THE ROLE OF NATIVE POINT DEFECTS AND SURFACE CHEMICAL REACTIONS IN THE FORMATION OF SCHOTTKY BARRIERS AND HIGH N-TYPE DOPING IN ZINC OXIDE

DISSERTATION

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ZnO has received renewed interest in recent years due to its exciting semiconductor properties and remarkable ability to grow nanostructures. As a wide band gap semiconductor, ZnO has many potential future applications including blue/UV light emitters, transparent conductors, biosensors, and electronic nanoscale devices. While the versatility of ZnO is exciting, many hurdles keep it from reaching full device potential. Chief among them are the role of native point defects and impurities in the fabrication of high quality contacts and high, yet controllable, n- and p-type doping. The scope of this work explores the electronic properties of ZnO surfaces and interfaces and the impact of native point defects on Schottky barrier formation and doping.

The results presented here use a complement of depth-resolved cathodoluminescence spectroscopy (DRCLS), atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), and surface photovoltage spectroscopy (SPS) to show that surface treatment and processing plays a significant role in the quality, stability, and efficiency of potential next generation devices. This is evident in our results showing that the Zn-polar surface is more stable and capable of forming higher quality Au Schottky barriers as compared to the O-polar surface. We go on to reveal a significant metal sensitivity and surface polarity dependence that correlates with defects and interface chemistry on ZnO. We’ve also shown the significant impact of surface preparation and
post processing techniques on the optical efficiency and stability of ZnO surfaces. Our measurements reveal that remote oxygen plasma (ROP) processing is capable of decreasing oxygen vacancy related defects (V\textsubscript{O}-R) on the O-polar surfaces as well as creating new zinc vacancy related (V\textsubscript{Zn}-R) defects on the Zn-polar surface. Furthermore, we have correlated the formation of native point defects with interface chemical reactions and surface morphology on ZnO. With this, we were able to determine the relationship between the strength of near band edge to deep level defect emissions finding a threshold dependence on surface roughness that can serve as a figure of merit for substrate polishing and etching. Further experiments reveal that ZnO nanostructures grow spontaneously on ZnO polar surfaces in air that generate strong potential variations which correlate with native defects. Using a staged annealing process we were able to determine the activation energy for ZnO nanostructured growth revealing that Zn-interstitial diffusion is the dominant mechanism feeding growth. In a separate study, we observed the strong interplay between V\textsubscript{Zn}-R defects and dopants in degenerately Ga-doped ZnO films. In doing so we found that the DRCLS Fermi level thresholds provide a useful indicator of carrier density, revealing depth variations that anticorrelate with V\textsubscript{Zn}-R densities.

The ability to understand and control native defects as well as surface and interface chemical reactions in ZnO could allow for efficient and stable n- and p-type doping and serve to making higher quality Schottky diodes for future device applications.
DEDICATION

Dedicated to my Mother and Father, Brother, and Grandparents.
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This work could not have been completed without the opportunity and mentorship given to me by my adviser, Dr. Leonard J. Brillson. I would like to express my deepest gratitude for his patience, advice, and guidance throughout my graduate career.

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CHAPTER 1   INTRODUCTION AND BACKGROUND

1.1 Motivation

ZnO has been actively studied for over 60 years\textsuperscript{1,2}, yet it is only within recent years that its remarkable semiconductor properties have emerged.\textsuperscript{3} ZnO has a large direct band gap (3.34 eV at 300K) and with its high exciton binding energy (60 meV) that persists at room temperature and lattice matching to GaN, ZnO based blue and ultraviolet (UV) optoelectronics have become an active area of research. In addition to highly efficient blue and UV lasers and light emitting diodes (LEDs), ZnO’s high optical transparency makes it an ideal candidate for transparent thin film transistors (TFTs). Other valuable qualities of ZnO include its abundance and low cost, its environmental friendliness, and non-toxicity in humans. Advances in crystal growth have allowed for greater control over crystal quality and doping which has led to additional next generation opto- and microelectronic applications such as gas sensors, buffer layers for solar cell applications, spintronic devices, and high electron mobility transistors (HEMTs). ZnO also has the remarkable ability to grow nanostructures with a wide array of geometries providing a foundation where many electronic applications may emerge.\textsuperscript{4} With advancements in nanostructured growth and processing\textsuperscript{5}, devices which employ
ZnO’s piezoelectric ability and high sensitivity to adsorbate charge transfer would serve as valuable bio-medical sensors.6

Figure 1.1: ZnO has many opto- and microelectronic device applications such as blue/UV diodes and lasers. Also, ZnO has the ability to grown nanostructures with a wide array of geometries.

Despite all of the potential uses for ZnO, for it to become a realistic candidate for next generation devices many challenges still need to addressed. Chief among them are the role of native point defects and impurities and how they affect electrical properties in ZnO. A firm understanding and control of the chemistry and physics at the metal/ZnO interface is not yet established. