Electrochemical Pinning of the Fermi Level: Mediation of Photoluminescence from Gallium Nitride and Zinc Oxide

Vidhya Chakrapani,[†] Chandrashekhar Pendyala,[‡] Kathleen Kash,[§]
Alfred B. Anderson,[||] Mahendra K. Sunkara,[‡] and John C. Angus*,[†]

Department of Chemical Engineering, Department of Physics, and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, 44106, and Department of Chemical Engineering, University of Louisville, Louisville, Kentucky, 40292

Received December 11, 2007; E-mail: john.angus@case.edu

Abstract: Charge transfer between diamond and an electrochemical redox couple in an adsorbed water film has recently been shown to pin the Fermi level in hydrogen-terminated diamond. Here we show that this effect is a more general phenomenon and influences the properties of other semiconductors when the band lineup between the ambient and electronic states in the semiconductor is appropriate. We find that the luminescent intensities from GaN and ZnO change in different, but predictable, ways when exposed to HCl and NH_3 vapors in humid air. The effect is reversible and has been observed on single crystals, nanowires, flakes, and powders. These observations are explained by electron exchange between the oxygen electrochemical redox couple in an adsorbed water film and electronic states in the semiconductor. This effect can take place in parallel with other processes such as defect formation, chemisorption, and surface reconstruction and may play an important, but previously unrecognized, role when electronic and optical measurements are made in air.

I. Introduction

A. Electrochemically Induced Charge Transfer to Semiconductors. Recent studies have confirmed that electron transfer takes place between hydrogen-terminated diamond and a redox couple in an adsorbed water film giving rise to p-type surface conductivity.[1−5] It has recently been confirmed that the redox couple involves oxygen and that the charge transfer also influences both the zeta potential and the contact angle in the diamond/water system.[6] In equilibrium the redox couple pins the Fermi level of diamond close to the valence band edge, leading to a positive space charge layer populated by holes. Similar charge transfer to diamond has been found using adsorbed C_{60}[7] or tetrafluorotetracyanoquino-dimethane.[8]

In this paper, we describe experiments showing that the luminescence from gallium nitride and zinc oxide changes in different, but predictable and reproducible, ways with changes of the electrochemical potential of the ambient. The results are

explained by electron exchange between the midgap states in GaN and shallow states in ZnO with the oxygen redox couple in an adsorbed water film. This reversible electron exchange will tend to pin the Fermi level in the semiconductor at the electron energy of the redox couple. We also briefly discuss the possibility of observing the effect in other semiconductors. The results have relevance for any semiconductor in contact with the ambient.

B. Prior Studies of Gallium Nitride and Zinc Oxide. Gallium Nitride. The near-band-edge luminescence (BEL) and yellow luminescence (YL) from gallium nitride have been widely studied. See Reshchikov and Morkoc[9] for a comprehensive review. There is general agreement that the YL arises from transitions either from the conduction band or shallow states to a band of midgap states.[9] The nature of the defect responsible for the YL has not been established with certainty although there is evidence that it involves a gallium vacancy or a gallium vacancy-complex.[9]

The nature of the ambient and adsorbed gases influences both the BEL and YL; however, the mechanism of this effect is still unresolved. Reshchikov et al.[10] and Iqbal et al.[11] showed that the intensity of near-band-edge photoluminescence of GaN decreases with exposure to air compared to the value in vacuum. A similar observation was made by Behn et al.[12] Several researchers have measured shifts in the Fermi level of GaN in

[†] Department of Chemical Engineering, Case Western Reserve University.
[‡] Department of Chemical Engineering, University of Louisville.
[§] Department of Physics, Case Western Reserve University.
[||] Department of Chemistry, Case Western Reserve University.
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air relative to vacuum. Hashizume et al.[13] measured the Fermi level position for homoepitaxial (2×2) rf-MBE grown GaN by *in situ* photoelectron spectroscopy. The as-grown Ga-terminated sample in UHV had a Fermi level 2.7 eV above the valence band edge; after the samples were exposed to air, the Fermi level was 2.0 eV above the valence band. Wu and Kahn[14] reported the Fermi level to be 2.6 eV above the valence band in UHV for clean MOCVD grown GaN. They found the Fermi level was 0.8 eV closer to the valence band maximum for samples that were exposed to air. Despite the differences in details, the upward band bending upon exposure to air is apparent.

Zinc Oxide. The electrical and optical properties of zinc oxide have recently been reviewed by Özgür et al.[15] Zinc oxide shows a green luminescence (GL) in addition to the near-band-edge (BEL) luminescence. The transitions giving rise to the green luminescence are still uncertain, although there is evidence that defects involving oxygen vacancies and copper impurities each play a role.[15] Reynolds et al.[16] found similarities in the GL from ZnO and the YL from GaN and suggested that these two bands arose from a similar mechanism, i.e., from transitions from shallow donor states to midgap states as proposed by Ogino et al.,[17] Hofmann et al.,[18] and Egelhaaf et al.[19]

There have been a number of reports of the effects of adsorbates on the electronic and optical properties of ZnO.[20-26] Schmidt et al.[20] pointed out that there has been a "failure to recognize and control" the effect of ambient on the properties of ZnO. Some workers have speculated that chemisorbed oxygen, perhaps adsorbed in oxygen vacancies, acts as a surface acceptor.[21,22,24] For n-type ZnO held under vacuum, the electron accumulation layer decreased and the resistance increased when exposed to air.[21] Lin et al.[22] reported marked sensitivity of the surface photovoltage and photoluminescence of ZnO nanorods to molecular oxygen. Fan et al.[23] found that exposure of ZnO field effect transistors to increasing partial pressures of air depleted the electron concentration in the surface conductive channel.

II. Experiments

A. Experimental Procedure. Photoluminescence (PL) measurements were done both at Case Western Reserve University (CWRU) and at the University of Louisville (UL). Steady state PL spectra at UL were obtained with a Renishaw Invia Micro Raman and PL

spectrometer using a He−Cd laser at 325 nm with maximum power of 1.7 mW and a spot diameter of 2 μm. Measurements were performed on single crystal films and flakes using 0.017 mW laser power and on nanowire samples using 1.7 mW laser power. No differences in the YL spectral shapes from the nanowires were observed at 0.017, 0.17, and 1.7 mW, and the YL signal intensities scaled linearly with excitation power, indicating that laser heating did not influence the results. Measurements at CWRU were done with a 5 mW He−Cd laser with multimode output at 325 nm. All spectra at CWRU were recorded with an excitation power of 0.13 mW and a spot diameter of 200 μm. Luminescence spectra were resolved using a 0.85 m double monochromator (SPEX model 1404) and detected using an RCA C31034A-02 cooled photomultiplier tube. Spectra are uncorrected for the wavelength dependence of the spectral response. Small oscillations superimposed on the broad peaks are measurement artifacts. The same effects on maximum intensity and wavelength shift were observed at both UL and CWRU. Duplicate measurements performed on the same sample in the same ambient were reproducible within 4%.

