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Interplay of native point defects with ZnO Schottky barriers and doping

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A combination of depth-resolved electronic and structural techniques reveals that native point defects can play a major role in ZnO Schottky barrier formation and charged carrier doping. Previous work ignored these lattice defects at metal–ZnO interfaces due to relatively low point defect densities in the bulk. At higher densities, however, they may account for the wide range of Schottky barrier results in the literature. Similarly, efforts to control doping type and density usually treat native defects as passive, compensating donors or acceptors. Recent advances provide a deeper understanding of the interplay between native point defects and electronic properties at ZnO surfaces, interfaces, and epitaxial films. Key to ZnO Schottky barrier formation is a massive redistribution of native point defects near its surfaces and interfaces. It is now possible to measure the energies, densities, and in many cases the type of point defects below the semiconductor-free surface and its metal interface with nanoscale precision. Depth-resolved cathodoluminescence spectroscopy of deep level emissions calibrated with electrical techniques show that native point defects can (1) increase by orders of magnitude in densities within tens of nanometers of the semiconductor surface, (2) alter free carrier concentrations and band profiles within the surface space charge region, (3) dominate Schottky barrier formation for metal contacts to ZnO, and (4) play an active role in semiconductor doping. The authors address these issues by clearly identifying transition energies of leading native point defects and defect complexes in ZnO and the effects of different annealing methods on their spatial distributions on a nanoscale. These results reveal the interplay between ZnO electronic defects, dopants, polarity, and surface nanostructure, highlighting new ways to control ZnO Schottky barriers and doping. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4732531>]

I. INTRODUCTION

The semiconductor ZnO is a prime candidate for next generation opto- and microelectronics. Applications include blue/UV light emitting diodes, lasers, transparent conducting

oxides, field effect transistors, biosensors, spintronics, and other nanoscale devices. Furthermore, ZnO possesses advantages over other semiconductors in terms of low cost, ease of growth, and wet chemical processing, as well as biocompatibility. The rapid development of ZnO electronic device applications^{1–3} has increased the need to understand and control its contact and doping properties. Here we review key challenges to ZnO Schottky barrier formation and

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doping, and we present results that highlight the interplay of native point defects with these electronic properties. ZnO provides an excellent test bed for such studies since one can obtain a wide range of Schottky barriers, carrier densities, and defect concentrations to distinguish between physical mechanisms. Several review articles on the nature of ZnO physical properties,⁴ native point defects,⁵ impurities and excitons,⁶ Schottky barrier formation and Ohmic contacts,⁷ and the relation of its interface properties to those of other compound semiconductors^{8,9} are now available. Key to evaluating the impact of various mechanisms is the ability to probe defect densities and carrier concentrations on a nanometer scale. We have used depth-resolved cathodoluminescence spectroscopy (DRCLS) on this scale combined with electrical, electronic, and chemical techniques to measure the impact of native point defects on contact rectification and doping. In terms of Schottky barriers, DRCLS reveals defect formation at metal–ZnO interfaces and corresponding changes in carrier densities that depend on the detailed interface chemical bonding on a microscopic scale. In terms of doping, DRCLS enables the identification of characteristic ZnO native point defects that are directly involved in degenerate donor doping, acceptor doping, as well as the sensitive dependence of free carrier density on specific annealing methods. Beyond the examples included in this review, we discuss new directions for controlling ZnO Schottky barriers and doping.

II. SCHOTTKY BARRIER INFLUENCE OF SURFACES AND INTERFACES

The study of ZnO Schottky barriers extends back to the 1960s with often conflicting results extending over a wide range of values.^{7,9,10} For semiconductors in general, the classical Schottky barrier height Φ_{SB} at a metal–semiconductor junction given by $\Phi_{\text{SB}} = \Phi_{\text{M}} - \chi_{\text{SC}}$, where Φ_{M} is the metal work function and χ_{SC} is the semiconductor electron affinity, is modified by an interface dipole $\Delta\chi$ due to a variety of extrinsic effects⁹, such that $\Phi_{\text{SB}} = \Phi_{\text{M}} - \chi_{\text{SC}} - \Delta\chi$. Such extrinsic effects are reflected in contacts to ZnO, where recent studies display major differences in Φ_{SB} even for the same metal on the same ZnO surface. For example, Fig. 1 illustrates the highest reported current–voltage (I – V) barrier heights Φ_{SB}^{I-V} for different metals on different oriented surfaces of single crystal ZnO.¹¹ Even for the same metal on the same orientation, Φ_{SB}^{I-V} can vary by several tenths of an eV. Thus Fig. 1 shows Φ_{SB}^{I-V} for Pt varying from 0.97 to 0.7 eV. Furthermore, there is a considerable variation in ideality factor n due to image force lowering, thermionic field emission, and/or lateral contact inhomogeneity such that Φ_{SB}^{I-V} decreases with increasing n . Ideality factor variations between 1 and 2 are commonly attributed to recombination via gap states.¹² Higher n values can also be attributed to defect state recombination,¹³ as well as trap-assisted tunneling,^{14,15} nonlinear shunts, or edge currents.¹⁶ Defects that increase the net carrier density can also enhance tunneling by decreasing the width of the semiconductor's depletion region. Assuming uniform semiconductor composition, variations in image force lowering,

