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The effect of an ambient environment on the surface photovoltage and photoluminescence observed for GaN is studied. In air ambient the upward band bending gradually increases under UV illumination and is explained by the photoinduced chemisorption of surface adsorbates. Specifically, the increase in negative surface charge is consistent with the transfer of electrons from surface states or bulk to oxygen species physisorbed at the GaN surface. In contrast, the upward band bending gradually decreases in vacuum under UV illumination and can be explained by the photoinduced desorption of these species. The photoadsorption and photodesorption of negatively charged species cause the surface depletion region to increase and decrease, respectively. This change in depletion region width is consistent with the observed decrease in photoluminescence intensity in air ambient and its significant increase in vacuum for a sample with low free electron concentration. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3122934]

The importance of the surface in controlling properties of semiconductors has been known for many years. Upward band bending due to negative charge at the surface and downward band bending due to positive charge at the surface are commonly observed in *n*- and *p*-type semiconductors, respectively.[1] The origin of such surface charge may be intrinsic, e.g., due to surface states from dangling bonds or defects, or extrinsic and due to adsorbed surface atoms or molecules. The surface of air-exposed, undoped *n*-type GaN grown on *c*-plane sapphire shows an upward band bending of approximately 1 eV due to negative charge at the surface.[2–5] This band bending can be reduced by 0.3–0.9 eV during illumination with ultraviolet (UV) light,[6–9] because of the accumulation of photogenerated holes at the surface. Such an illumination-induced change in surface band bending, known as surface photovoltage (SPV), is commonly measured by the contactless Kelvin probe technique.[1] The upward band bending in *n*-type semiconductors also leads to a depletion region that suppresses the recombination of photogenerated carriers. As a consequence, photoluminescence (PL) intensity depends on band bending and may drastically decline when the electric field in the depletion region is sufficiently strong to separate photogenerated carriers before they can be captured by defects or form excitons. In this work we have studied the effect of UV illumination on both the SPV and PL observed for GaN placed in vacuum or air ambient environments.

Undoped and Si-doped GaN layers with thicknesses in the range of 1–2 μm were grown on *c*-plane sapphire by molecular beam epitaxy. This study characterizes two samples designated as sample A (undoped) and sample B (Si-doped), which have room temperature free electron concentrations of 3×10^{16} and 7×10^{18} cm^{-3}, respectively. A Kelvin probe apparatus mounted in an optical cryostat was used to measure the contact potential difference between the probe and GaN surfaces. Prior to illumination, samples were maintained in dark for an extended period in order to minimize any residual potential from previous light exposure. In most experiments the samples were illuminated from the back side through a sapphire window and sapphire sample substrate using a 75 W xenon lamp filtered through a 0.25 m grating monochromator and longpass filters. The 365 nm light was chosen for band-to-band excitation of electrons since its absorption in the depletion region is substantial due to the Franz–Keldysh effect.[10] To compare SPV data for this backside illumination geometry with a traditional front side geometry, control experiments were done using an unfocused HeCd laser beam (325 nm, 40 mW) directed to the front sample surface through a special window port and a perforated Kelvin probe. PL data were also acquired in the same optical cryostat using a HeCd laser excitation source, where the same experimental conditions were used as for the Kelvin probe measurements.

We found that the PL behaviors for the undoped sample A and doped sample B, which have different depletion region widths that affect carrier recombination, were significantly different. In the case of sample B with a relatively narrow depletion region, the PL spectrum and intensity did not change with UV illumination time and the PL intensity increased by about 20% when changing from air ambient to midvacuum (10^{-5} mbar). In contrast, the PL intensity for sample A with a wide depletion region was very sensitive to the experimental conditions. The insert for Fig. 1 indicates how the PL intensity gradually decreased in air ambient under continuous UV illumination at sufficiently high excitation power density. After evacuation, the PL intensity increased significantly with the largest increase being in the region of excitonic emission (Fig. 1). When air ambient was introduced again, as seen in Fig. 2, the PL intensity decreased very slowly, nearly as a logarithm of time. Interestingly, there was no noticeable change in the PL intensity measured just before turning off the UV illumination for a few minutes and just after turning it back on again, indicating that the decreasing PL intensity required UV light exposure.