We note that the photoexcitation process under these conditions is simply a probe of the system and does not change its Fermi energy appreciably. This assertion is borne out by our observation that the shapes of the photoluminescence spectra are independent of photoexcitation intensity.

All spectra were taken at room temperature in air. Samples were exposed to different environments by placing aqueous solutions of NH_4OH, HCl and LiCl of known concentration adjacent to the sample in a closed chamber. Analytical grade chemicals were used in all cases. Unless otherwise stated, HCl solutions of pH = 1 and NH_4OH solutions of pH = 11 were used.

All photoluminescence measurements are reported after equilibrium was reached. The typical time constant for the approach to equilibrium was approximately five minutes for both GaN and ZnO.

B. Photoluminescence Results from Gallium Nitride. Undoped Ga-terminated (+c) GaN, 6.7 μm thick, deposited on a c-plane sapphire substrate by molecular beam epitaxy (MBE), was purchased from University Wafers. GaN nanowires (10 to 15 nm diameter) with the [10$\bar{1}$0] direction along the wire axis were synthesized via reactive vapor transport of Ga in dissociated ammonia.[27] GaN flakes with (0001) faces, several mm in lateral dimension and 5−10 μm thick, were synthesized by directly nitriding molten Ga in an ECR plasma reactor.[28] The polarity of the faces, i.e., (+c) Ga-terminated or (−c) N-terminated, was determined from the morphologies of the etched surfaces.[29]

Figure 1a shows yellow band luminescence (YL) spectra from a single crystal GaN film recorded in different environments. Exposure to NH_3 reduces the yellow band luminescence intensity; exposure to HCl vapors increases the intensity. The effect was greatest for the GaN nanowire samples (Figure 1b). Figure 1b also shows that the peak energy of the YL spectrum from GaN in equilibrium with HCl is blue-shifted compared to the peak energy when in equilibrium with NH_3. Similar, but smaller, shifts were observed for the single crystal and flake samples (Table 1).

The intensity of the near-band-edge luminescence (BEL) shows the opposite trend, i.e., the intensity increases upon exposure to NH_3 and decreases with exposure to HCl vapors. See Figure 2. No shift in peak position of the near-band-edge peak was observed.

Table 1 and Figure 3 summarize the changes occurring in the yellow band luminescence upon exposure to HCl and NH_3 vapors for a variety of GaN samples.

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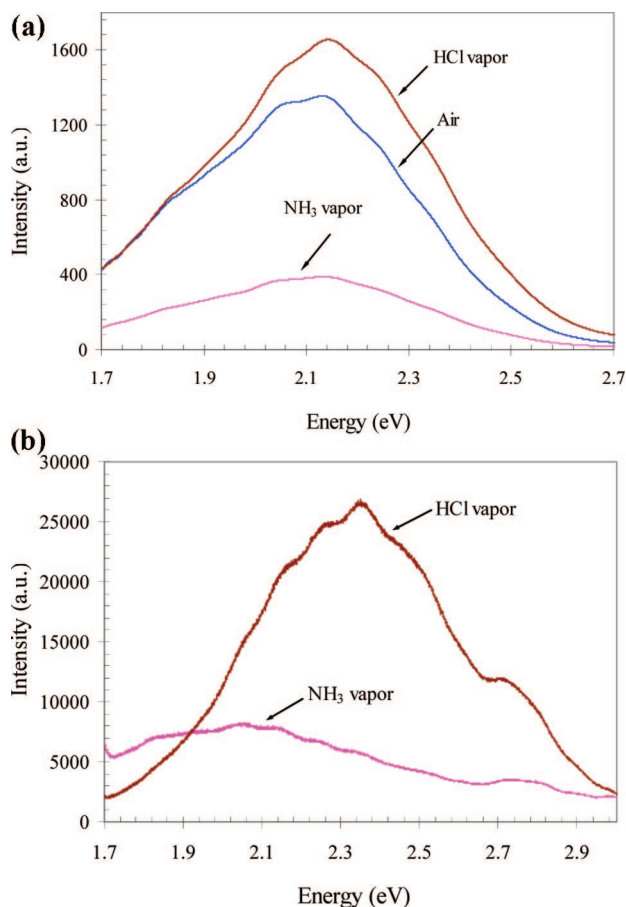**Figure 1.** (a) Yellow luminescence spectra from a single crystal GaN film in contact with air and with HCl vapor and NH₃ vapor in air. The HCl vapors were in equilibrium with an HCl solution of pH = 1; the NH₃ vapors with an NH₄OH solution of pH = 11. (b) Yellow luminescence spectra from GaN nanowires in air in the presence of HCl and NH₃ vapors. The HCl vapors were in equilibrium with an HCl solution of pH = 1; the NH₃ vapors with an NH₄OH solution of pH = 11.

In Figure 4, the intensities of near-band-edge (BEL) and yellow luminescence (YL) from GaN from two separate experiments are shown during cycles in which the air ambient is replaced by argon and then replaced again with air. The BEL intensity increases from its steady state value in air when the air is replaced with argon; the intensity returns to its original value upon reintroduction of air. The YL intensity shows the opposite behavior.

C. Photoluminescence Results from Zinc Oxide. We made luminescence measurements on an undoped ZnO single crystal, ZnO nanowires, and ZnO powder in humid air. Zinc face, single crystal ZnO, 500 μm thick, was obtained from Cermet Inc. and MTI corporation; 40 μm powder from Alfa Aesar. ZnO nanowires, 30 to 100 nm in diameter, were synthesized by reacting Zn metal powder with an oxygen-containing plasma without the use of a substrate in a microwave plasma jet reactor.[30] The procedure for the PL measurements on ZnO was the same as that used for GaN.

The effect of pH on the green luminescence (GL) from single crystal film of ZnO and a ZnO nanowire is shown in Figure 5a and b. The intensity of the GL increases with exposure to HCl vapor and decreases with exposure to NH₃ vapor, the same as the intensity changes of the yellow band luminescence from GaN shown in Figure 1b. The intensity change is larger from the ZnO nanowire samples than from the ZnO single crystal film, also similar to the observations with GaN. However, in contrast to the distinct red- and blue-shifts in the YL of GaN, there is no shift of the GL from ZnO at different pH.