FIG. 1. Maximum values of Φ_{SB}^{I-V} and n obtained from I – V measurements for various metals on ZnO showing the wide range of values for the same metal. Reprinted with permission from M. W. Allen, S. M. Durbin, and J. B. Metson, *Appl. Phys. Lett.*, 91, 053512, 2007. Copyright 2007, American Institute of Physics.

semiconductor work function, and band bending can be attributed to surface dipole changes due to local electronic states near the semiconductor surface or induced at the surface by adsorbates. In each case, localized electronic states are involved. These states can alter the potential difference and hence the barrier between metal and semiconductor, or they can decrease the effective barrier by variety of trap-assisted tunneling processes. In the case of Ag, higher Φ_{SB}^{I-V} may also be due to formation of Ag oxide interlayers¹⁷ or an increase in effective work function.¹⁸

The same metal on the same ZnO surface can also exhibit significant Φ_{SB}^{I-V} and capacitance–voltage-measured Φ_{SB}^{C-V} variations. Figure 2 illustrates the difference between Φ_{SB}^{I-V} and Φ_{SB}^{C-V} for Pd diodes on ZnO.¹⁹ The lower Φ_{SB}^{I-V} are due to inhomogeneities within a single diode area that weight conduction preferentially through lower barrier patches. The fluctuations in Φ_{SB} can be modeled by a Gaussian distribution of barrier heights with a standard deviation around a mean value and a temperature-dependent effective barrier height $\Phi_{\text{SB,eff}}(T)$. The inset shows the difference between $\Phi_{\text{SB,eff}}(T)$ and Φ_{SB}^{C-V} versus temperature such that extrapolation to the origin yields a standard deviation of barrier height and thereby a method to quantify barrier height inhomogeneity.

ZnO surface orientation also has a strong influence on Φ_{SB}^{I-V} . Figure 3 illustrates the variation of Φ_{SB}^{I-V} for Ag (oxide) on Zn- vs O-polar ZnO, showing a 0.2 eV higher Zn-polar barrier for all diodes, regardless of n .¹¹ The decrease in Φ_{SB}^{I-V} with increasing n again indicates extrinsic states near the interface reducing the effective Φ_{SB} .

Early measurements of ZnO Φ_{SB}^{I-V} and Φ_{SB}^{C-V} for different metals without air exposure display a wide range of values that are in contrast to the much smaller range found for the same metals on more covalent semiconductors such as GaAs.²⁰ A characteristic transition from low to high Φ_{SB} common to ZnO and other compound semiconductors was found with an interface heat of reaction ΔH_R .^{21,22} In turn,

FIG. 2. Effective $\Phi_{SB,eff}$, $\Phi_{SB,C-V}$, and $\Phi'_{SB,C-V}$ vs temperature for Pd/ZnO(0001). The inset plots the difference between $\Phi_{SB,eff}$ and $\Phi'_{SB,C-V}$ such that a line through the origin yields a standard deviation of barrier height. Reprinted with permission from H. von Wenckstern, G. Biehne, R. A. Rahman, H. Hochmuth, M. Lorenz, and M. Grundmann, *Appl. Phys. Lett.*, 88, 092102, 2006. Copyright 2006, American Institute of Physics.

this thermodynamic relation suggests that chemical interactions at the metal–ZnO interface can play a role in barrier formation. Similarly, the barriers for metals on chemically treated ZnO do not seem to follow the difference in work functions.²³ They attributed the much larger ideality factors for these diodes either to tunneling, interface states, and/or the presence of deep recombination centers.

In general, these variations in Φ_{SB} for ZnO (and other semiconductors) can be understood in terms of multiple transport mechanisms at the metal interface. Figure 4 illustrates schematically the major pathways for transport across the metal–semiconductor interface. Charge can transfer from the metal into the semiconductor either over the barrier (thermionic emission), through the barrier by tunneling (field

FIG. 4. Complementary charge transport mechanisms in ZnO including thermionic emission, tunneling, and hopping transport through defect levels in the bandgap. Reprinted with permission from L. J. Brillson and Y. Lu, *J. Appl. Phys.*, 109, 121301, 2011. Copyright 2011, American Institute of Physics.

emission), a combination of the two (thermionic field emission), and through the barrier by hopping through gap states within the semiconductor space charge region, termed trap-assisted tunneling. The metal–semiconductor interface without applied voltage, i.e., with Fermi levels aligned, and only for charge transport from the metal to the semiconductor is commonly used to illustrate the internal photoemission spectroscopy method for measuring Schottky barrier heights.²⁴ Analogous illustrations of thermionic and thermionic field emission under forward or reverse bias are commonly shown in textbooks,²⁵ albeit without trap-assisted tunneling.^{14,15} Increased doping in the surface space charge region decreases the depletion width, thereby increasing thermionic field, field emission, and trap-assisted or hopping transport *through* the barrier. The results presented in the sections to follow provide evidence that electrically active native point defects near the intimate metal–semiconductor interface can form that (1) alter the carrier concentration and change the surface space charge region to influence tunneling and (2) introduce new gap states within the bandgap that can promote hopping transport. Likewise, following sections provide evidence that the presence of native point defects either at a growing ZnO surface or within the bulk can enable ZnO doping by providing lattice vacancy sites for dopant atoms to fill.

