A. Smart, J. R. Shealy, and L. F. Eastman, IEEE Electron Device Lett. **21**, 268 (2000).
- ²⁷P. Javorka, J. Bernat, A. Fox, M. Marso, H. Luth, and P. Kordos, Electron. Lett. **39**, 1155 (2003).
- ²⁸T. Hashizume, S. Ootomo, S. Oyama, M. Konishi, and H. Hasegawa, J. Vac. Sci. Technol. B **19**, 1675 (2001).
- ²⁹T. Hashizume, S. Ootomo, T. Inagaki, and H. Hasegawa, J. Vac. Sci. Technol. B **21**, 1828 (2003).
- ³⁰T. Hashizume and H. Hasegawa, Appl. Surf. Sci. **234**, 387 (2004).
- ³¹E. V. Konenkova, Vacuum **67**, 43 (2002).
- ³²C. Huh, S. Kim, I. Lee, and S. Park, J. Appl. Phys. **87**, 4591 (2000).
- ³³G. Martinez, M. Curiel, B. Skromme, and R. Molnar, J. Electron. Mater. **29**, 325 (2000).
- ³⁴J. O. Song, S.-J. Park, and T.-Y. Seong, Appl. Phys. Lett. **80**, 3129 (2002).
- ³⁵S. Chevtchenko, M. A. Reshchikov, K. Zhu, Y.-T. Moon, A. A. Baski, and H. Morkoç, Mater. Res. Soc. Symp. Proc. **892**, 0892–FF23–09 (2005).
- ³⁶Y. T. Moon, Y. Fu, F. Yun, S. Dogan, M. Mikkelsen, D. Johnstone, and H. Morkoç, Phys. Status Solidi A **202**, 718 (2005).
- ³⁷D. G. Park, M. Tao, D. Li, A. E. Botchkarev, Z. Fan, H. Liang, J. R. Abelson, A. Rockett, H. Morkoç, A. R. Heyd, and S. A. Alterovitz, J. Vac. Sci. Technol. B **14**, 2674 (1996).
- ³⁸M. A. Reshchikov and H. Morkoç, J. Appl. Phys. **97**, 061301 (2005).
- ³⁹M. Z. Iqbal, M. A. Reshchikov, L. He, and H. Morkoç, J. Electron. Mater. **32**, 346 (2003).
- ⁴⁰M. A. Reshchikov, Appl. Phys. Lett. **89**, 232106 (2006).
- ⁴¹S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. **86**, 1 (1999).
- ⁴²O. Mitrofanov, M. Manfra, and N. Weimann, Appl. Phys. Lett. **82**, 4361 (2003).
- ⁴³J. Z. Li, J. Y. Lin, H. X. Jiang, and G. J. Sullivan, Appl. Phys. Lett. **77**, 4046 (2000).
- ⁴⁴O. Mitrofanov and M. Manfra, J. Appl. Phys. **95**, 6414 (2004).
- ⁴⁵D. F. Blossey, Phys. Rev. B **2**, 3976 (1970).
- ⁴⁶J. F. Muth, J. H. Lee, I. K. Shmagin, R. M. Kolbas, Jr. H. C. Casey, B. P. Keller, U. K. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **71**, 2572 (1997).
- ⁴⁷U. Behn, A. Thamm, O. Brandt, and H. T. Grahn, J. Appl. Phys. **87**, 4315 (2000).
- ⁴⁸S. R. Lunt, G. N. Ryba, P. G. Santangelo, and N. S. Lewis, J. Appl. Phys. **70**, 7449 (1991).
- ⁴⁹H. Hasegawa, H. Ishii, T. Sawada, T. Saitoh, S. Konishi, Y. Liu, and H. Ohno, J. Vac. Sci. Technol. B **6**, 1184 (1988).
- ⁵⁰B. J. Skromme, C. J. Sandroff, E. Yablonovitch, and T. Gmitter, Appl. Phys. Lett. **51**, 2022 (1987).
- ⁵¹K. Kumakura, T. Makimoto, N. Kobayashi, T. Hashizume, T. Fukui, and H. Hasegawa, Appl. Phys. Lett. **86**, 052105 (2005).
- ⁵²S. Sabuktagin, Y.-T. Moon, S. Dogan, A. A. Baski, and H. Morkoç, IEEE Electron Device Lett. **27**, 211 (2006).
- ⁵³G. Koley, V. Tilak, L. F. Eastman, and M. G. Spencer, IEEE Trans. Electron Devices **50**, 886 (2003).
- ⁵⁴W. S. Tan, M. J. Uren, P. A. Houston, R. T. Green, R. S. Balmer, and T. Martin, IEEE Electron Device Lett. **27**, 1 (2006).