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Transient photovoltage in GaN as measured by atomic force microscope tip

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We studied restoration of the band bending at the surface of undoped GaN layers after illumination with above-bandgap light. The photovoltage saturated with illumination at about 0.2–0.3 eV at room temperature, although the upward band bending for GaN in the dark is of the order of 1 eV. We attribute the photovoltage effect to charging of the surface states, the density of which is estimated at about 10^{12} cm^{-2} . Restoration of the barrier after a light pulse is simulated by a phenomenological model whereby the acceptorlike surface states are emptied of electrons under illumination and filled back in dark due to thermionic transfer of free electrons from the bulk to the surface states over the near-surface barrier. Photoinduced desorption of oxygen also affects the value of the photovoltage if the illumination is prolonged. © 2004 American Institute of Physics. [DOI: 10.1063/1.1774245]

I. INTRODUCTION

Recent progress in development of GaN-based optical and electronic devices contrasts with weak understanding of processes at the surface and interfaces that are certain to play a pivotal role in the performance and reliability of many devices based on this material system. Surface states are formed at the GaN surface due to Ga or N termination, reconstruction, structural and point defects, adsorbates, oxidation, etc. The surface of the air-exposed undoped GaN grown on *c*-plane sapphire shows an upward band bending, reported as 0.4, 0.75, and 0.9 eV in various studies.^{1,3} It is established that a thin ($\sim 9 \text{ Å}$) Ga_2O_3 layer,⁴ as well as chemisorbed oxygen atoms (up to one monolayer) cover the GaN surface.^{1,5} The band bending may also be affected by spontaneous polarization.⁶

Scanning Kelvin probe microscopy (or electrostatic force microscopy) has been successfully used in recent years for the surface potential mapping of GaN.^{7–11} Surface potential fluctuations in the dark typically range from less than 20 mV up to 300 mV in different samples.^{7–11} Hsu *et al.*⁷ reported that the surface potential fluctuations were not seen on oxidized surfaces, whereas after cleaning in hot H_3PO_4 , the fluctuations appeared. Remarkably, the variations in the surface contact potential image correlated with the distribution of edge dislocations, consistent with excess local negative fixed charges at dislocation sites.⁷

Illumination of GaN with ultraviolet (UV) light has been reported to reduce band bending by about 0.35 (Ref. 12) or 0.5 eV (Ref. 13) due to screening of the electric field by photogenerated electrons and holes (photovoltage effect).¹⁴ Traditionally,^{14,15} the surface states in semiconductors are divided into “fast states” (presumably located at the interface between a semiconductor and the surface oxide layer) and “slow states” (predominantly located inside or outside of the oxide and arising from adsorbed gas atoms). Usually the fast

states are characterized by time constants of the order of microseconds or less, while the slow states have time constants ranging from a fraction of a second to several hours.¹⁵ In the present work, we studied transient photovoltage in GaN and developed a phenomenological model which accounts only for the recombination between the bulk electrons and holes bound to the acceptorlike surface states. The model predicts accurately the logarithmic transients in the photovoltage after cessation of light. It also explains the experimental transients containing fast and slow components.

II. EXPERIMENT

A number of undoped GaN layers with thickness in the range of 1–2 μm were grown on *c*-plane sapphire by molecular beam epitaxy (MBE). Two undoped GaN layers (6 and 30 μm thick) were grown on *c*-plane sapphire using hydride vapor phase epitaxy (HVPE) by TDI, Inc. Ga polarity of the samples was established from etching characteristics, surface morphologies, x-ray diffraction data, and in a few cases it was confirmed by cross-section transmission electron microscopy.¹⁶ The concentration of electrons at room temperature, determined from the Hall effect measurements, varied from 10^{17} to 10^{18} cm^{-3} .

We measured the absolute value of the surface band bending with atomic force microscopy (AFM) in the surface potential mode (Kelvin probe method). The gold-coated tips were calibrated with respect to a 100 nm gold film. In this method, a dc bias on the tip is varied so that, when it equals the potential at the conductive sample surface, the force felt by the tip vanishes. By measuring the dc bias required for vanishing tip force, we obtained the value of the contact potential V_{cp} between the gold tip and GaN surface. V_{cp} varied not more than 30 mV as the distance between the tip and the surface was increased from ~ 0.05 to 1 μm .