III. EXPERIMENTAL METHODS

In order to probe defects and doping near surfaces, interfaces, and within thin films on a nanometer scale, we used a combination of techniques centered on DRCLS with single crystal ZnO provided by numerous vendors. The DRCLS technique typically employs a relatively low energy electron beam to excite electronic transitions at depths below a free surface that are controllable on a nanometer scale.^{26–28} Briefly, an incident electron beam introduces a cascade of secondary electrons that produce electron–hole pairs that recombine and produce optical luminescence at characteristic depths. Figure 5 illustrates a Monte Carlo simulation that includes backscattering of the rate of energy loss due to the electron–hole pair creation.²⁹ With increasing incident beam

FIG. 3. Effective Ag–ZnO Φ_{SB}^n for hydrothermal ZnO for opposite polar orientations showing consistently higher Zn- vs O-polar Φ_{SB}^n , both increasing with decreasing n . Reprinted with permission from M. W. Allen, S. M. Durbin, and J. B. Metson, *Appl. Phys. Lett.*, 91, 053512, 2007. Copyright 2007, American Institute of Physics.

FIG. 5. (Color online) Monte Carlo simulations for rate of energy loss due to electron-hole pair creation in ZnO for $E_B = 1\text{--}5$ keV.

energy E_B , excitation can occur at a surface, an interface below the surface, or deep within the bulk semiconductor. The resultant emission energies are characteristic of band-to-band, band-to-defect, as well as interface-specific transitions. At E_B of a few kilovolts or less, excitation depths can be controlled on a scale of tens of nanometers or less. This control permits investigation of both ultrathin layers as well as micrometer-thick materials. Evidence from both depth ranges contribute to the results presented here. The electron beam creates a cascade of secondary electrons in three dimensions, “blooming” laterally with increasing depth. To compensate for such volume changes, all defect spectra are normalized with respect to near-band edge (NBE) peak intensities. As Fig. 5 shows, the depth range of excitation also becomes wider with increasing E_B . For $E_B > 5$ keV, DRCLS depth resolution is improved with a relatively simple differential method: renormalizing spectra from shallower layers for subtraction from deeper layer spectra, resulting in depth resolution comparable to other depth-resolved techniques.³⁰ Measurements of depth-resolved cathodoluminescence (DRCL) spectra versus metal thickness show no distortion of spectra features through the metal diodes due to attenuation or internal reflection.

Several other experimental techniques complement DRCLS to describe how native point defects impact ZnO's electronic properties. Positron annihilation spectroscopy (PAS) provides densities of Zn vacancies and vacancy clusters as a function of depth.^{31,32} Hall measurements coupled with modeling provide detailed values of donors and acceptors for our ZnO samples as a function of growth and processing conditions.^{33,34} I - V (Refs. 35 and 36) provides a Φ_{SB}^{I-V} , while C - V (Refs. 37–40) provides both Φ_{SB}^{C-V} as well as net carrier densities as a function of depth. Deep level optical spectroscopy (DLOS)⁴¹ and surface photovoltage spectroscopy (SPS)^{42,43} provide information on energy levels within the ZnO bandgap that correspond with the optical emission energies detected by DRCLS, often within 100 meV, notwithstanding possible Franck-Condon shifts.

Schottky barrier studies employed ZnO single crystal wafers grown by vapor phase transport from ZN Technology, Inc. These exhibit typical defect density luminescence

intensities several orders of magnitude below those of the NBE emission. Degenerate n -type doping studies employed films grown by pulsed laser deposition (PLD) under argon or forming gas ambients. Li-doped studies employed both Li-doped melt-grown- (MG) and hydrothermal (HT)-ZnO with different temperature anneals and cooling rates, as described in Sec. VI.

IV. SUBSURFACE AND INTERFACE DEFECTS

DRCLS studies of ZnO single crystals from numerous sources reveal defect emission intensities that can vary by orders of magnitude relative to NBE emissions within the bulk and that lie deep within the energy bandgap.²⁷ Calculations of formation energy for the most common native point defects in ZnO indicate that zinc vacancies (V_{Zn}) and oxygen vacancies (V_O) are energetically the most favorable under O-rich or Zn-rich conditions, respectively, under n -type conditions.^{44,45} Indeed, both have relatively low formation energies under both conditions. Hybrid Hartree-Fock density function first-principles theory positions the energy levels of these defects above midgap for the $2^+/0$ V_O transition energy and below midgap for $0/-$ V_{Zn} transition energy.⁴⁴

There is considerable electronic evidence that carrier densities can increase by orders of magnitude near metal-ZnO interfaces. For example, a $1/C^2$ - V plot of net carrier density at Ir-ZnO (000 $\bar{1}$) contacts reveals a threefold increase in electron density from a depth of 200 to 90 nm, reaching 10^{17} cm⁻³ at 90 nm with an increasing slope that suggests at least an order of magnitude higher density at the metal interface. Even at 10^{17} cm⁻³, such carrier densities are comparable or larger than bulk doping densities. Forward current leakage prevents measurements at even shallower depths. DRCLS excitation at depths of 200 to $\sim$ 50 nm reveals threefold midgap defect increases that correspond to the $1/C^2$ - V data. DLOS and deep level transient spectroscopy (DLTS) measurements exhibit energy level transitions that correspond to the DRCLS features under bias conditions that probe comparable depths.⁴⁶

