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Surface band bending in as-grown and plasma-treated *n*-type GaN films using surface potential electric force microscopy

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The surface band bending, as well as the effect of plasma-induced damage on band bending, on GaN surfaces, was investigated. The upward band bending, measured by surface potential electric force microscopy (a variant of atomic force microscopy), for the as-grown *n*-type GaN was about 1.0 eV which increased to ~1.4 eV after reactive ion etching (RIE). UV illumination decreased the band bending by 0.3 eV with time constants on the order of seconds and hundreds of seconds for the as-grown and RIE treated GaN, respectively. This implies that there is a higher density of the surface states in the samples subjected to the RIE process. After the RIE treatment, the shape of the photoluminescence spectrum remained unchanged, but the intensity dropped by a factor of 3. This effect can be attributed to nonradiative defects created near the surface by the RIE treatment. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1703843]

GaN is an important wide band gap material for a broad range of applications including high power/temperature electronics, and visible and ultraviolet (UV) emitters and detectors.[1] In many of these devices, particularly amplifier types and for basic materials characterization, it is essential to know the extent of the surface band bending. It is also important to gain some knowledge of the effect of processing methods on the surface band bending. Plasma based dry etching methods are necessary for GaN device fabrication, as GaN is somewhat impervious to wet chemical process, and the photoresists used for patterning are attacked by wet chemicals. However, plasma-induced damage[2,3] during dry etching can produce high density of surface states and consequently affects band bending on the GaN surface,[4] resulting in significant degradation/alteration of Schottky characteristics.[5–7] Naoi suggested that during reactive ion etching (RIE) using BCl_3, the boron is driven below the surface to a considerable distance, and plays a part along with the etching damage in the formation of surface states.[8]

The band bending of GaN may be created by surface states, adsorbed atoms, and oxidation, and has recently been attributed to spontaneous and piezoelectric polarization in conjunction with Schottky barriers, and it can be affected also by screening.[9]

Bermudez reported that chemisorbed O_2 coverage saturates at 0.4 ML and removes surface states near the valence band edge.[10] However, this has little effect on surface band bending, reducing the band bending only by 0.15 eV.[10] The spontaneous polarization has been reported to be much smaller for N-polar GaN (as compared to Ga-polar samples),[9] and thus band bending is much smaller.[11] Band bending causes depletion in the underlying layers requiring a correction to be made in analyses such as Hall measurements where the conducting layer thickness is an important parameter. The impact of such a depletion layer and its dependence on the type of ambient has been investigated in the context of photoluminescence (PL).[12] Band bending would also affect the minority charge accumulation in underlying layers, and thus would have an impact on optical processes such as the lifetime of excitons. With such a large effect of adatoms, and surface states, it is important to characterize the effects of RIE and wet etching in order to determine and/or place the band bending in a controllable, known state amenable to device operation.

The GaN layer used in this study was grown on *c*-plane sapphire substrate by molecular beam epitaxy (MBE). The GaN wafer was cut into 1 cm×1 cm pieces and cleaned in acetone and methanol with ultrasonic agitation, rinsed in flowing de-ionized water (DI H_2O), and blown dry with N_2. This was followed by boiling aqua regia treatment and DI H_2O rinse ending with blow drying in N_2. RIE was performed in a Plasma-Therm RIE system under slightly different etching conditions (200–250 W rf power, 100 sccm BCl_3 flow rate, 54 mTorr). Some samples underwent subsequent treatment in either boiling aqua regia or molten KOH solution for 10 min and 15 s, respectively, in an effort to remove either the surface contaminants such as metal and perhaps etch away the damaged region caused by the plasma treatment. For band bending measurements, a Dimension 3100™ surface potential electric force microscope (SP-EFM) was used to measure the surface potential by adjusting the voltage on the tip so that the tip experiences a minimum electric force from the sample. In this state, the voltage on the tip and the sample surface is the same, which allowed the surface potential to be obtained. In calculations of the band bending, the electron affinity of GaN was assumed to be 3.2 eV.[10] In addition, the evolution of band bending was measured under UV illumination (with photon energy of 3.68 eV). The PL was also measured at room temperature following each of the surface treatments.

