Yellow luminescence and Fermi level pinning in GaN layers

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A correlation between Fermi level pinning and yellow luminescence in Pt/n-GaN junctions has been studied using Schottky barrier measurements by internal photoemission spectroscopy and complementary deep level spectroscopies. The results show that illumination by photons with energies in the yellow luminescence range causes an unpinning of the interface Fermi level, accompanied by a significant increase of the Schottky barrier height from $\sim$1 to $\sim$1.9 eV. This strongly suggests the presence of acceptor states related to the yellow luminescence at the Pt/GaN interface. These states are charged in equilibrium and pin the interface Fermi level but can be optically discharged, resulting in a nearly unpinned interface. © *2000 American Institute of Physics.* [S0003-6951(00)02033-7]

In recent years, technological breakthroughs in GaN growth, doping, and contacting technologies have resulted in numerous devices, notably the blue GaN-based laser.[1] This has led to a considerable revival of interest in GaN fundamental bulk and surface properties. One surface property that is of particular relevance to device design is the height of the metal-GaN Schottky barrier, ϕ_b. The degree to which the interface Fermi level, and hence ϕ_b, are influenced by interface states is usually characterized by the slope parameter, $S \equiv d\phi_b/d(\phi_m\text{-}\chi_s)$, where ϕ_m is the work function of the metal and χ_s is the electron affinity of the semiconductor. S ranges from 0, obtained in the case of a complete pinning of the interface Fermi level by interface states (''Bardeen limit'') to 1, obtained in a complete absence of interface states (''Schottky limit'').[2] For GaN, S was found to be $\sim$0.385.[3] This value is typical of ionic semiconductors[2] and clearly indicates partial pinning by interface states.

The predominant manifestation of gap states in GaN is probably the ubiquitous yellow luminescence (YL).[4] While the related gap states are usually analyzed as bulk states, we have recently provided evidence indicating that they possess significant *surface* densities at both the external free surface[5] and internal grain surfaces[6] of GaN films. An increasing density of YL-related states toward the free surface was also reported recently by Brillson *et al.*[7] This has led us to hypothesize that YL-related states may also be present at metal/GaN interfaces. Moreover, because these states seem to be acceptor states that are charged in equilibrium,[5,6] they may play a significant role, together with other mechanisms, such as metal induced gap states,[8] in the observed interface Fermi level pinning of n-GaN, if present at the interface.[9] In this letter, we examine this hypothesis experimentally by correlating the Schottky barrier height with the charge state of the YL-related states.

Our experimental approach relies on the observation that the YL-related acceptor states are easily discharged by illumination of appropriate sub-band gap photon energy, which excites the electrons trapped in the states to the conduction band.[4,5] Such sub-bandgap illumination can therefore be used to ''unpin'' the Fermi level. For a metal where ϕ_m is larger than χ_s, Fermi level unpinning, whether partial or complete, should result in an increase of the Schottky barrier height towards a value closer to the Schottky limit.

For measuring Schottky barrier heights, we use internal photoemission (IPE) spectroscopy.[10] IPE is based on the classical description of the photoelectric effect given by Fowler.[11] When a metal–semiconductor junction is illuminated with photons of energy $h\nu$ higher than ϕ_b, charge carriers may be optically excited from the metal over the Schottky barrier into the semiconductor. These carriers are then swept in the built-in electric field of the metal–semiconductor junction, giving rise to a photocurrent. The photoyield, Y, i.e., the photocurrent per absorbed photon, is given for photon energies exceeding the Schottky barrier height by[11]

$$Y = C\frac{k^2T^2}{(E_F-\mu kT)^{1/2}}\left\{\frac{\pi^2}{6}+\frac{\mu^2}{2}+\sum_{n=1}^{\infty}\left[(-1)^n\frac{\exp(-n\mu)}{n^2}\right]\right\}, \quad (1)$$

where $\mu \equiv (h\nu\text{-}\phi_b)/kT$, C is a constant that depends on the metal, E_F is the Fermi energy measured from the bottom of the metal conduction band, q is the (absolute value of the) electron charge, k is the Boltzmann constant, and T is the temperature. Typically, in some intermediate range of μ's