At Pd-ZnO(0001) contacts with relatively low native point defect emissions, DRCL spectra exhibit a midgap defect emission at 2.45 eV that grows more than twofold with decreasing excitation depth in the <20–100 nm range. $1/C^2$ - V net carrier concentrations exhibit a corresponding increase by $>2\text{--}5\times$ from the bulk to $\sim$ 70–80 nm. Similarly, an $E_C - E_S = 0.5$ eV trap measured by DLTS at this junction appears and grows by $>2\times$ from 150 to 60–90 nm.³⁸ Taken together, these results show that near-surface defects can introduce new donors. Thus nanoscale DRCLS reveals subsurface native point defects whose densities can vary by orders of magnitude as seen from (1) deep level optical emission, (2) carrier densities, and (3) trap densities. These subsurface and interface defect densities are large enough to impact Schottky barriers.

Although $1/C^2$ - V measurements often reveal increased defect densities within tens of nanometers of surfaces and interface, such variations can depend on surface polarity, interface preparation, subsequent process, and the variations

in defect densities versus depth within the initial ZnO crystal.⁷ Thus, for example, Pd diodes on hydrothermally grown ZnO can exhibit decreased near-junction carrier densities,⁴⁷ and Ag oxide contacts to hydrothermally grown, highly compensated as well as melt-grown ZnO showed little change within ~ 50 nm of the surface.¹⁷ Likewise, remote oxygen plasma treatments that increase compensating defects can decrease net carrier density as described in the following.³⁸

V. METAL-INDUCED DEFECTS AND SCHOTTKY BARRIERS

The densities of native point defects at the nanoscale metal–ZnO interface can be directly related to the corresponding Schottky barrier heights measured macroscopically. To illustrate the correlation of defects with Φ_{SB}^{V-V} , consider atomically clean ZnO contacts with the common metals Al and Au, which produce Ohmic versus rectifying behavior, respectively, when deposited on the same ZnO surface. Figure 6(a) shows a comparison of DRCL spectra for an Al–ZnO diode interface versus the bare ZnO surface within a few nanometers of the diode.³⁶ This diode exhibits Ohmic behavior with nearly equal forward and reverse current characteristics. At room temperature, the bare surface exhibits an NBE transition at 3.36 eV and phonon replicas extending to lower energies plus midgap emission at ~ 2.5 eV that is more than 3 orders of magnitude lower than the NBE intensity. Under the Al diode, this midgap emission intensity increases by an order of magnitude. In contrast, an Au diode on the *same surface* has a rectifying $\Phi_{\text{SB}} = 0.48$ eV and negligible change in this ~ 2.5 eV emission under the Au diode at room temperature even though peak excitation for $E_B = 5$ keV through Au is tens of nanometers closer to the interface. Since DRCLS showed uniformly low defects from the surface extending hundreds of nanometers into the ZnO, the dramatically higher defect densities induced by Al compared to the relatively unchanged defect emission for Au can only be attributed to the creation of new defects by Al. Furthermore, as depth-dependent carrier density measurements will show, these metal-induced changes can extend tens of nanometers away from the interface due to atom and/or defect segregation, the nature of which is currently under investigation.

After annealing at higher temperature, however, the Au diode characteristic changes dramatically.³⁶ The room temperature I – V characteristic remains rectifying until temperatures above 550 °C, where the reverse current increases by more than 2 orders of magnitude. Figure 6(b) shows that a new defect feature appears at ~ 1.9 eV at $T = 650$ °C, exceeding by 2 orders of magnitude the background emission at that energy for the unannealed junction. We attribute this ~ 1.9 eV emission to V_{Zn} -related defects since the Au–Zn phase diagram includes an eutectic at 642 °C.⁴⁸ Formation of this eutectic must involve Zn atoms from the ZnO adjacent to the Au diode. Diffusion of Zn out of the ZnO into the Au layer then would leave behind V_{Zn} sites and account for the appearance of new gap state emission. These defects reside within a few nanometers of the Au–ZnO junction and are

Fig. 6. (Color online) (a) Micro-cathodoluminescence (CL) spectra of bare ZnO(0001) through vs at the periphery of an Al diode showing the increase of defect emission at the Al/ZnO interface. (b) Micro-CL spectra of bare ZnO(0001) through vs at the periphery of an Au diode showing the increase of defect emission at the Au/ZnO interface above the threshold for Au–Zn eutectic formation. Reprinted with permission from H. L. Mosbacker, S. El Hage, M. Gonzalez, S. A. Ringel, M. Hetzer, D. C. Look, G. Cantwell, J. Zhang, J. J. Song, and L. J. Brillson, *J. Vac. Sci. Technol. B*, 24, 1405, 2007. Copyright 2007, American Institute of Physics.

detectable because DRCLS can probe the first few nanometers of ZnO below the Au–ZnO interface selectively.