The band bending for each sample measured by SP-EFM

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TABLE I. Band bending measured by SP-EFM.

	As grown	RIE
Control	1.0±0.1 eV	1.4±0.15 eV
Aqua regia	1.1±0.1 eV	1.55±0.15 eV
KOH	1.0±0.1 eV	1.35±0.15 eV

is given in Table I. Each of the as-grown samples with or without wet treatment had a band bending of 0.9–1.1 eV. The band bending in each of the RIE samples was 0.3–0.5 eV greater than the respective as-grown samples. Figure 1 shows the band bending measured by SP-EFM as a function of time under UV illumination for the as-grown surface and RIE surface. The initial conditions show the RIE surface starting at a larger band bending, as given in Table I. Then, both the as-grown and etched samples have a delay in the variation of band bending under illumination. The RIE treated surface requires a much greater photon flux (time of UV exposure) than the as-grown surface to decrease the band bending. With further illumination, both saturate, although at different levels. The band bending for the as-grown surface saturates much faster, on the order of 1 s, as opposed to hundreds of seconds for the RIE treated surface. The total shift, 0.3 eV reduction in band bending with illumination, is approximately the same for each. When the UV illumination is turned off, the recovery process back to the dark steady-state condition takes much longer time for the RIE treated surface than for the as-grown surface as shown in Fig. 2.

Illumination generates electron-hole pairs and consequently electrons drift away from the surface while holes accumulate at the surface. The holes accumulated at the surface will empty the surface states from electrons. Therefore, the surface will be positively charged with respect to the bulk region, resulting in a decrease in band bending due to electric field formed toward the bulk, as can be seen in the behavior of a Schottky barrier under forward bias condition.

Recapture of electrons may take place prior to drift away from the depletion region to the bulk region by cascade capture through successively deeper surface states, however we neglect this process. Free electrons can be thermionically emitted over the barrier from bulk to the surface and be captured by the surface states. Equilibrium is established

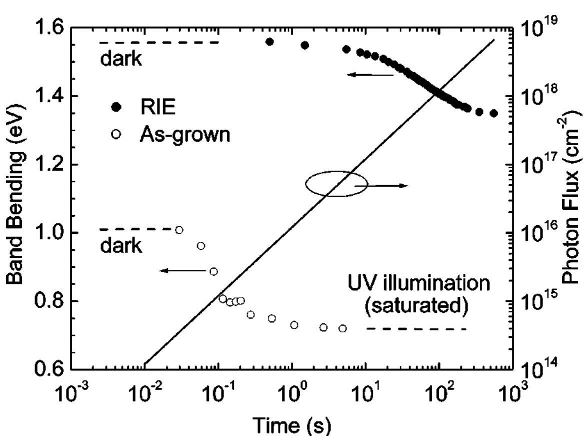

FIG. 1. Band bending as a function of time under UV illumination for as-grown and RIE GaN measured by surface potential electric force microscopy.

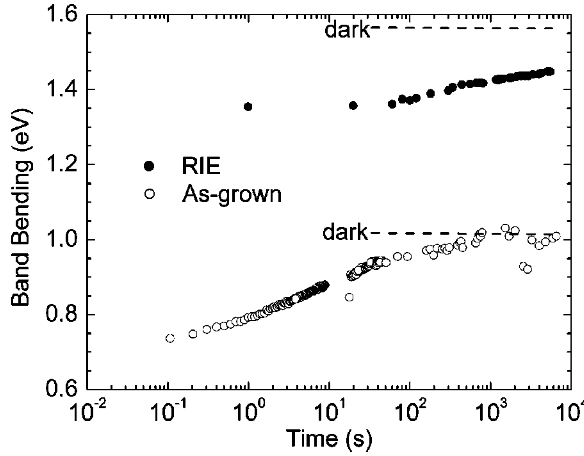

FIG. 2. Band bending as a function of time after stopping UV illumination for as-grown and RIE GaN.