In order to better distinguish the influence of surface band bending from changes in depletion region width, we used a Kelvin probe to measure the surface contact potential and SPV signal in a variety of gas environments. As shown

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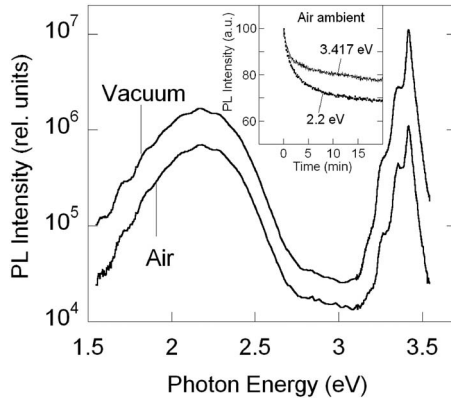
FIG. 1. PL spectra of sample A in air and vacuum (HeCd laser, P_{exc} =0.3 W/cm^2). PL intensity at 3.4 eV for sample B (not included) changed by only 20% in air vs vacuum. The insert shows decreasing PL intensity in air ambient under continuous exposure of sample A. PL intensity at 3.4 eV for sample B did not change during UV illumination in air ambient.

in Fig. 3, samples A and B exhibit similar behavior in the SPV data during UV exposure as a function of the environment. In vacuum, after an initial fast rise (to 0.53 eV in sample A and to 0.50 eV in sample B), the SPV signal gradually *increased* for both samples (to 0.64 eV for sample A and to 0.60 eV for sample B) under continuous UV illumination with P_{exc}=0.03 W/cm^2. In a nitrogen gas environment (industrial grade purity), the SPV signal slightly decreased for sample A and significantly increased for sample B. In air ambient, however, the SPV signal almost instantly reached a maximum (0.62 eV for sample A and 0.41–0.46 eV for sample B) and then gradually *decreased* by at least 0.1–0.2 eV. The SPV signal also decreased significantly in the presence of oxygen (99.999%, <1 ppm H$_2$O), as shown for sample B in Fig. 3(b). This result indicates that the primary component in air likely responsible for the observed decrease in SPV is oxygen. Such an assumption is consistent with previous findings that the presence of oxygen gas or air causes nearly identical changes in PL measurements for GaN.[11] After switching off the light, the SPV in air ambient or oxygen dropped to its initial dark level or close to it in only 1 min and then continued to decrease slowly. In contrast, the SPV in vacuum or a nitrogen gas environment decreased much less during the first minute after ceasing illumination and continued to decrease with a nearly logarithmic behavior. Figure 4(a) illustrates the effect of UV exposure
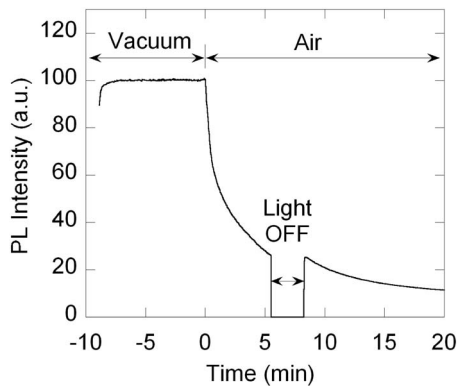

FIG. 2. Evolution of PL intensity at 3.417 eV for sample A before and after exposure to air at time t=0 (P_{exc}=0.3 W/cm^2). The laser was blocked between 5.5 and 8 min.
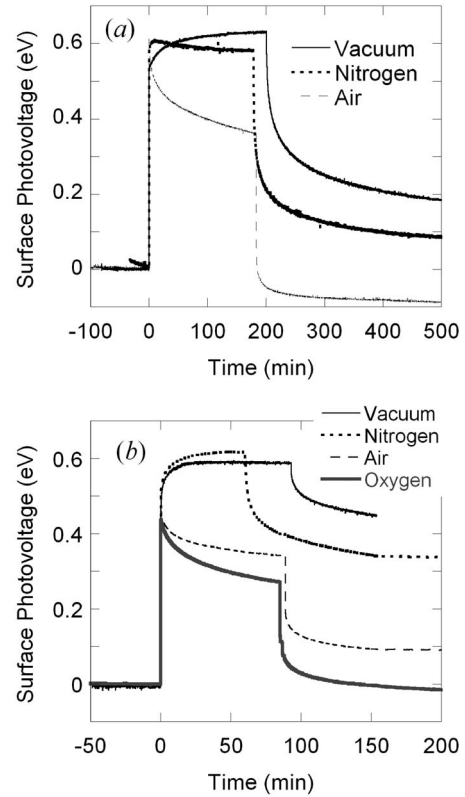

FIG. 3. Evolution of SPV in different gas environments for (a) sample A and (b) sample B (P_{exc}=0.03 W/cm^2). The UV illumination is turned on at t=0 min and turned off 60 to 200 min later. Note that the SPV signal significantly decreases under illumination in air or oxygen for both samples.