Native point defects can also account for the significant differences in Φ_{SB} between Zn and O surface polarities. Figure 7 illustrates $1/C^2$ – V determination of Φ_{SB} from extrapolated intercepts to the baseline for Pd and Au on Zn- and O-polar ZnO surfaces of the same crystal.³⁷ C – V -measured barriers have fewer artifacts than I – V measurements since barrier inhomogeneities and current leakage through low barrier regions are avoided. For the Pd diode, the Zn-polar face exhibits a 0.05 eV higher Φ_{SB} than the O-polar face. For the Au diode, Zn-polar face has a 0.13 eV higher Φ_{SB} . The net carrier densities in the ZnO near the metal diodes can account for these differences in Φ_{SB} . Figure 7 (inset) shows net carrier densities obtained from $1/C^2$ – V measurements that exhibit a clear

FIG. 7. (Color online) C^{-2} vs V barrier height plots for Au and Pd diodes on Zn- and O-polar surfaces of ROP-cleaned ZnO. The inset shows corresponding carrier densities vs depth. Higher O-polar diodes exhibit higher subsurface carrier densities and lower $\Phi_{\text{SB}}^{\text{e}}$. Reprinted with permission from Y. Dong, Z.-Q. Fang, D. C. Look, G. Cantwell, J. Zhang, J. J. Song, and L. J. Brillson, *Appl. Phys. Lett.*, 93, 072111, 2008. Copyright 2008, American Institute of Physics.

decrease in net carrier density for the Zn-polar surface. The Pd and Au diodes exhibit similar carrier density profiles, indicating that this contact behavior is due to the different polarity rather than differences in metal. SIMS results showed no differences in any residual impurities between the two polarities. Associated with the increased donor density on the O-polar surface for the Au diode, DLTS reveals a trap located 0.9 eV below the

conduction band E_C that increases toward the metal interface. Significantly, the position of this trap corresponds to an energy level $3.36 - 0.9 = 2.46$ eV above the valence band, nearly identical to the ~ 2.45 eV defect energy measured by DRCLS. Indeed, SPS features due to filling gap states locate a level at ~ 2.45 eV above the valence band E_V .⁴³

It is now possible to control the rectifying versus Ohmic nature of ZnO Schottky barriers by controlling the defect densities with polarity and plasma processing. Figure 8 illustrates schematically a diode of Au deposited on an as-received and chemically cleaned ZnO surface (Au I) and another Au diode deposited subsequently on the same surface after this surface was exposed to a remote oxygen plasma (ROP) (Au II). The ROP treatment is known to remove surface adsorbates such as OH and C, remove H from within the ZnO, and reduce ~ 2.45 eV emission attributed to V_{O} .^{35,49} Figure 8(a) shows $1/C^2$ - V -derived net electron density and DRCLS spectra obtained from the same depth range on a Zn-polar surface.³⁸ For the as-received surface, optical emission from the intimate Au–ZnO interface consists of the NBE emission, phonon replicas, and a single gap state feature at ~ 2.5 eV nearly 3 orders of magnitude lower in intensity. ROP treatment introduces a second gap state at ~ 2.1 eV attributed to V_{Zn} according to the results presented in Fig. 6(b). The inset of Fig. 8(a) shows the net electron densities corresponding to these DRCLS spectra. For the Au I diode, carrier density remains roughly constant to within 80 nm of the metal interface. For the Au II diode, carrier density exhibits a pronounced decrease within proximity to the surface. This is clear evidence that the ROP-generated ~ 2.1 eV emission is due to a compensating acceptor-type defect. Indeed, according to the same analysis used in Fig. 7, the Au II diode exhibits higher rectifying character, as

FIG. 8. (Color online) Comparison of micro-CL spectra for Au I and II diodes at their Zn and O-polar interfaces. Without ROP treatment, ~ 2.5 eV defect emissions increase at the Au–ZnO(0001) interface. With ROP treatment, ~ 2.1 eV defect emission increases at the Au–ZnO(0001) interface. The corresponding C - V carrier profiles appear in the inset showing higher electron densities for Au I and O-polar surface diodes. Reprinted with permission from Y. Dong, Z.-Q. Fang, D. C. Look, D. R. Dutt, G. Cantwell, J. Zhang, J. J. Song, and L. J. Brillson, *J. Appl. Phys.*, 108, 103718, 2010. Copyright 2010, American Institute of Physics.

expected for a lower free carrier density and hence wider barrier width.

As-received and ROP-treated Au diodes formed on the O-polar ZnO face exhibit significant differences that can account for the lower Φ_{SB} shown in Figs. 3 and 7. In Fig. 8(b), Au I diodes exhibit proportionally higher ~ 2.5 eV emission, which ROP treatment reduces nearly twofold. No ~ 2.1 eV emission is evident with ROP treatment. The corresponding carrier density for Au II on the O-polar face is higher than on the Zn-polar face. Carrier densities for Au I diodes on the O-polar face were precluded by excessive leakage current, indicating even higher carrier densities than for Au II on the same surface. Thus Fig. 8(b) shows that emissions associated with V_O are higher on the O-polar face and correlate with higher carrier densities below the metal–ZnO interface.

In general, these interface defect findings show that (1) metal reactions can increase defect densities by orders of magnitude within tens of nanometers of the metal–ZnO interface; (2) the nature of chemical reaction induces different defects and interfacial layers; (3) surface polarity alters defects and free carrier densities within the surface space charge region; and (4) interface defect densities and Schottky barriers can be controlled by remote plasma techniques.