Also, in marked contrast to GaN, the intensity of the near-band-edge luminescence (BEL) from ZnO varies in the same direction as the green luminescence, that is, it increases in HCl vapor and decreases in NH₃ vapor, see Figure 5c. These results show that, despite some similarities, the nature of the interaction of the ambient with the ZnO differs substantially from that observed with GaN.

Effect of Relative Humidity. The influence of relative humidity (RH) on the intensity changes was studied by controlling the relative humidity in the sample chamber. The RH was controlled by placing an open reservoir of LiCl solution with known water vapor pressure[31] in the chamber adjacent to the sample; a near-saturated environment (100% RH) was accomplished by using a reservoir of pure water. The magnitude of the intensity changes from both GaN and ZnO increased with increase in RH and is shown in Figure 6.

III. Electrochemical Pinning of Fermi Level in GaN and ZnO

A. Band Lineups. Electrochemical Couple. The electrochemical potential is reported in volts, often with respect to the standard hydrogen electrode (SHE). In this paper, we use the physical scale with electron energies referred to the vacuum level. The relationship between the electrochemical potential, U, in volts versus the standard hydrogen electrode (SHE), and the electron energy of the redox couple, μ_e, in electron volts, with respect to the vacuum level, is: $\mu(eV) = (-1)U - 4.44$.[32,33] In humid air, the electron energy (Fermi level) in the adsorbed water film will be determined by the oxygen redox couple. The reaction is

$$O_{2,aq} + 4H^+_{aq} + 4e^- = 2H_2O_{aq} \qquad (1)$$
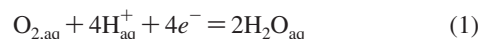
In equilibrium, the electron energy, $\mu_e(eV)$, relative to the vacuum level is given by the Nernst equation applied to reaction 1:

$$\mu_e(eV) = -4.44 + (-1)(+1.229) + \frac{0.0592}{4}[4pH - \log_{10}(P_{O_2})] \qquad (2)$$

Here the activity of H₂O is assumed to be unity, the ideal gas approximation is used, and P_{O_2} is in bar. The standard electrode potential of reaction 1 is +1.229 V vs SHE.[34] The pH of the water film is fixed by dissolved CO₂ from the air at pH ≈ 6 or at other values by using acidic or basic vapors, for example, HCl and NH₃, intentionally added to the ambient.

The maximum practical energy range of the oxygen couple is from −5.66 eV at pH = 0 to −4.83 eV at pH = 14. In our experiments, the pH ranged from 1 to 11, which from eq 2 corresponds to a range in electron energies from −5.60 to −5.01 eV.

GaN and ZnO Band Lineup with Redox Couple. The relationship between the electrochemical energies and the electron energies in GaN and ZnO is shown in Figure 7.

The electron affinity of a clean (+c) GaN surface in UHV has been reported to be $\chi = 3.0 \pm 0.3$ eV.[35,36] This value together with the band gap of 3.4 eV was used to set the band lineup shown in Figure 7. Also shown is the approximate range

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Table 1. Changes in the Yellow Band Peak Intensity and Peak Position for Several GaN Samples under Air, Air with HCl Vapor, and Air with NH$_3$ Vapor[a]
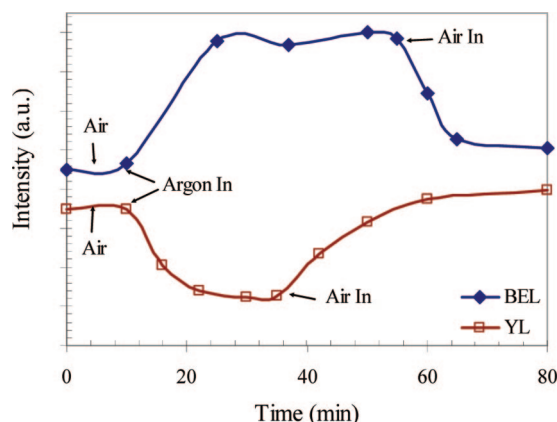
	single crystal	nanowires	(+c) flakes Ga-terminated	(−c) flakes N-terminated
		effect of HCl		
$(I_{p,HCl} - I_{p,Air}/ I_{p,Air}) \times 100$	+23	+140	+160	+26
$\Delta E_{p,HCl} = E_{p,HCl} - E_{p,Air}$ (eV)	+0.007	+0.31	+0.0067	+0.0038
		effect of NH$_3$		
$(I_{p,NH_3} - I_{p,Air}/I_{p,Air}) \times 100$	−62	−60	−17	−9.6
$\Delta E_{p,NH_3} = E_{p,NH_3} - E_{p,Air}$ (eV)	−0.015	−0.11	−0.0043	−0.014

[a] I_p and E_p denote the peak intensity and peak position of the yellow band luminescence respectively. Duplicate measurements performed on the same sample under the same ambient were reproducible to within several percent. Frequency shifts were estimated by the change in the peak position.
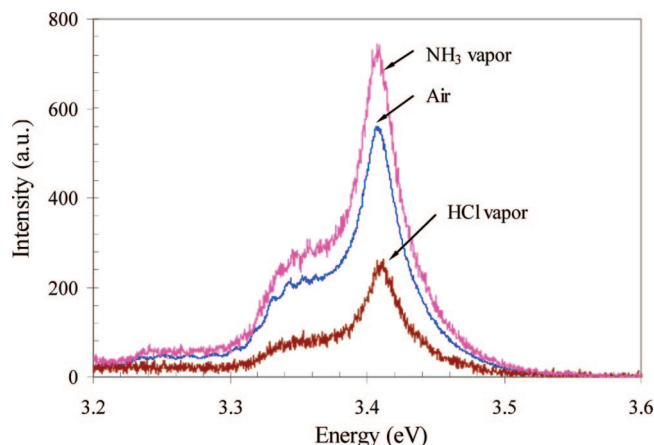
Figure 2. Near-band-edge luminescence spectra from a single crystal GaN film in contact with air and with HCl vapor and NH$_3$ vapor in air. The HCl vapors were in equilibrium with an HCl solution of pH = 1; the NH$_3$ vapors with an NH$_4$OH solution of pH = 11.
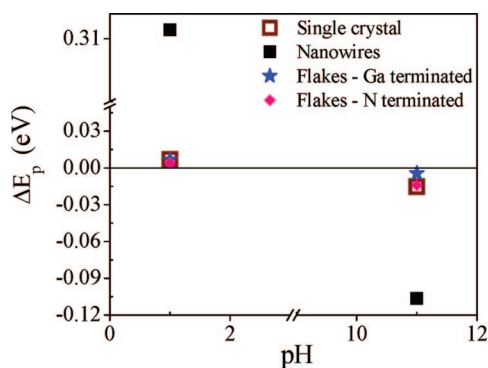
Figure 3. Shift in the peak position of yellow luminescence with exposure to HCl and NH$_3$ vapors in air. Exposure to HCl caused a blue-shift of the peak position relative to the position in air. Exposure to NH$_3$ resulted in a red-shift of the peak position. The zero corresponds to the peak position in air, pH ≈ 6.