The band bending near GaN surface, or potential barrier height in dark, Φ_b , can be found as

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FIG. 1. Schematic diagram showing the band bending and the vacuum level (E_{VAC}) near the surface of GaN in vicinity of the metal tip.

$$\Phi_d = \phi_M - qV_{cp} - \Phi_s - \chi + E_F, \quad (1)$$

where ϕ_M is the metal work function ($\phi_M = 5.1$ eV for Au), χ is the electron affinity of the semiconductor, and E_F is the Fermi level measured with respect to the conduction band minimum E_C (Fig. 1). The parameter Φ_s includes potential drop across the oxide film, arising from a possible distribution of charge in it, surface dipole due to adsorbate species, and microscopic dipole at the surface which is determined by the exact arrangement of the atoms near the surface.¹⁴ Based on the findings of Bermudez,¹ Wu *et al.*,² and Nienhaus *et al.*,¹⁷ we assumed $\chi = 3.3 \pm 0.3$ eV for GaN. The variation in values of χ reported in the literature may be due to different microscopic surface dipoles, different degrees of oxidation, and presence of different adsorbed species in the experimentally studied GaN.

Photovoltage effect, or variation of the band bending under illumination, was measured with the help of a pulsed nitrogen laser (photon energy of 3.68 eV) or a Xe lamp in conjunction with a grating monochromator. Neutral-density filters were used to attenuate the incident light, and color filters were used to cut the unwanted orders of the grating. All experiments were performed at room temperature.

III. MODEL

The upward band bending at the surface of n -type GaN with uncompensated concentration of shallow donors N_D is characterized by the barrier height Φ and associated depletion region width W ,¹⁸

$$W = \sqrt{\frac{2\Phi\epsilon\epsilon_0}{q^2 N_D}}. \quad (2)$$

The band bending is caused by negative charge at the surface with density n_s and the charge balance requires that

$$n_s = WN_D. \quad (3)$$

The origin of n_s is in part the acceptorlike surface states below the Fermi level and in part uncompensated negative charge of ions adsorbed at the surface. Previously we have obtained that in a large set of GaN samples with different concentration of electrons the barrier height at the surface is of the order of 1 eV,³ and thus, the depletion region width is about 100–30 nm for the concentrations of shallow donors in the range 10^{17} – 10^{18} cm⁻³, respectively, and the density of

FIG. 2. Schematic diagram showing the band bending near the surface of GaN in dark (a) and after UV light pulse (b). Electrons are shown with solid circles and holes—with empty circles. The Fermi level E_F is shown as the same for electrons and holes in nonequilibrium case (b) in assumption that recombination in bulk is much faster than recombination over the barrier, and concentration of traps in the depletion region is much less than density of the surface states.

the negative charge at the surface is in low 10^{12} cm⁻³ according to Eqs. (2) and (3).

A pulse of light creates electron-hole pairs. Since the depletion region width in a typical undoped GaN is comparable with the effective absorption depth of light [about 80 nm at 3.68 eV (Ref. 19)], a substantial part of the photogenerated holes is swept towards the surface by the strong near-surface electric field (Fig. 2) and quickly (in $\sim 10^{-10}$ – 10^{-8} s) captured by surface states. On the other hand, the photogenerated electrons are quickly swept towards the bulk, increasing concentration of free electrons in the bulk, likely in close vicinity of the surface barrier since the diffusion is relatively small in GaN. The holes captured by the surface states reduce the negative charge of the surface and, consequently, reduce the depletion region width from its dark value W_d to the light value W_l and the band bending from Φ_d to Φ_l , according to Eqs. (2) and (3). One may expect that these values tend to zero with increasing excitation intensity due to complete filling of the acceptorlike surface states with holes. However, in addition to surface states, other charges such as negatively charged adsorbed ions and spontaneous polarization, may contribute to the upward band bending near the GaN surface. Thus, in general, the photovoltage may differ from the band bending in the dark even when it saturates with increasing excitation intensity.

We assume that thermionic transfer of free electrons from the bulk to the surface states over the barrier dictates the restoration of the charge equilibrium after the light is turned off. In the first-order approximation we neglect tunneling of electrons through the near-surface barrier and even two-step transfer via deep traps because the localization of the electrons at deep traps is too high to provide a discernible overlap between the wave function of an electron bound to a trap and that for a hole bound to a surface state at a spatial separation comparable to the depletion width. For simplicity let us assume that only acceptorlike surface states located below the Fermi level (with the density n_s) participate in the photovoltage transients. After the surface states are partially or completely filled with photogenerated holes and the light is off the dynamics of the recombination is determined by the following rate equation:

$$\frac{\partial p_s}{\partial t} = -C_n p_s N_D \exp\left(-\frac{\Phi}{kT}\right). \quad (4)$$

Here, the rate of the electron-hole recombination is proportional to the density of the holes at the surface acceptor-like states, p_s , and concentration of free electrons at an energy Φ from the bottom of the conduction band, which approximately equals $N_D \exp(-\Phi/kT)$. C_n is the capture coefficient, which is related to the capture cross section, σ_n , as

$$C_n = \sigma_n v_{th} = \sigma_n \sqrt{\frac{8kT}{\pi m_n}}, \quad (5)$$

where v_{th} ($\sim 2 \times 10^7$ cm/s) and m_n ($0.22 m_0$) are the thermal velocity and effective mass of electrons in the conduction band of GaN.