VI. DEFECT ROLES IN ACHIEVING CONTROLLED DOPING

There is now great interest in controlled doping of ZnO to achieve: (1) *p*-type doping for light emitting diodes and lasers and (2) degenerate *n*-type doping for transparent conducting oxides. *p*-type ZnO is achievable but difficult to control and stabilize over time. Examples include *p-i-n* homojunctions,⁵⁰ *p-n* homojunction light emitting diodes,⁵¹ and *p-Cu:ZnO/n-6H:SiC* *p-n* heterojunctions,⁵² each of which emit light with electric current. Very recently, Liu *et al.* have demonstrated lasing within ZnO nanorods.⁵³ The *p*-type layers in these structures can change with time, suggesting the movement of defects within the semiconductor that change carrier properties. Such electrically active native point defects can act as donors, e.g., V_O complexes or Zn interstitials Zn_i , that can compensate *p*-type dopants, or as acceptors, e.g., V_{Zn} , that can compensate residual donor impurities such as Al, In, and Ga. Thus native point defects can supply or balance dopant sites. However, the physical nature of defect donors and acceptors that dominate charge densities as well as their behavior under various growth and processing conditions are still unresolved. The ability to correlate optical emissions with the energetics of these defects can help monitor the densities and spatial distributions of electrically active sites in ZnO.

In order to identify specific optical emissions with specific native point defects, we correlated DRCLS measurements with PAS and SIMS of the same crystal films.³⁰ DRCLS of hydrothermally grown ZnO, unintentionally doped with 5×10^{17} Li/cm³, *n*-type and highly resistive, were implanted with $^7\text{Li}^+$ and annealed under controlled conditions.^{54,55} The preannealed ZnO exhibited midgap defect and NBE emissions that were relatively uniform with

depth. With a 20 ms 1200 °C flash anneal, DRCLS indicates orders-of-magnitude increases in deep level emissions at ~ 2 and ~ 2.45 eV with the former dominating at all depths. In contrast, a 1 h 800 °C furnace anneal reverses this behavior, with the ~ 2.4 eV emission larger at all depths. Both emissions vary with depth for both processes, and the large differences in their magnitude and variation with depth for the same starting material demonstrate the strong effect of different annealing conditions.

Since both DRCLS and PAS provide defect information as a function of depth, we compared the results of both for the same crystal films. Figure 9 illustrates schematically the comparison of the two techniques and the data obtained. For DRCLS, an incident electron beam generates secondary electrons and ultimately electron–hole pairs that can recombine and emit light at depths calculated from Monte Carlo simulations. For PAS, an incident positron beam emitted with a 1.27 MeV γ ray penetrates the solid and thermalizes until it recombines with an electron and emits two 0.51 eV γ rays. As with electrons, the depth of excitation can be controlled with the kinetic energy of the incident positron. The time elapsed between the initial and final γ ray emissions determines the lifetime of the recombination, increasing for regions with low densities of electrons such as V_{Zn} sites and thus providing a measure of vacancy density. The 0.51 MeV line shape or S parameter reflects the annihilating electron's Doppler shift and provides a measure of its momentum, which is useful for distinguishing between different open volume defects. For the crystal flash annealed at 1200 °C,

FIG. 9. (Color online) (a) Schematic illustration comparing DRCLS and PAS excitation mechanisms vs depth from the free surface. (b) DRCLS defect emission intensities and PAS V_{Zn} densities vs depth for 1200 °C flash annealed $I(2.0\text{ eV})/I(3.4\text{ eV})$ (black square) and $I(2.4\text{ eV})/I(3.4\text{ eV})$ (red hexagons) vs V_{Zn} (blue dots), showing the 2.0 eV emissions correlate with V_{Zn} . Reprinted with permission from Y. Dong, F. Tuomisto, B. G. Svensson, A. Yu. Kuznetsov, and L. J. Brillson, Phys. Rev. B, 81, 081201, 2010. Copyright 2010, American Institute of Physics.

the S parameter versus sample depth shows a V_{Zn} concentration peaking at $\sim 1 \mu\text{m}$. This feature is not due to implanted Li density, which peaks considerably deeper, i.e., $\sim 1.6 \mu\text{m}$.⁵⁵ The graph in Fig. 9 comparing PAS S parameter with ~ 2.0 and ~ 2.45 eV DRCLS emissions shows a clear correspondence between the V_{Zn} density and the ~ 2.0 eV emission intensity. Conversely, the ~ 2.45 eV peak intensity does not. Similar PAS–DRCLS comparison for the 800°C furnace annealed sample yields the same results—good correlation between V_{Zn} and ~ 2.0 eV emission intensities and strikingly different behavior for the ~ 2.45 eV intensities.³⁰ Similar correlations with other ZnO films also show a variation of the ~ 2 eV peak energy with V_{Zn} cluster size, ranging from 1.6 eV for isolated V_{Zn} to ~ 2 eV for V_{Zn} clusters.³⁰ The different ~ 2.45 eV behavior suggests that this feature is related to the other dominant defect in ZnO, V_{O} or a V_{O} complex. Considerable previous work supports this assignment.^{36,56}

In order to determine the energy levels within the ZnO bandgap that correspond to the ~ 2 and ~ 2.45 eV emissions, we employed SPS to identify energies corresponding to optical transitions between gap states and E_{C} versus gap states and E_{V} . These measurements revealed that ~ 2 eV optical excitation depopulates electrons from states located 2 eV below E_{C} , while ~ 2.45 eV excitation populates states located ~ 2.45 eV above E_{V} with electrons. These processes result in opposite changes in work function as the surface band bending and Fermi level E_{F} vary with changing concentration of electrons at the surface. The resultant energy level assignments can be compared with theory. In particular, the 1.6–2 eV level for V_{Zn} and V_{Zn} clusters below the conduction band can be compared with calculations of the V_{Zn} 0/– transition obtained from plane wave pseudopotential total-energy and force methods plus local density approximation,⁵⁷ first-principles, hybrid functional with finite size corrections,⁴⁵ and density functional theory within a local density approximation,⁵⁸ which yield a wide range of values, i.e., ~ 3.8 , ~ 2.7 , and ~ 3.2 eV below E_{C} , respectively. Hence our energy level assignments can provide a guide for assessing different calculational approaches.