of the midgap state energies centered about 2.2 eV below the conduction band minimum, that is, approximately 5.2 eV below the vacuum level. Note that the energies of these midgap states in GaN are in the same range as the electron energy of the oxygen redox couple.

The band gap of ZnO is 3.3 eV, very close to that of GaN. The electron affinity of the ZnO surface is reported to be 4.4[37] and 4.5 eV,[38,39] which places the energy range of the oxygen redox couple just below the conduction band minimum in the midgap region.

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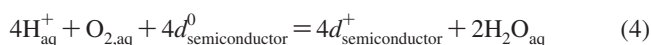(37) Kobayashi, H.; Mori, H.; Ishida, Y. *J. Appl. Phys.* **1995**, *77*, 1301.

Figure 4. Intensities in arbitrary units of the near-band-edge (BEL) and yellow luminescence (YL) from GaN upon replacement of ambient air with argon and subsequent reintroduction of air in two separate experiments. The solid lines are drawn to guide the eye.

B. Proposed Model. Reaction with Ambient. We note that in humid environments adsorbed water films on solid surfaces are ubiquitous and increase in thickness with increase in relative humidity.[40] The atmosphere provides a source of acceptors/donors (the O$_2$ molecules). Therefore, in equilibrium the surface Fermi level, E_F, will be fixed by the electron energy of the oxygen redox couple. If initially $E_F > \mu_e$, electrons will transfer into the water film until $E_F = \mu_e$. Reaction 1 proceeds in the forward direction and H$^+$ ions are consumed, leaving excess anions in the water film. In equilibrium, a positive space charge layer in the semiconductor is charge balanced by uncompensated anions in the water film.

The processes that take place depend on the nature of the site exchanging electrons with the oxygen redox couple. When exchange is with ionized acceptor sites, the reaction can be formally written as

$$4H^+_{aq} + O_{2,aq} + 4a^-_{semiconductor} = 2H_2O_{aq} + 4a^0_{semiconductor} \qquad (3)$$
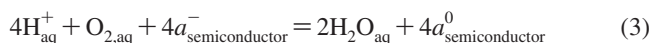
where a^- and a^0 are ionized and un-ionized acceptor sites, respectively. For the case of $E_{F,semiconductor} > \mu_{e,aq}$, the reaction proceeds to the right as ionized acceptors, a^-, are oxidized and protons are consumed. For oxidation of an uncharged donor site, d^0, the formal reaction is

$$4H^+_{aq} + O_{2,aq} + 4d^0_{semiconductor} = 4d^+_{semiconductor} + 2H_2O_{aq} \qquad (4)$$

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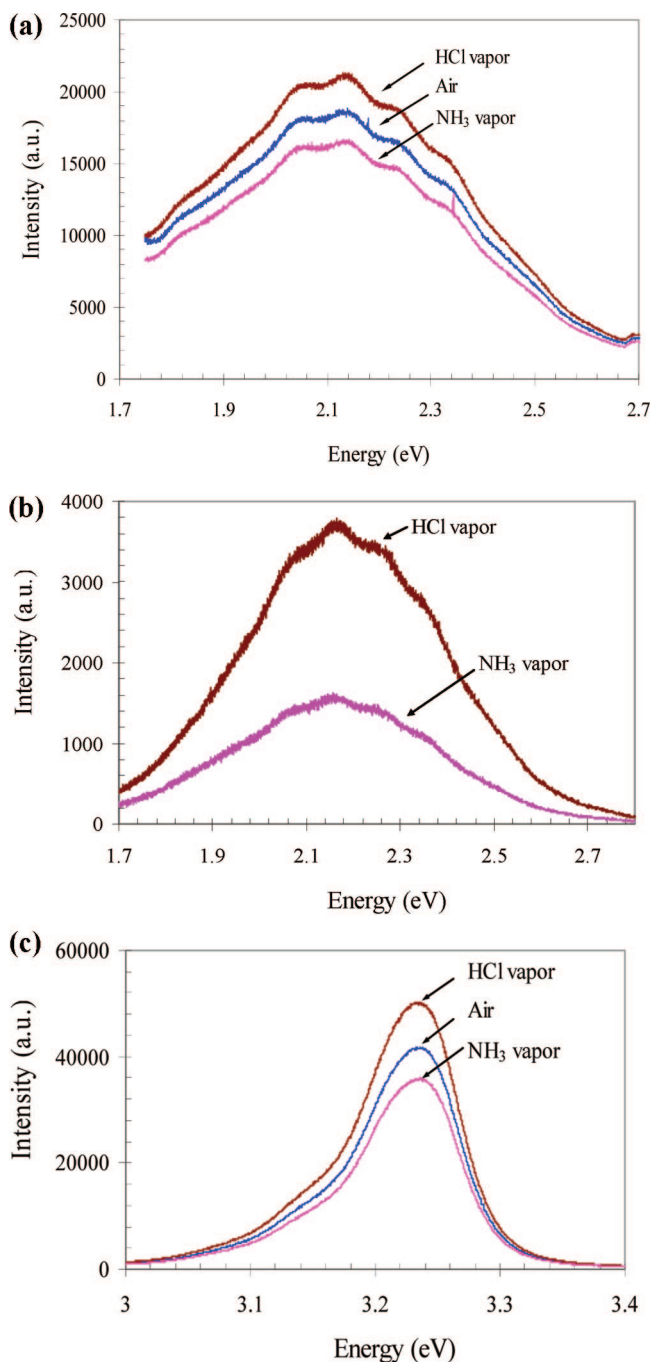(40) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; John Wiley: New York, 1982.