For a single pulse and small values of photovoltage the time dependence of Φ can be ignored, and the solution of Eq. (4) can be found in the form

$$P_s(t) = P_0 \exp\left(-\frac{t}{\tau}\right), \quad (6)$$

where τ can be construed as the recombination lifetime²⁰ and $P_0 = (W_d - W_l)N_D$. Substitution of Eq. (6) into Eq. (4) gives

$$\tau = N_D^{-1} C_n^{-1} \exp\left(\frac{\Phi}{kT}\right). \quad (7)$$

Finally, equating the expression for p_s from Eq. (6) to its expression following from Eq. (3), $P_s = [W_d - W(t)]N_D$, and taking into account that the photovoltage signal after pulse excitation, determined as $\Delta\Phi(t) = \Phi_d - \Phi(t)$, is small compared to Φ_d , we obtain a solution for the time evolution of $\Delta\Phi$ in the form

$$t \approx N_D^{-1} C_n^{-1} \exp\left(\frac{\Phi_d - \Delta\Phi(t)}{kT}\right) \ln\left(\frac{\Delta\Phi(0)}{\Delta\Phi(t)}\right). \quad (8)$$

Analysis of Eq. (8) shows that at times $t \ll N_D^{-1} C_n^{-1} \exp(\Phi_d/kT)$ and $t \gg N_D^{-1} C_n^{-1} \exp(\Phi_d/kT)$, $\Delta\Phi$ equals $\Phi_d - \Phi_l$ and 0, respectively. $\Delta\Phi$ decreases to half its initial value $\Delta\Phi(0)$ at

$$t = t_0 = N_D^{-1} C_n^{-1} \exp\left(\frac{\Phi_d - 0.5\Delta\Phi(0)}{kT}\right) \ln 2, \quad (9)$$

and $\Delta\Phi(t)$ varies as $\sim \ln(t)$ close to t_0 . Examples of the calculated $\Delta\Phi(t)$ dependences for $\Delta\Phi(0) = 0.2$ eV and different values of the band barrier are shown in Fig. 3. In these calculations the capture cross section was taken equal to 10^{-15} cm², a typical value for semiconductors, although values from 10^{-22} to 10^{-12} cm² have been reported in the literature.¹⁵ According to Eq. (8), if the actual value of σ_n is larger or smaller than 10^{-15} cm² by m orders of magnitude, a curve for a particular Φ_d should be shifted to the left or to the right, respectively, by m orders of magnitude in Fig. 3. The numerical solution of Eq. (4) accounting for the variation of Φ with time gives similar results if $\Delta\Phi(0) \ll \Phi_d$.

FIG. 3. Transients of photovoltage, calculated using Eq. (8) with $\Delta\Phi(0) = 0.2$ eV, $N_D = 3 \times 10^{17}$ cm⁻³, $C_n = 2 \times 10^{-8}$ cm³/s ($\sigma_n = 10^{-15}$ cm²), and Φ_d varied from 0.4 to 1.0 eV. Typical experimental transient is shown for comparison.

IV. RESULTS AND DISCUSSION

The samples selected for this study had smooth surfaces with the root-mean-square roughness of about 0.5 nm in the 1×1 μm area. The surface potential images did not reveal any significant features, and the variation of the contact potential V_{cp} in the 5×5 μm² area did not exceed ~ 20 mV. This result is in agreement with the findings of Hsu *et al.*⁷ and Losurdo *et al.*,⁸ although others observed larger fluctuations of the potential.⁹⁻¹¹ We repeated measurements of the photovoltage transients at different spots of the samples, and the results were reproducible. To assure that the transients are representative of the entire surface, and not of dislocations, we have measured the transient photovoltage on the Ga-face surface of a freestanding template, having the dislocation density less than 5×10^6 cm⁻² (Ref. 21), and obtained similar transients.

Figure 4 shows a typical example of the dependence of the photovoltage value after pulse excitation, $\Delta\Phi(0)$, on excitation intensity. Each point was measured as a variation of the band bending after approximately 10^{-2} s (the best temporal resolution in our setup) from a single pulse of UV light,

FIG. 4. Photovoltage after illumination with a single pulse of UV light $\Delta\Phi(0)$ as a function of the excitation intensity.