when the carrier photogeneration rate is equal to the surface recombination rate. Further understanding can be obtained from a comparison to the time constant involved when the illumination is stopped. Another possibility for the change in the band bending is that due to the adsorbed oxygen being removed by the light. However, other measurements have indicated that the effects of adsorbed oxygen on the surface states are minimal, and reduce rather than increase the surface potential.[10]

Emission of electrons from bulk to the surface states and reestablishment of the dark band bending condition take longer time than the charging process for both the as-grown and RIE GaN surfaces as shown in Fig. 2. Also, the discharging process is longer for the RIE treated surface than for the as-grown GaN surface. This is consistent with thermionic emission of electrons from bulk to the surface states, as the larger surface band bending for the RIE treated surface would result in much slower emission for the same temperature.

The delay in shift of the surface potential with illumination implies that there is a high density of surface states. As the illumination proceeds, the occupations of the discrete surface states with electrons decrease until they are emptied. The dynamics of emptying the surface states under UV illumination and that of recovery process in a particular sample are related but they both depend on the sample history. So, the dynamics is fast for as-grown samples, while it becomes very slow after the RIE treatment. After the aqua-regia treatment the dynamics remained unchanged, whereas after a shallow etching in hot KOH the dynamics became almost as fast as in as-grown samples. We explain this by removing some surface states by KOH etching, but not with aqua-regia which tends to remove metals and other contaminants from the surface.

Photoluminescence spectrum was measured for the as-grown and RIE treated GaN samples at room temperature, the results of which are shown in Fig. 3. After the RIE treatment, the near band edge and yellow luminescence intensity decreased by approximately three times while the shape of the PL spectrum remained unchanged. This effect can be attributed to creation of nonradiative defects near the surface of the RIE treated GaN.

In conclusion, surface band bending on GaN layers has

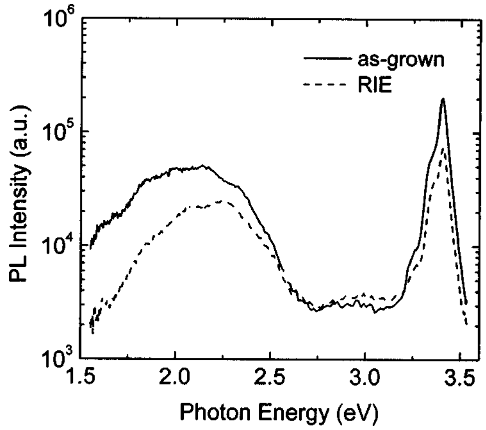

FIG. 3. PL spectrum of MBE grown GaN samples before and after RIE measured at room temperature. After RIE, the near-band-edge PL and YL band intensity decreased by approximately three times, presumably due to creation of nonradiative defects near the surface.

been measured for as-grown and reactive ion etched (RIE) surfaces. RIE damage causes an increase in the band bending. The band bending in the as-grown GaN is 1.0 eV, increasing to 1.4 eV after RIE treatment using BCl_3. Furthermore, the UV illumination time required to saturate the surface states for a given illumination power increases significantly for the RIE treated surface. RIE treatment followed by aqua-regia treatment is similar to RIE alone, increasing the band bending by 0.4 eV. The delay in the shift of the band bending, when the illumination is initiated, is related to a high density of surface states both in the as-grown GaN surface and in the RIE treated GaN surface. The delay in shift of band bending with illumination was much longer with the RIE treated GaN surface, indicating a higher surface state density created by the RIE treatment. KOH etching returned the dynamics of photoinduced changes to that in as-grown sample. This implies that RIE induced surface states can be reduced by KOH etching. Over the range of etching power used in these studies, the difference in band bending was not significant, nor was the difference in photoluminescence response.

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