Figure 5. (a) Green luminescence spectra from ZnO single crystal in air in the presence of HCl vapor and NH_3 vapor in air. The HCl vapors were in equilibrium with an HCl solution of pH = 1; the NH_3 vapors with an NH_4OH solution of pH = 11. (b) Green luminescence spectra from ZnO nanowires in air in the presence of HCl and NH_3 vapors. Unlike for GaN, there was no appreciable shift in the GL peak position with pH. (c) Near-band-edge luminescence spectra from ZnO single crystal film in contact with air and with HCl vapor and NH_3 vapor in air. The HCl vapors were in equilibrium with an HCl solution of pH = 1; the NH_3 vapors with an NH_4OH solution of pH = 11.

For interaction with the valence band to form a hole, one has

$$4H^+_{aq} + O_{2,aq} + 4(e^- h^+)^0_{semiconductor} = 4h^+_{semiconductor} + 2H_2O_{aq}$$

$$(5)$$
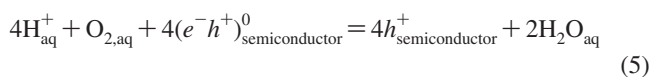
The protons arise from the dissolved carbon dioxide or from other acidic or basic components in the ambient. For CO_2 in air, protons are generated by

$$CO_{2,air} + H_2O_{aq} = HCO^-_{3,aq} + H^+_{aq} \qquad (6)$$

From reactions 3 and 6, one obtains the overall chemical reaction for oxidation of an ionized acceptor.

$$4a^-_{semiconductor} + O_{2,air} + 2H_2O_{air} + 4CO_{2,air} = 4a_{semiconductor} + 4HCO^-_{3,aq} \quad (7)$$
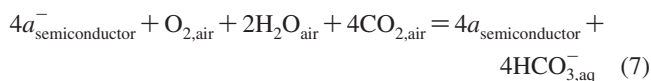
Equation 7 shows that as oxidation proceeds, compensating ions are generated in the aqueous phase.

The electron exchange between GaN and the oxygen redox couple is schematically illustrated in Figure 8. From Figure 8a one can see that in an NH_3 environment in equilibrium with an NH_4OH solution at pH = 11, midgap states up to $E \approx -5.0$ eV are filled. Therefore, the average intensity of the YL transitions is lowered and the peak red-shifted. The intensity of the BEL is increased. Making the water film acidic lowers the electron energy in the water film. For HCl vapors in equilibrium with an HCl solution at pH = 1, midgap states are filled only up to $E \approx -5.6$ eV. See Figure 8b. This increases the YL intensity, decreases the intensity of the BEL, and results in a blue-shift of the YL spectrum.
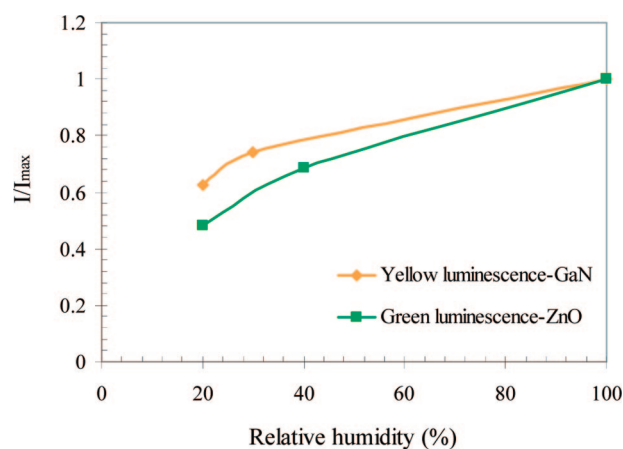

Figure 6. Normalized peak intensities of the yellow luminescence from GaN and the green luminescence from ZnO versus relative humidity (RH).
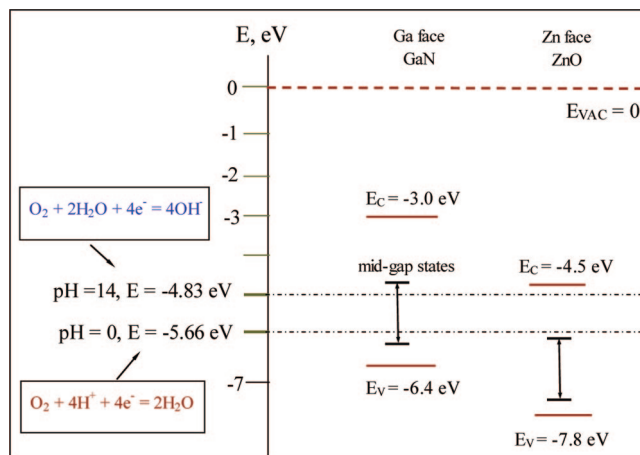