FIG. 5. Transient of photovoltage, $\Delta\Phi(t)$, after pulse of UV light, attenuated 10^3 (1) and 10^2 (2) times. Solid curves—calculated using Eq. (8) with $C_n = 2 \times 10^{-8} \text{ cm}^3/\text{s}$ ($\sigma_n = 10^{-15} \text{ cm}^2$) $\Phi_d = 0.64 \text{ eV}$, and $\Delta\Phi(0) = 0.05 \text{ eV}$ (1) and 0.22 eV (2).

and we waited for complete restoration of the dark value of Φ between measurements. As depicted in Fig. 4, $\Delta\Phi(0)$ increases linearly with excitation intensity and completely saturates above $\sim 1\%$ of the maximal laser intensity. We explain the saturation of $\Delta\Phi(0)$ at high excitation intensities by saturation of the surface states with photogenerated holes after the UV light pulse. Transition from the linear increase of $\Delta\Phi(0)$ to saturation corresponds to the density of the photogenerated electron-hole pairs of about $2 \times 10^{12} \text{ cm}^{-2}$, as estimated from the laser power accounting for the geometry of the experiment. Ignoring losses due to bulk recombination, we conclude that about the same density of surface states participate in the photovoltage effect. Corrections for losses would decrease this value.

Figure 5 demonstrates transients of $\Delta\Phi$ for two excitation intensities (below and near the saturation point). The experimental dependencies can be well fitted with Eq. (8) using the same parameters except for $\Delta\Phi(0)$. Note that the apparent independence of $\Delta\Phi$ on t for $t < 0.1 \text{ s}$ for the case of $\Delta\Phi(0) = 0.05 \text{ eV}$ supports the accuracy of the values of $\Delta\Phi(0)$ in Fig. 4 below the saturation point, although the values of $\Delta\Phi(0)$ above the saturation point may be slightly underestimated due to the absence of experimental data below 10^{-2} s in the transient curves. To check any possible contribution of very fast transients (below 10^{-2} s), we studied transients in $\Delta\Phi$ for the same sample illuminated with continuous-wave (cw) UV light. In this case, $\Delta\Phi(0)$ saturated at a value somewhat larger (about 0.4 eV) than that at 10^{-2} s after a single pulse. However, after turning off the light the dynamics of the fast component of decay of $\Delta\Phi$ was nearly identical to that after a single pulse excitation, and only the amplitude of the slow component of $\Delta\Phi$ was larger in the former case. Thus, we conclude that in this particular case the contribution of fast variation of $\Delta\Phi$ below 10^{-2} s is negligible.

We observed also a slow increase of the photovoltage under extended illumination with pulses at a repetition rate of 30 Hz (up to 0.1 eV increase compared to a single pulse). However, the larger photovoltage under extended illumination (cw or pulsed) does not necessarily mean a higher de-

gree of filling of the surface states of GaN with holes as compared to the single pulse illumination. It is possible that prolonged high-intensity illumination modifies states located in the oxide layer, as well as facilitates desorption of ions from the surface (photoinduced desorption).

We attempted to estimate the value of Φ_d from Eq. (1). For the majority of our GaN samples, including the sample analyzed in detail in this work, $\Phi_d + \Phi_s \approx 1.0 \text{ eV}$. It can be noted from Fig. 3 that the experimental data can be equally well fitted by Eq. (8) with the sets of (Φ_s, σ_n) gradually varied from $(0 \text{ eV}, 10^{-9} \text{ cm}^2)$ through $(0.35 \text{ eV}, 10^{-15} \text{ cm}^2)$ and up to $(0.6 \text{ eV}, 10^{-19} \text{ cm}^2)$. It should be stated that the present experiments do not allow independent determination of Φ_s and σ_n , although we believe that the cross section of 10^{-9} cm^2 is unreasonably large to justify the assumption that $\Phi_s = 0$.

We observed very similar transients of photovoltage in different GaN samples grown by MBE and HVPE. As follows from Eq. (8) the observed logarithmic transient of the photovoltage (sometimes treated as containing fast and slow components¹⁵) can be explained solely by thermionic transition of electrons from bulk to the surface states over the barrier at the surface. Note that the exact position of the surface states in the gap does not affect the calculations carried out in this work, as the method employed is sensitive to only the density of all acceptorlike states below the Fermi level at the surface in the dark. The density of these states is $(1.1 - 1.6) \times 10^{12} \text{ cm}^{-2}$ in the analyzed sample, as can be estimated from Eqs. (2) and (3) for all the plausible values of band bending in dark ($\Phi_d = 0.4 - 0.8 \text{ eV}$ in case of $\sigma_n \approx 10^{-19} - 10^{-12} \text{ cm}^2$, respectively).

V. CONCLUSIONS

In conclusion, we investigated transient behavior of the photovoltage in GaN after pulsed illumination. Logarithmic variation of the photovoltage, typically observed in the range $10^{-2} - 10^2 \text{ s}$ in undoped GaN layers, is attributed to thermionic emission of electrons from bulk to the surface states over the barrier near the surface. The phenomenological model developed explains the dynamics of the photovoltage transients (both fast and slow components) using first-order assumptions and two fitting parameters.

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