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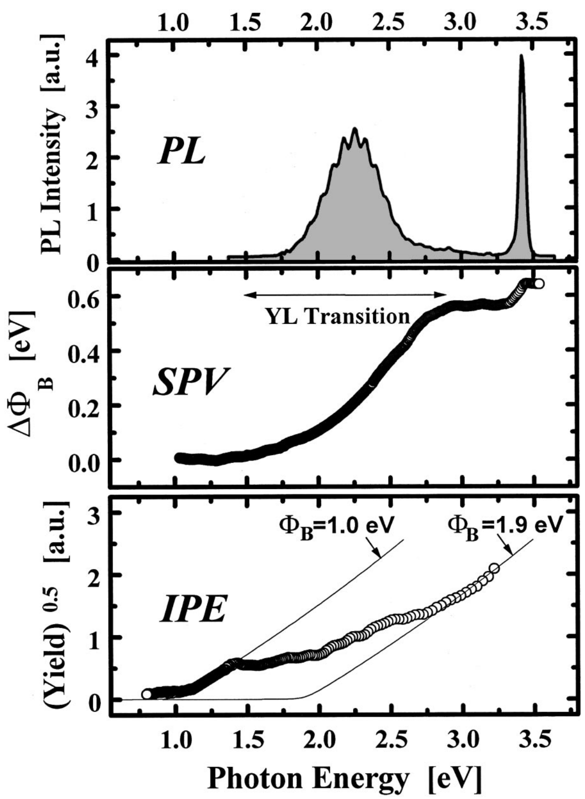

FIG. 1. PL (top), SPV (middle), and IPE (bottom) spectra obtained from the same typical GaN sample. Dashed lines on the internal photoemission spectrum indicate a fit of the data using Eq. (1).

the μ^2 term is dominant and plotting $\sqrt{Y}$ vs $h\nu$ yields a linear curve whose extrapolation to $Y=0$ yields ϕ_b. For higher μ's the curve becomes superlinear.

The GaN films used in this work were grown using metalorganic vapor phase epitaxy on (0001) oriented sapphire substrates.[5] The samples were ~3 μm thick with an effective doping level of $n\sim4\times10^{17}\,\mathrm{cm}^{-3}$. Schottky barriers were produced by depositing Pt contacts using a mechanical mask with 500 μm diameter holes, surrounded by large area ohmic Ti/Pt/Au contacts. Prior to the deposition, the GaN surface was etched in an aqueous solution of 10% HCl for 10 s and then blown dry with N_2 gas.

For characterizing the YL-related states, photoluminescence (PL) and surface photovoltage (SPV) spectroscopies were used to characterize the bare sample. Details of the experimental setup have been given elsewhere.[5,6] After deposition of contacts, IPE measurements were conducted within the same spectroscopic setup used for SPV. Photon yields were calculated by measuring the photocurrent across the Schottky diode using a picoampermeter (Keithly, model 614) and the photon flux transmitted through the sample using a pyroelectric detector. All samples were maintained in the dark for an extended period prior to illumination in order to eliminate persisting effects of previous light exposure.[12] All spectroscopies were conducted step-by-step from low energy to high energy and carried out at room temperature.

Typical spectra obtained from the three techniques are shown in Fig. 1. The PL spectrum [Fig. 1(a)] features a band gap-related peak at ~3.4 eV, as well as a broad subband gap peak, centered at ~2.2 eV. This is the well-known YL peak, resulting from defect states, shown to be distributed ~2.2 eV below the conduction band edge.[4,5] A band gap-related feature at ~3.4 eV is also observed at the SPV spectrum [Fig. 1(b)]. However, as SPV senses absorption, rather than emission, this feature is observed as a *knee* and not as a peak.[5] In the sub-band gap energy range, the SPV data feature a significant signal. It starts at ~1.6 eV, i.e., at the onset of the YL, and levels off at ~2.9 eV, i.e., at the outset of the YL. This correlation arises because SPV probes the ''yellow absorption.''[5,6] This absorption involves the transition inverse to that of the YL, i.e., the excitation of electrons from YL-related states into the conduction band.