Figure 7. Band lineups of GaN and ZnO with respect to the oxygen electrochemical redox couple. E_C and E_V are the conduction band minimum and valence band maximum, respectively. The approximate energy range of the midgap states is shown. The electron affinity of GaN (3.0 eV) is from refs 35 and 36; the electron affinity of ZnO (4.5 eV) is from refs 38 and 39.
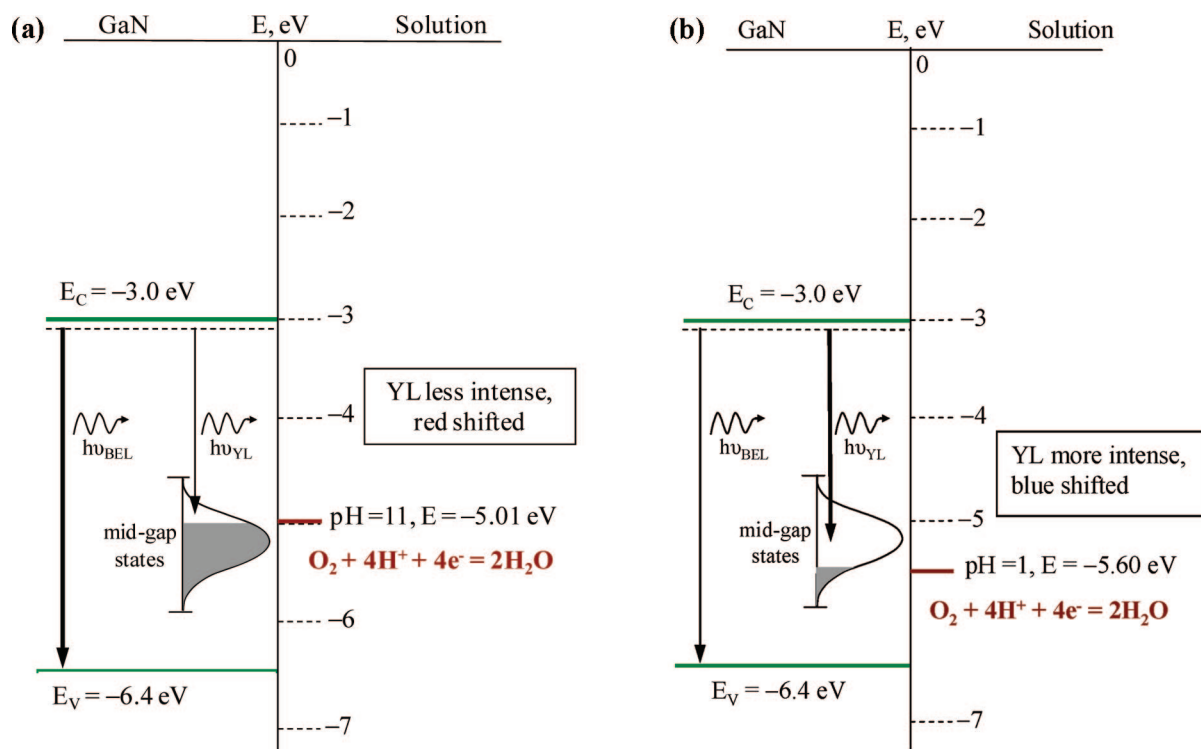
Figure 8. (a) Schematic energy diagram showing the yellow band and near-band-edge transitions in an NH_3 ambient. The transitions are shown occurring from a shallow level slightly below the conduction band minimum.[41] (b) Schematic energy diagram showing the yellow band and near-band-edge transitions in an HCl ambient. The transitions are shown occurring from a shallow level slightly below the conduction band minimum.[41]

Steady State Transition Rates. Any proposed model must explain the significant differences in the effect of pH on the luminescent intensity changes from GaN and ZnO. It is now generally accepted that the yellow luminescence (YL) from GaN centered around 2.2 eV arises from electron transitions from shallow states to midgap states.[9] For ZnO the nature of the upper and lower states is less clear,[15] but there is evidence that the green luminescence (GL) from ZnO arises from a similar process.[16−19] Schematic diagrams of the major transitions in GaN and ZnO are shown in Figure 9a and b.

Referring to Figure 9a for GaN, a steady state electron balance on the shallow level, D, leads to

$$\dot{N}_{CD} = \dot{N}_{DV} + \dot{N}_{DM} \tag{8}$$

where $\dot{N}_{ij}$ is the transition rate from level i to level j. Referring next to Figure 9b for ZnO, the steady state balance about shallow level D is

$$\dot{N}_{CD} = \dot{N}_{DV} + \dot{N}_{DM} + (\dot{N}_{DR} - \dot{N}_{RD}) \tag{9}$$

In steady state the transitions between the redox couple, R, and level D are equal and opposite so $(\dot{N}_{DR} - \dot{N}_{RD}) = 0$. Therefore, in steady state, eq 9 reduces to eq 8, which applies to both GaN and ZnO.

The transition rates, $\dot{N}_{ij}$, are proportional to $n_i v_j$, where n_i is the number of electrons in the upper level, i, and v_j is the number of empty states in the lower level, j. Therefore, eq 8 can be written

$$k_{CD} n_C v_D = k_{DV} n_D v_V + k_{DM} n_D v_M \tag{10}$$

Figure 9 and eq 10 provide a straightforward interpretation of the luminescence changes for both GaN and ZnO. For GaN, Figure 9a, raising the Fermi level by increasing the pH results in the filling of midgap states, reducing v_M, thus leaving fewer empty states available for the yellow band transition, DM. Conversely, lowering the Fermi level empties midgap states, increasing v_M, thus increasing the rate of the yellow band transition, DM. Since the CD transition rate, $\dot{N}_{CD}$, is essentially constant at the low excitation intensities used here, competition between the DV and DM channels means that the luminescence intensity of the BEL and YL will change in opposite directions.

For ZnO, Figure 9b, the range of electrochemical energies is close to the position of the shallow level, D. The CD transition is in competition with the transition, CV. Raising the Fermi level by increasing the pH will fill empty states in D, reducing v_D, which will decrease the transition rate, $\dot{N}_{CD}$. From eq 8, this decrease in turn will decrease the transition rates for both the DV and DM luminescent channels. Therefore, the GL and BEL intensities should change in the same direction, as is observed. Since channel CD is in competition with channel CV and the excitation rate, $\dot{N}_{VC}$, is constant, the transition rate through the nonradiative channel, CV, will change in the opposite direction to changes in the transition rate of CD. We also note that because the shallow levels form a significantly narrower band than the midgap levels, the frequency shift will be small compared to that observed in GaN.

The nature of the shallow levels, D, shown in Figure 9 is not known, but we note that all of our samples were nominally undoped. In Figure 9 we show the transitions giving rise to the luminescence arising from the same upper level, D. However, for both GaN and ZnO, the single shallow level, D, can be replaced with two noninteracting shallow levels and the steady state analysis and conclusions remain the same.

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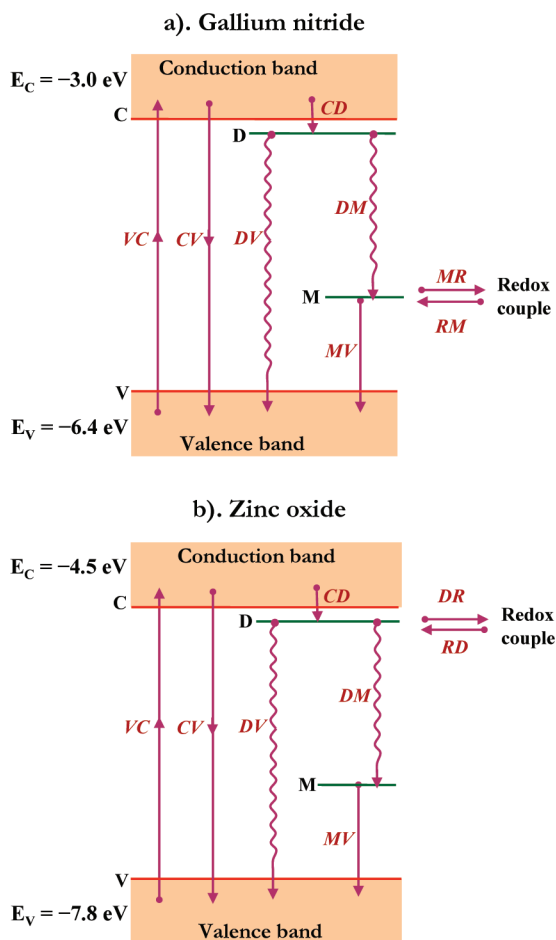
a). Gallium nitride

