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Unpinned behavior of the surface Fermi level of GaN detected by photoreflectance spectroscopy

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The photoreflectance signal from GaN films is sensitive to the ambient medium. A large decrease in the photoreflectance amplitude is observed, when the ambient medium is changed from air to vacuum. This effect is attributed to ultraviolet-light-induced desorption of oxygen from the sample surface leading to a reduction of the surface barrier height. The effect is absent, when a thin Ti layer is deposited on top of the GaN film. A simple model is used to demonstrate that the surface photovoltage can be strongly reduced with a decrease of the surface barrier height. © *2000 American Institute of Physics.* [S0021-8979(00)05009-X]

I. INTRODUCTION

Modulation spectroscopy is a very powerful tool to characterize semiconductor microstructures. In particular, photoreflectance (PR) spectroscopy, which is a contactless variation of electroreflectance spectroscopy, has been successfully applied to investigate surface Fermi levels and photovoltage effects in different semiconducting material systems such as GaAs,[1–4] (Al, Ga)As,[5] InP,[6] and (In, Al)As.[7] From the analysis of the Franz–Keldysh oscillations (FKOs) in intermediate electric-field PR spectra, the surface electric field and the corresponding surface Fermi level can be estimated. For *n*-GaAs, a Fermi level pinning near the center of the energy gap has been found independently of the ambient medium and the treatment of the surface.[2–4] Similar results have been obtained for (Al, Ga)As.[5] However, for *p*-GaAs, a reduced surface state density has been reported[8] resulting in a lower band bending than for *n*-GaAs. Strong changes in the surface band bending and the PR amplitude have been reported for *p*-GaAs, on which Cs[3,9] and O_2 overlayers[3] had been deposited. An influence of the ambient medium on the surface barrier and surface recombination velocity has been reported for wide gap materials such as CdSe, CdS, and ZnS quite some time ago.[10]

In this letter, we study the room temperature PR spectra for *n*-GaN films exposed to different ambient media. We find a remarkable change in the PR amplitude and line shape, when the sample cryostat is evacuated under simultaneous ultraviolet (UV)-light illumination. We attribute these variations to a change of the surface barrier height caused by a UV-light-induced desorption of oxygen. The sensitivity of the PR spectra to the ambient medium was directly confirmed by exposing the system to He. Furthermore, by depositing a Ti layer on top of the GaN film, the effect could be removed.

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II. EXPERIMENT

A variety of samples has been investigated in this work, including GaN layers grown by plasma-assisted and reactive molecular-beam epitaxy (MBE) on 6H–SiC substrates as well as by metalorganic vapor phase deposition (MOCVD) on sapphire substrates. We stress that all these layers exhibit Ga-face ([0001]) polarity and that for all samples a temporal change of the photoreflectance signal is observed. In the following, we will focus on a single sample, which has been thoroughly characterized by various methods. The sample consists of a 1.2-μm-thick GaN layer deposited directly onto 6H–SiC(0001) by reactive MBE, utilizing an unheated injector for introducing NH_3 into the system. Details of the growth conditions can be found in Ref. 11. Atomic force microscopy reveals the surface of this layer to be smooth (1.3 nm peak-to-valley and 0.17 nm rms roughness) with clearly visible monatomic step arrays. The background electron concentration, as determined by capacitance voltage profiling, is in the upper $10^{16}\,cm^{-3}$ range. Photoluminescence spectra taken at room temperature are dominated by the free-exciton transition at 3.401 eV with a full width at half maximum of 45 meV, while the intensity of the yellow band is more than two orders of magnitude lower.

Room temperature PR spectra were recorded in a dual monochromator setup.[12] The light of a 75 W Xe arc lamp was dispersed by a 0.64 m grating monochromator and directed onto the sample under nearly normal incidence. The sample was mounted on the cold finger of a continuous-flow He cryostat allowing measurements in the temperature range from 5 to 500 K. To minimize the effects of spurious light such as luminescence and stray light, the reflected beam from the sample was passed through a second 1 m grating monochromator and then collected with an UV-enhanced Si photodiode. This second monochromator was synchronized with the first one in order to act as an adjustable narrow bandpass filter. The signal $\Delta R/R$ was detected by a conventional lock-in setup in combination with a computer. The modulation was achieved by illuminating the sample with chopped light of an attenuated 50 mW HeCd laser ($\lambda = 325\,nm$). The average modulation intensity was approxi-