We have previously attributed the observed SPV signal conclusively to a discharge of YL-related *surface* acceptor states that are charged in equilibrium.[5] If the same, or similar, surface states are still present after deposition of Pt, a high work function metal, they are expected to affect the Schottky barrier by pinning the interface Fermi level, resulting in a barrier height below the Schottky limit. This is readily observed by analyzing the IPE spectrum in Fig. 1(c). For Pt and GaN, the Schottky limit is expected to be ~2.25±0.1 eV, which is the difference between the work function of Pt (5.65 eV)[13] and the electron affinity of GaN (3.3 or 3.5 eV).[14,15] However, a fit of the lower energy part of the $\sqrt{Y}$ vs $h\nu$ curve shown in Fig. 1(c) using Eq. (1), yields a Schottky barrier height of only ~1 eV, a value which is much smaller than the Schottky limit and is in very good agreement with previous studies.[3,16–18]

At higher photon energies, the IPE curve becomes significantly *sublinear*. The energy range of this sublinear deviation coincides with the energy range of the YL-related signal in both the PL and SPV spectra. The curve apparently becomes superlinear only at ~2.9 eV, i.e., beyond the range of the YL-related transitions, where the SPV curve levels off. This behavior is interpreted as follows: As the interface YL-related states are discharged by optical excitation of their electrons into the conduction band, the net interface charge decreases, the interface Fermi level is unpinned, and the Schottky barrier height increases. This increase in barrier height reduces the internal photoemission yield [see Eq. (1)], resulting in an IPE signal below the initial trend. Indeed, fitting the data in the second superlinear regime (beyond ~2.9 eV) using Eq. (1) yields a value of ~1.9 eV, which is much closer to the Schottky limit. However, it is the trend that should be emphasized rather than the exact value of the height of the second barrier since the second superlinear regime of the curve is near the edge of the light source spectral range and has few data points.

It is important to note that several other mechanisms involving YL-related states are all easily *rejected* as causes for the behavior of the IPE curve. First, sub-band gap absorption in gap states is typically very weak as compared to absorption in metals, owing to the low density of gap states and their limited optical cross section. Therefore, the direct contribution of this absorption to the IPE curve is negligible. Second, a significant YL-related photoconductivity would, if at all, increase the photocurrent. This would cause a superlinear deviation of the IPE curve, whereas the opposite trend is observed experimentally. Third, the contribution of the semiconductor space charge to interface Fermi level pinning is usually negligible.[2] Therefore, even if the YL-related absorption results in a significant increase in the semiconductor free carrier density, this is unlikely to result in a major shift of the Schottky barrier height. Fourth, if the observed YL-related transitions occur at the semiconductor bulk (or at internal grain boundaries), then the excitation of electrons to the conduction band would not induce a cancellation of the *interface* charge since the latter is also negative. Another possible mechanism (not directly involving YL-related states) is that of a ''patched'' contact, consisting of two or more phases of different barrier heights contacting the semiconductor surface in parallel.[19,20] However, in this case the current should again *increase* each time the photon energy exceeds the Schottky barrier of another ''patch.'' Thus, this would also result in a superlinear dependence, in disagreement with the current results. Finally, one may argue that a thick metal contact constitutes a quasi-infinite reservoir of electrons, under which conditions it would seem very difficult, if not impossible, to considerably discharge interface states in the case of IPE. However, this may not apply to a ''real'' metal–semiconductor junction, where substrate surface contamination excludes an intimate contact. This may hamper repopulating the discharged states, resulting in the observed unpinning.

We thus conclude that the observed correlation of the unpinning of the Schottky barrier height with YL-related transitions strongly suggests that YL-related states are present as charged *interface* acceptor states, affecting the Schottky barrier height by pinning of the interface Fermi level. This is in line with our previous assignment of YL-related acceptor states to grain boundary surfaces.[5,6]

We wish to emphasize that our results by no means indicate that YL-related states constitute a universal pinning mechanism at metal/GaN interfaces. The general metal/GaN interface Fermi level position is likely to be the result of a complex interplay, involving native defects, metal-induced defects, and most notably metal-induced gap states and metal-GaN interface reactions.[7,8,15] Thus, other effects may eclipse the YL contribution, depending on both the metal and its deposition procedure. However, our results indicate that YL-related *interface* states may dominate the interface Fermi level under certain conditions. This observation may play a significant role in both the science and technology of practical passivation of metal/GaN interfaces.

In conclusion, we have used two complementary deep level spectroscopies in conjunction with internal photoemission based Schottky barrier measurements for studying the relation between Fermi level pinning and YL in Pt/*n*-GaN junctions. We find that illumination with photons with energies in the YL range causes an unpinning of the interface Fermi level, accompanied by a significant increase of the Schottky barrier height (from ~1 to ~1.9 eV). This strongly indicates the presence of acceptor states related to the YL at the Pt/GaN interface. In equilibrium, these states are charged and pin the interface Fermi level, but can be discharged optically using sub-band gap illumination, resulting in a nearly unpinned interface.

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