The depth dependence of optical emissions attributed to V_{Zn} - and V_{O} -related defects provides a useful tool to understand surface spreading resistance measurements (SSRM) for the ZnO films with DRCLS–PAS correlations. With the expectation that V_{Zn} act as acceptors to increase ρ , that V_{Zn} clusters deactivate Li acceptors to decrease ρ , and that V_{O} -related complexes act as donors to decrease ρ ,³⁰ one can account for the SSRM variations of ρ with depth for dramatically different ρ variations on a nanometer scale.⁵⁵ The success of these DRCLS–SSRM correlations requires that a combination of defects be used to account for nanoscale resistivity variations.

In general then, DRCLS–PAS correlations provide an identification of the commonly observed ~ 2 eV as V_{Zn} clusters and the ~ 1.6 – 1.7 eV emissions as isolated V_{Zn} . SPS provides a determination of the energy levels corresponding to the DRCLS emissions that can be used for comparison with theory. Different annealing methods alter V_{Zn} and V_{Zn} clus-

ter distributions spatially in ion-implanted ZnO, and a combination of V_{Zn} , V_{Zn} clusters, and V_{O} -related defects are required to account for ρ versus depth variations on a nanometer scale.

With these defect assignments, the role of vacancies in ZnO doping can be further understood. Figure 10 illustrates the interplay between V_{Zn} -related emissions measured by DRCLS and Hall-measured carrier density for ZnO degenerately doped with Ga, termed “GZO.”⁵⁹ This material exhibits carrier densities and mobilities that rival the leading transparent conducting oxide, indium tin oxide.^{34,60,61} Previously we showed from SIMS and Hall measurements that donors in GZO can only be due to Ga on Zn sites, Ga_{Zn} , since residual donor impurity densities are orders of magnitude lower.³³ Similarly, SIMS measurements and the application of density functional theory show that acceptors in GZO can be explained only by V_{Zn} and not by any other impurity. The inset of Fig. 10 contains DRCLS spectra for a GZO sample with an electron density of $4.92 \times 10^{20} \text{ cm}^{-3}$ grown at 400°C by PLD in a forming gas (FG) atmosphere. The degenerate n -type ZnO spectra show both V_{Zn} -related features at 1.84–2.05 eV and emission at energies above the conduction band minimum due to transitions involving filled conduction band states. Figure 10 includes data from GZO samples grown under both Ar and FG atmosphere at various temperatures ranging from 100 to 600°C . V_{Zn} intensities normalized to intensity at 3 eV (shown) or integrated conduction band intensity⁵⁹ both show a monotonic decrease with increasing Hall carrier density n_{Hall} over a range 1 – $10 \times 10^{20} \text{ cm}^{-3}$. The 3 eV intensity reflects conduction band intensity near the renormalized band edge and appears in the inset as a shoulder on the leading edge of conduction band emission. Integrated area 1.84–2.05 eV versus full conduction band emissions yield almost exactly the same ratios.⁵⁹ This decreasing intensity of V_{Zn} and V_{Zn} clusters with increasing n_{Hall} thus demonstrates

FIG. 10. (Color online) V_{Zn} -related defect intensity $I(V_{\text{Zn}})/I(3.0 \text{ eV})$ vs Hall carrier density n_{Hall} for degenerately doped GZO crystals showing decreasing V_{Zn} with increasing n_{Hall} indicating Ga filling Zn vacancies. The inset contains DRCLS spectra showing both V_{Zn} -related and filled conduction band states. High energy emission cutoff provides E_{F} vs depth.

the filling of Zn vacancies by Ga that increase Ga_{Zn} donors and decrease V_{Zn} acceptors. This relation holds for both Ar and FG growth ambients. The highest electron density occurs for GZO grown at 200°C for both ambients and decreases with increasing growth temperature. The temperature dependence of dopant incorporation depends on the dynamics of the growth process⁶⁰ and the availability of V_{Zn} sites. Hence this interplay suggests growth strategies for maximizing donor dopant incorporation.