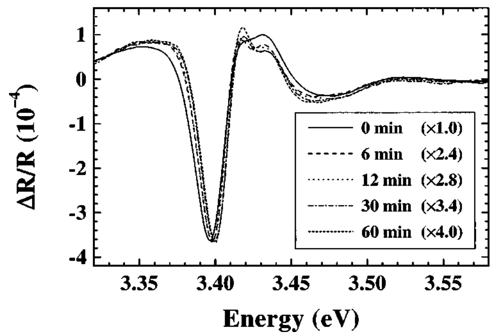

FIG. 1. Photoreflectance spectra of the GaN film measured at different times as indicated after starting the evacuation of the cryostat at 300 K. For a better comparison, the amplitude of all spectra has been normalized to the spectrum taken without evacuation (0 min).

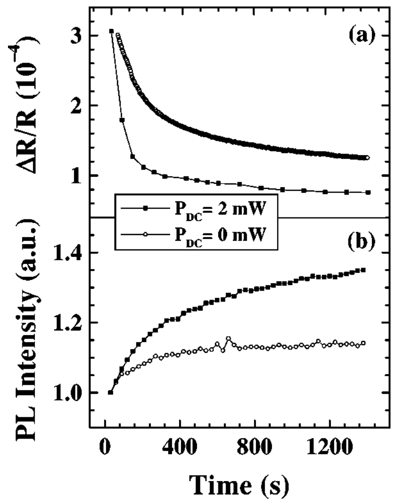

FIG. 2. (a) PR amplitude and (b) integrated photoluminescence intensity as a function of evacuation time of the cryostat without and with additional unmodulated UV illumination for the same sample as in Fig. 1 measured at 300 K.

mately $3\,\mathrm{mW\,cm^{-2}}$. For the photoluminescence (PL) measurements, we employed the same set-up using a liquid N_2-cooled charge-coupled-device array as the detector. The excitation conditions were exactly the same as in the PR measurements. For the experiments with additional UV illumination, the laser beam was divided in two parts by an adjustable beam splitter. One portion was modulated providing the pump beam, while the other unchopped portion yielded the additional UV illumination.

III. RESULTS AND DISCUSSION

In all investigated GaN samples, we found that the PR spectra are strongly influenced by the ambient medium. A typical example for a single sample is shown in Fig. 1, where several spectra recorded at different times after starting the evacuation of the cryostat are displayed. During this evacuation, the ambient medium changes from air to vacuum. Figure 1 clearly shows that the main effect of the evacuation is a decrease of the PR amplitude by a factor of as much as 4 accompanied by a small shift of the main peak near 3.4 eV to higher energies. At the same time, the full width at half maximum of the main minimum is decreased from 22 to 18 meV. We believe that the observed line shapes shown in Fig. 1 are Franz–Keldysh like, but with a significant influence of the electron-hole interaction, i.e., excitonic effects. First-principle calculations of Blossey[13] and Heesel *et al.*[14] have shown that the inclusion of the electron-hole interaction into the Franz–Keldysh theory of electromodulation spectra mainly results in an enhancement of the near-band-gap minimum and an energy shift of the FKOs. We attribute the dominant minimum near 3.4 eV (same spectral position as PL line maximum) to a superposition of the A and B exciton, which are not spectrally resolved in our PR spectra. The small shoulder at about 3.425 eV is probably due to a contribution from the C exciton. At higher energies ($E > 3.44\,\mathrm{eV}$), two Franz–Keldysh-like oscillations are observable. However, they are strongly damped due to an inhomogeneity of the electric field in the space-charge layer caused by the residual doping of the sample. A quantitative analysis of the surface electric field using only two FKOs does not seem to be practicable, but it is well known that the energy axis of intermediate field PR spectra and therefore the position of FKOs in relation to the gap energy scales as $F^{2/3}$,[15] where F denotes the surface electric field. From the fact that the FKOs move closer towards the main peak and that the FWHM of the main peak decreases, when the cryostat is evacuated, we conclude that the surface electric field is reduced. Within the Schottky model, this decrease results in a reduced surface barrier V_B and consequently in a reduced surface Fermi level eV_F as defined by $V_B = V_F - V_F^{\mathrm{bulk}}$, where the reference energy is the conduction band edge.