$E_C = -3.0$ eV — Conduction band

C

D

CD

DM

VC CV DV

MR — Redox couple

M

RM

MV

V

$E_V = -6.4$ eV — Valence band

b). Zinc oxide

$E_C = -4.5$ eV — Conduction band

C

D

CD

DR — Redox couple

RD

DM

VC CV DV

M

MV

V

$E_V = -7.8$ eV — Valence band

Figure 9. Schematic diagrams of major transitions and relationships with the oxygen redox couple in (a) GaN and (b) ZnO. Radiative transitions observed in the spectra are indicated by curvy lines. Here C refers to conduction band; V, valence band; D, shallow level; M, midgap states; R, redox couple. The energies given on the diagram refer to the conduction band minima and valence band maxima.

IV. Discussion

A. Comparision with Experimental Results. Comparison with Prior Results of Others. Reshchikov et al.[9,10] observed a reduction in the intensity of near-band-edge luminescence of GaN with exposure to air or oxygen compared to its value in vacuum. Air-saturated water has a pH ≈ 6 from dissolved CO_2. From eq 3 at this pH, $E \approx -5.3$ eV, and thus the oxygen redox couple can act as an acceptor to the midgap states that lie above this energy. This process enhances the YL intensity and decreases the BEL intensity as reported by Reshchikov et al.[9,10] and described above. Exposure to nitrogen has little effect[9,10] because there are no nitrogen redox couples with sufficiently positive electrochemical potentials to participate in electron transfer from GaN. Small changes in intensity observed in the presence of hydrogen[9,10] may arise from electron transfer to the hydrogen redox couple, which can act as an electrochemical acceptor for the higher midgap states. The electron energy of the hydrogen redox couple, $2H^+ + 2e^- = H_2$, is −4.09 eV for a hydrogen partial pressure of 1 bar and pH = 6.

Our results are consistent with the conclusions of Ogina et al.,[17] Hofmann et al.,[18] Egelhaaf et al.,[19] and Reynolds et al.[16] that both the GL transition in ZnO and the YL transition in GaN are from shallow levels to midgap states. We emphasize, however, that other models of the transitions are also consistent

with the ZnO data. Furthermore, the precision of the redox probe, as currently implemented, is not sufficient to distinguish excitonic states near the conduction band minimum. We also note that filling of trap states in ZnO by increasing the Fermi level would have the opposite effect of that observed, that is, would increase the luminescence intensity of both the near-band-edge and green luminescence.

Frequency Shifts. The observed blue and red shifts of the YL spectra from GaN are consistent with the view that the dominant radiative transition is from shallow states to midgap states as indicated in Figure 8 and Figure 9a and proposed by numerous workers.[9] If the dominant YL transition were from midgap states to the valence band, the frequency shifts would have been in the opposite direction. In the present experiments large differences in pH were used so frequency shifts would dominate over red shifts arising from spatially indirect transitions.[9,10]

Effect of Oxygen and Relative Humidity. Replacement of O_2 from the ambient by an inert gas reduces the number of electrochemical acceptors and therefore should reverse the effects of the air on the intensity changes, that is, should increase the near-band-edge luminescence and decrease the yellow luminescence from GaN. The changes shown in Figure 4 are consistent with these predictions.

Thicker water films in equilibrium with air will contain more dissolved O_2, thus increasing the number of electrochemical acceptors/donors. Therefore, one would expect to see an increase in the magnitudes of the effects with increased relative humidity, which increases the thickness of adsorbed water films.[40] The responses of both the GaN and ZnO to relative humidity changes shown in Figure 6 are similar in magnitude and in agreement with the model predictions.

B. Size Effects and Surface Band Bending. A striking feature of the data is the greater intensity changes observed for the GaN nanowires (10 to 15 nm diameter) and, to a smaller extent, for the ZnO nanowires (30 to 100 nm diameter) than from the single crystal samples, see Figures 1 and 5. Also note the greater changes in YL peak position for the GaN nanowire samples than for the single crystal samples (Figures 1 and 3). We believe that the most likely cause for these differences is the larger area to volume ratio, A/V, for the nanowires than for the single crystal film samples. A larger A/V leads to a larger mass ratio of adsorbed water to semiconductor and, therefore, to a larger ratio of electrochemical acceptors/donors to midgap states.

For a thick planar film we approximate the effective value of A/V as the reciprocal of the absorption length, $1/\alpha$, where α is the absorption coefficient. For GaN at the He−Cd laser wavelength of 325 nm, α is 1.2×10^5 cm^{-1},[41] so $1/\alpha$ is approximately 80 nm. Therefore, we may assume that the GaN nanowires are excited uniformly throughout their volume, so that the effective A/V ratio is equal to the geometric value, 4/d, where d is the nanowire diameter. For the largest GaN nanowires $(A/V)_{nanowire}/(A/V)_{film} \approx 4/(d\alpha) \approx 20$. For ZnO, $\alpha = 1.6 \times 10^5$ cm^{-1},[42] and similar considerations apply: for the largest ZnO nanowires $(A/V)_{nanowire}/(A/V)_{film} \approx 2.5$.

We emphasize that these estimates of A/V are for the largest nanowires and assume the sampling depth for a single crystal film is limited to $1/\alpha$ and therefore they give minimum estimates of $(A/V)_{nanowire}/(A/V)_{film}$. Also, excited carriers will tend to

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diffuse before trapping and recombining, increasing the sampling volume for the thick film and resulting in an increase in this ratio.

While differences in A/V are likely to be the most important source of differences in the luminescence from the nanowires and thick films, other factors can contribute. Band bending, which tends to lower photoluminescence transition energies in the high field region, will be different in the nanowires as compared to the thick film. The doping level of the GaN nanowires is $\sim 10^{18}$ cm^{-3},[43] which leads to a depletion layer thickness of ~ 30nm. This estimate indicates that the entire GaN nanowire is depleted and that the internal field is low compared to that in an epilayer of similar doping level. For the GaN single crystal wafer the doping level is $\sim 10^{17}$ cm^{-3}, for an estimated depletion layer thickness of ~ 100 nm. These estimates indicate that depletion widths for GaN are greater than the nanowire diameters and of the same order as the lower bound of the sampling depth. The estimates are thus consistent with the conclusions drawn above. (The doping level of the ZnO nanowires is not known so a similar comparison cannot be made.)