The DRCL spectra shown in the inset of Fig. 10 provide a measure of E_F from the high energy cutoff of emission intensity. The energy at which conduction band emission decreases to 50% of its maximum provides a Fermi level position $E_{F\text{max}}$ from which filled conduction band state densities can be calculated, depending on the electron effective mass m^* and the shape of the renormalized conduction band.⁶² Comparison of $E_{F\text{max}}$ with absorption threshold measurements of $E_F - E_V$ on the same samples shows consistently higher $E_{F\text{max}}$ energies that vary with probe depth. The difference between absorption threshold and $E_{F\text{max}}$ can be understood if carrier density varies within the absorption depth since the onset of absorption occurs at $E_F - E_V$ minima while conduction-to-valence band free carrier recombination can extend to energies where doping and hence $E_{F\text{max}} - E_V$ is higher. DRCLS measurements of $E_{F\text{max}}$ versus depth indeed reveal variations in free carrier density.⁶⁰ Furthermore, the V_{Zn} -related intensities exhibit an anticorrelation with $E_{F\text{max}}$, decreasing for depths at which $E_{F\text{max}}$ is high and vice versa.⁶⁰ These V_{Zn} -related intensities vary by nearly a factor of 2 with depth on a scale of tens of nanometers versus $E_{F\text{max}}$ variations that correspond to $\leq 10\%$ variations in carrier density, precise values depending on the renormalized conduction band shape

FIG. 11. (Color online) 5 keV CL spectra comparison of V_{Zn} - and Li_{Zn} -related defects in Li-doped MG-ZnO after quenching and slow cooling process. The slow-cooled MG-ZnO exhibits an additional 3.0 eV peak and a decrease of V_{Zn} -related defect intensity.

FIG. 12. (Color online) (a) SPS spectra showing pronounced cpd increase at 3.0 eV corresponding to surface gap state emptying and (inset) lower band bending, raising E_F in the gap. (b) Schematic optical transitions for V_{Zn} (2.1 eV), V_{O} -related (2.45 eV), and Li_{Zn} (3.0 eV) defects in a ~ 3.3 eV ZnO bandgap, showing energy level positions for the corresponding defects.

but consistent with the magnitude of Hall-measured acceptor densities.⁶⁰ This anticorrelation further confirms the acceptor nature of the V_{Zn} -related emissions, and the $E_{F\text{max}}$ profile identifies primary Hall conduction channels for modeling donor and acceptor densities.

Another example of interplay between dopants and defects is Li-doped ZnO, where Li on a Zn site Li_{Zn} acts as an acceptor. Figure 11 illustrates DRCL spectra for Li-doped ZnO normalized to constant NBE intensity.⁶³ This hydrothermally (HT) grown HT-ZnO was unintentionally doped with $1\sim 5 \times 10^{17} \text{ Li/cm}^3$ and annealed in 10% Li_2O and ZnO powder for 1 h then either (1) quenched in de-ionized H_2O or (2) annealed in air at 600°C for an additional 10 min with slow cooling in air. The as-grown crystals exhibit high resistivity ρ and high V_{Zn} -related emission at ~ 2.1 eV. Rapid quenching decreased ρ to 0.1 $\Omega \text{ cm}$ and increased V_{Zn} -related emission. On the other hand, additional 10 min annealing and slow cooling in air produces high ρ , decreased V_{Zn} -related emission, and the appearance of a new peak at 3.0 eV. The intensity of this 3.0 eV peak varies with depth with a profile that mirrors the Li density [Li] measured by SIMS. Furthermore, the [Li] profile follows the SSRM depth profile of ρ , indicating that the 3.0 eV DRCLS peak intensity follows the Li_{Zn} acceptor density.

The energy level position of this 3.0 eV emission follows from SPS spectra of the same Li-doped ZnO. Figure 12(a)

illustrates a strong onset of contact potential difference (cpd) at 3.0 eV that corresponds to optical transitions that empty traps located 3.0 eV below E_C . The inset of Fig. 12 illustrates how emptying negative charge from this state reduces n -type band bending and raises E_F toward the vacuum level E_{VAC} . Slope changes are also apparent at 2.15 and 2.45 eV corresponding to emptying and filling transitions involving V_{Zn} - and V_O -related defects, respectively. The position of the Li_{Zn} acceptor level agrees with theoretical predictions⁶⁴ and with photoluminescence spectroscopy features of Li diffused into ZnO.⁶⁵ Figure 12(b) illustrates all three transitions within the ZnO bandgap. As with Ga-doped ZnO, these results for Li-doped ZnO illustrate how V_{Zn} -related defect densities decrease as zinc vacancy sites are filled with Li. The major difference in Li incorporation between quenched and slow-cooled samples can be viewed in terms of the time required for Li to diffuse to V_{Zn} sites. Without sufficient time to diffuse, Zn atoms remain as interstitials that act as donors, reducing ρ as observed experimentally.

VII. CONCLUSIONS

The results presented here serve to illustrate numerous ways in which native point defects play a major role in ZnO Schottky barrier formation and doping. Native point defect densities near ZnO and other semiconductor interfaces are much higher than previously believed. Their electrical activity introduces additional free carriers that reduce depletion widths and increase tunneling, while the defect gap states themselves provide sites for hopping conduction through barriers. The densities of these native defects and free carriers are sufficient to dominate charge transport across metal–semiconductor interfaces. Chemical interactions between metals and ZnO produce new defects at their intimate junction whose physical nature depends on the metal interaction with Zn or O in the adjacent lattice. DRCLS studies identify optical signatures of V_{Zn} , V_{Zn} clusters, V_O -complexes, Ga_{Zn} , and Li_{Zn} defects whose distributions depend sensitively on annealing. Therefore DRCLS serves as a tool for monitoring these defects to optimize Schottky barriers and to enable n - or p -type doping. New avenues to control densities and spatial distributions of native point defects are now available using the plasma, annealing, and metal bonding techniques illustrated here.

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