An important factor determining the time dependence of the PR spectra during evacuation is the intensity of the UV illumination caused by the pump and probe light. In Fig. 2(a), the development of the signal strength of the main minimum near 3.4 eV is shown as a function of evacuation time without (open circles) and with (solid squares) additional unmodulated UV illumination. During the first 200 s of the evacuation, the signal strength of the minimum decays much faster with than without any additional UV illumination. At the same time, the integrated intensity of the near-band-gap PL increases with increasing evacuation time as shown in Fig. 2(b) so that the PL signal exhibits the opposite behavior as the PR signal. The observed increase of the PL signal during the evacuation of the cryostat can be attributed to the decrease of the surface band bending or of the velocity of nonradiative surface recombination, which competes with radiative recombination channels as observed in the PL signal.

To confirm the sensitivity of the PR spectra of GaN films to the ambient medium, we measured PR spectra exposing the sample to different media. The results are shown in Fig. 3(a) for air, He, and vacuum. First, the spectrum for the GaN/vacuum surface was measured after evacuating the cryostat for approximately 1 h under additional UV illumination ($P = 10\,\mathrm{mW}$). Second, the cryostat was filled with He gas ($p = 1$ bar), and subsequently the PR spectrum labeled GaN/He was recorded. Finally, the cryostat was filled with air ($p = 1$ bar), and the PR spectrum labeled GaN/air was measured. Note that the spectrum for the GaN/air surface is

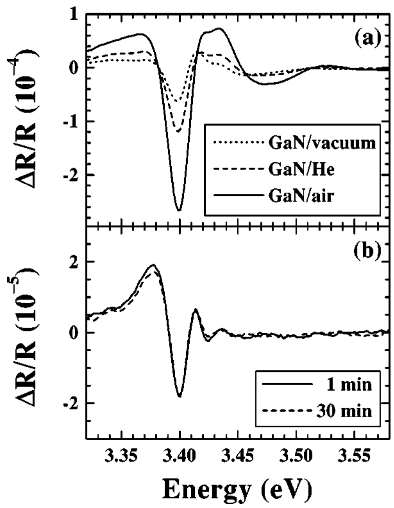

FIG. 3. PR spectra for different ambient media on the same sample as in Fig. 1 as indicated (a) and for the sample with a 7 nm Ti layer measured at different evacuation times as indicated with additional UV illumination (b) at 300 K.

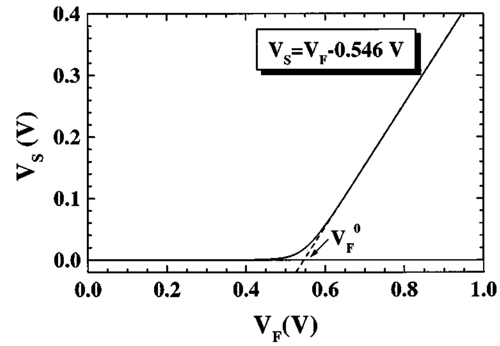

FIG. 4. Surface photovoltage V_S as a function of surface Fermi voltage V_F calculated using Eq. (1) with the parameters $A^*=2.4\times10^5\ \mathrm{A(m\,K)^{-2}}$, $B=4.63\times10^{-5}\ \mathrm{K^{-3/2}}$, $J_{PC}=11.4\ \mathrm{A\,m^{-2}}$, $T=300\ \mathrm{K}$, and $\eta=1$.

the same as the spectrum shown in Fig. 1 recorded before any evacuation, i.e., the process is reversible. The spectrum of the GaN/He surface is clearly different from the one of the GaN/vacuum surface, but its signal is still much smaller than the one for the GaN/air surface. We believe that the change from the GaN/vacuum to the GaN/He surface is due to residual oxygen, which entered the cryostat, when it was flushed with He gas. In order to obtain further information, we deposited a semitransparent Ti overlayer of 7 nm thickness on top of the already investigated GaN film. The resulting PR spectra are shown in Fig. 3(b). The Ti layer passivates the surface and almost completely removes the influence of adsorbates, since hardly any changes in the PR amplitude and linewidth are observed with increasing evacuation time [cf. Fig. 3(b)]. However, the PR signal is strongly reduced (by a factor of about 15) and the line shape significantly changed in comparison to the PR spectra of GaN films without any Ti layer. The reduction of the PR amplitude has probably two reasons. First, a considerable part of the reflected light is unmodulated and originates from the Ti/air surface reducing the signal $\Delta R/R$. Second, the density of surface and interface states as well as their energies are different, which could result in a lower band bending accompanied by a reduction of the PR aplitude as observed in the spectra for GaN films without a Ti overlayer. Since no FKOs could be identified in the spectra with the Ti overlayer, no conclusion about the surface electric field can be drawn.