We also note that quantum confinement in the nanowires will modify the energies of electronic states, including those of the mid gap defects, as well as affect the electron affinity. Finally, spatially indirect transitions induced by band bending would show a different signature, i.e., red shifts in both acidic and basic vapors and smaller shifts in the nanowires than in thick films because of a lower internal field.

C. Dynamics of Effect. The atmosphere provides a quasi-infinite reservoir of oxygen and CO$_2$ that maintains the electron energy of the redox couple at a fixed value. However, pinning the Fermi level requires that electron exchange must take place sufficiently rapidly that equilibrium is approached within the time of measurement. Oxide layers or adsorbed hydrocarbon films can block electron exchange and thus attainment of equilibrium.[4] The oxygen reduction reaction, eq 1, is sluggish in the absence of metallic catalysts. Processes that do not involve electron exchange, for example, chemical ionization of functional groups on the surface and capacitively induced charge,[44] may mask the effect in some instances.[6] Furthermore, the increase in counter-ions (eq 7) may eventually cause the water film to become saturated, limiting further charge transfer.

The measurements reported here are taken at room temperature after equilibrium has been approached. Consequently, no information on activation energies and the height of surface barriers may be inferred. Time-resolved measurements will be required to establish intermediate steps in the process.

D. Other Redox Couples. In our analysis, we assumed equilibrium of the full oxidation of O$_2$ to H$_2$O (eq 1). Partial reduction could, in principle, also play a role. However, these reactions have energies that are not in the range where the observed transitions take place. For example, the electron affinity O$_2$ to form O$_2^-$ in the absence of water is 0.45 eV,[45] which corresponds to an energy of -0.45 eV on the vacuum scale. From Figure 7 one can see this is far above the conduction band minima for both GaN and ZnO. Superoxide (O$_2^-$) formation can also take place in neutral and basic solutions.

$$O_{2,g} + H_2O_{aq} + e^- = O_{2,aq}^- \qquad (11)$$
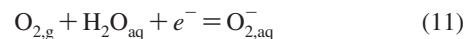
for which the standard reversible potential is -0.284 V. Because the pK_a for OOH is 4.8,[34] OOH will form in acidic solutions

$$O_{2,g} + H_{aq}^+ + e^- = HOO_{aq} \qquad (12)$$

for which the standard reversible potential is -0.046 V.[34] From the Nernst equation, the energies on the vacuum scale for reactions 11 and 12 are, respectively, -3.33 eV for pH = 14 and -4.39 eV for pH = 0. These limits define an energy range above the midgap states in GaN but below its conduction band edge; the limits are well above the conduction band minimum of ZnO. We conclude that partial oxidation to superoxide intermediates does not play a significant role for either of these semiconductors.

E. Polarity of Surface. The difference in the electronegativities of Ga and N (Ga = 1.6, N = 3.0) results in polarization of the surface bonds along the *c*-axis. For the Ga-terminated (+c) (0001) face, the polarization creates a surface dipole that reduces the electron affinity. Polarization on the N-terminated (−c) (0001) face results in a surface dipole of opposite polarity that increases the electron affinity. Since the electron affinity is different on the (+c) and (−c) faces, the band lineup with the electrochemical redox couple will be different, and this difference should influence the observed luminescence properties. Evidence from Schottky barrier heights[46,47] and high resolution photoemission spectroscopy[48] suggests that the band lineup of the (−c) face is lower than the (+c) face by as much as 1 eV, which may explain the smaller changes in the YL intensities and peak shifts observed with the N terminated samples. See Table 1.

F. Additional Issues. Uncertainties in Electronic and Thermodynamic Properties. Interpretation of the results depends on the absolute position of the energy bands of the semiconductor with respect to the electron energy of the aqueous redox couple. This relationship is usually obtained by measurement of the electron affinity of the semiconductor in ultra high vacuum. The electron affinity is a sensitive function of surface treatment and adsorbed contaminants, including water.[49] Therefore, using results acquired in vacuum for semiconductors exposed to humid air must be done with caution.

The thermodynamic properties of water and dissolved species, and hence the redox potential, in an adsorbed water film may differ from bulk values because of orientation effects near the surface. Furthermore, there is an uncertainty of as much as 0.2 eV in the relative position of the electron energy scale and the electrochemical potential scale.

Irreversible Effects. The luminescence from GaN can be strongly influenced by chemical surface treatments that affect the surface recombination velocity. For example, Martinez et al.[50] found that sulfide treatments increased the near-band-edge luminescence of GaN by three to four times for periods of up to seven months. In contrast, the effect reported here is reversible with changes of the pH, humidity and oxygen content of the

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ambient. Therefore, irreversible changes in the chemical state of the surface are not believed to play a role in the present experiments.

G. Other Semiconductors. Water films appear on many solids exposed to humid air.[40] Furthermore, adsorption will be enhanced by the electrostatic attraction between the space charge layer in the semiconductor and solvated counter-ions in the adsorbed film.[6] Therefore, the effect can be expected to occur in other semiconductors if the band lineup is appropriate.

For example, the energy range of the water redox couple essentially spans the band gap of semiconducting, single-walled carbon nanotubes (s-SWNT).[6] Indeed, charge transfer to an adsorbed layer has been posited by Ristein[5] and Chakrapani et al.[6] as the source of the observed changes in conductivity type of s-SWNT with changes in ambient. However, other evidence suggests that the effect also occurs in the absence of water.[51] Additional experiments under carefully controlled ambients will be required to sort out the several effects that may be taking place.

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V. Summary and Conclusions

Electrochemical pinning of the Fermi level by the oxygen redox couple can occur in semiconductors exposed to humid air. This effect may play an unrecognized role when electrical and optical measurements are made in air and may be responsible for disparate results in the literature. Charge transfer to adsorbed films can take place in parallel with other processes, *e.g.*, defect formation, surface reconstruction and chemisorption. The signature of electrochemical charge transfer to adsorbed water films is a systematic, reversible dependence on ambient conditions of humidity, pH and oxygen concentration. The response of luminescence and electronic properties such as Seebeck coefficient and charge carrier density to changes in pH provides another means for study of the density of states and electronic and optical transitions in semiconductors.

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