time after switching off illumination for sample B in air ambient. Note that these measurements were conducted 8 months prior to the data shown in Fig. 3(b). After a long UV exposure (78 min), the SPV dropped below its initial
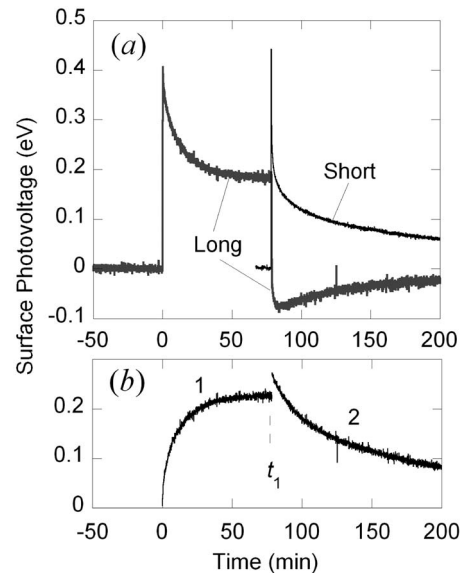

FIG. 4. (a) Evolution of SPV for sample B in air for short (few seconds) and long (75 min) exposures to 365 nm light (P_{exc}=0.03 W/cm^2). The light is switched off at time t=t_1=78 min. (b) Adsorption-related component of SPV derived from (a) assuming that SPV due to internal mechanism does not change during UV exposure and decays in dark as for short exposure. Part 1 is equal to the initial SPV offset value (0.41 eV) minus the "long" curve for $0 < t < t_1$; part 2 is equal to the difference between the "short" and long curves for $t \geq t_1$.

dark level and then slowly increased to the dark level. After a short UV exposure (few seconds), however, only logarithmic decay was observed. Such behavior implies a competition between two mechanisms for restoration of the SPV signal to its dark value after ceasing illumination, as will be discussed below.

The observed transients in the SPV data result from a number of different processes. The initial fast increase in SPV upon illumination for both samples is due to the creation of holes in the depletion region and their fast accumulation at the surface, which decreases band bending and increases SPV. After this initial fast rise, the slower decrease in SPV in air ambient during UV exposure is attributed to another mechanism: the photoinduced adsorption of oxygen species. The accumulation of electrons at these surface species (chemisorption process) results in increased surface band bending and the observed decrease in SPV. In vacuum, however, the SPV gradually increases due to the slow desorption of any surface species. These processes are slow because they require the transfer of electrons between the bulk or surface states and the oxygen species, where the electrons may tunnel through a thin oxide layer. It should be noted that some GaN samples demonstrate a relatively constant SPV under illumination after the initial fast rise. The susceptibility of the surface to photoinduced chemisorption can therefore be sample dependent and further studies are necessary to investigate this effect. The adsorption-related component of the SPV is isolated for sample B in Fig. 4(b). It is assumed that the slow decrease in SPV during illumination is due to the transfer of electrons from GaN to oxygen species, and that the difference in SPV decay after short and long illumination is attributed to electron transfer from oxygen species to GaN, which is logarithmic in time. Observation of the SPV decrease under UV illumination in oxygen and air but not in nitrogen indicates that adsorption of oxygen species rather than water vapor is responsible for the accumulation of negative charge on the surface and the subsequent increase in band bending in air ambient. Reports concerning photoinduced adsorption and desorption for semiconductors can be found;[12] however, this is the first observation of both effects in GaN.

The PL results can also be qualitatively explained within the above photoinduced chemisorption model, given the assumption that the depletion region does not contribute to PL due to a strong electric field that quickly separates photogenerated carriers. The upward band bendings in samples A and B are estimated as 0.9 and 1.3 eV, respectively, in agreement with a previous study of GaN with different free electron concentrations.[5] The depletion region widths under dark conditions for samples A and B are then estimated to be 170 and 13 nm, respectively. During the first few seconds of illumination, the band bendings for samples A and B abruptly decrease by approximately 0.6 and 0.4 eV, respectively, corresponding to depletion region widths of 100 and 11 nm. During continuous UV illumination in air for 2 h, the depletion region width gradually increases to about half of its initial change. After switching off illumination, the depletion region width abruptly increases to its initial dark value or slightly above. Since the absorption coefficient in GaN at 325 nm is about 10^5 cm^{-1} (Ref. 13), the depletion region width and its variation under illumination can be disregarded in sample B but plays a significant role in sample A. In air ambient, the PL intensity in sample A decreases substantially under UV illumination due to a gradual increase in the depletion region width. In vacuum, the PL intensity in this sample increases due to a decreasing depletion region width.

In conclusion, we have observed an increase in upward band bending in air ambient and a decrease in vacuum under continuous UV illumination. These changes in band bending are explained by the photoinduced adsorption of surface species in air ambient and photoinduced desorption in vacuum, where the major adsorbate is assumed to be oxygen. The observed changes in PL intensity under continuous illumination and for transitions between air ambient and vacuum are consistent with changes in surface potential determined by the Kelvin probe technique. The results of this work show that the electrical and optical properties of GaN are sensitive to changes in ambient, and therefore special attention should be given to surface passivation during the development of GaN-based optoelectronic devices.

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