We attribute the observed changes in the PR spectra during the evacuation of the cryostat to an UV-light-induced desorption of oxygen from the sample surface. As shown in Fig. 2, the typical time scale of this process is of the order of several hundred seconds, whereas the reverse process, i.e., the adsorption of oxygen, is instantaneous on our time scale. After flushing the evacuated cryostat with air, the immediately recorded PR spectra consist of the typical GaN/air signal strength and line shape as shown in Figs. 1 and 3(a). Note that we observed the same effect in a number of different GaN samples grown either by MBE or MOCVD using different growth conditions so that the quality of the investigated GaN films varied. In some cases, the change in line shape was more pronounced than the one shown in Fig. 1. The characteristic decay times as well as the final value of the PR amplitude varied from sample to sample, but the observed sensitivity to the ambient medium was always present. Obviously in samples with Ga-face ([0001]) polarity, V_F appears to be not strongly pinned. The desorption of oxygen from the surface changes the number of surface states and/or their energy resulting in a reduced V_B. This is apparent from the shift of the FKOs to lower energies as shown in Fig. 1.

The strong decrease of the PR amplitude seen in connection with the decrease of V_F can be explained within a transport model for the surface photovoltage V_S proposed by Yin *et al.*[1,16] Based on this model, V_S can be expressed as

$$V_S=\frac{\eta k_B T}{e}\ln\left[1+\frac{J_{PC}(1+BT^{3/2})}{A^*T^2}\exp\left(\frac{eV_F}{k_BT}\right)\right], \tag{1}$$

where η denotes an ideality factor, k_B Boltzmann's constant, T the sample temperature, e the elementary charge, $B=(1/300v_0)\sqrt{k_B/(2\pi m^*)}$, $A^*=(m^*ek_B^2)/2\pi^2\hbar^3$ the modified Richardson constant, m^* the effective mass, and v_0 the saturation velocity at room temperature. J_{PC} is the photoinduced current density, which is directly proportional to the optical pump intensity. Using Eq. (1), the temperature dependence of the surface photovoltage for GaAs was successfully described in Ref. 1. For higher temperatures ($T\geqslant300\ \mathrm{K}$), V_S tends to zero. In Fig. 4, V_S is shown as a function of V_F for the parameters $A^*=2.4\times10^5\ \mathrm{A(m\,K)^{-2}}$, $B=4.63\times10^{-5}\ \mathrm{K^{-3/2}}$, $J_{PC}=11.4\ \mathrm{A\,m^{-2}}$, $T=300\ \mathrm{K}$, and $\eta=1$ using $m^*=0.2m_0$ and $v_0=2.5\times10^5$ m/s.[17] For temperatures near 300 K, V_S depends strongly on V_F exhibiting a threshold-like behavior. For values of V_S larger than the threshold value V_F^0, V_S becomes linearly dependent on V_F as apparent from Eq. (1) with a slope of exactly one and a threshold value of $V_F^0=-(k_BT)/e\ln\{[J_{PC}(1+BT^{3/2})]/A^*T^2\}=0.54$. For values of V_F slightly above V_F^0, an increase of V_F from 0.6 to 0.8 V results in an increase of V_S by a factor of 4.6. Since in the small modulation limit, the PR amplitude is directly proportional to the surface photovoltage,[18,19] a small reduction of V_F can significantly decrease the PR amplitude confirming our experimental observation. A similar correlation between the surface band bending and the PR amplitude was observed for Cs and O_2 overlayers deposited on p-GaAs(100).[3]

IV. SUMMARY

In summary, we have observed a sensitivity of the photoreflectance signal from GaN films to the ambient medium. A small decrease of the surface band bending and a large change in the PR amplitude is observed, when the ambient medium is changed from air to vacuum. We attribute this effect to the UV-light-induced desorption of oxygen from the sample surface leading to a reduction in the surface Fermi level. The observed effects are absent, when a thin Ti layer is added on top of the GaN film. To obtain information on the surface chemistry as well as the character and energy of the surface states, additional work is required. It is important to take the observed effect into consideration in order to avoid misinterpretations of PR spectra on GaN films and heterostructures.

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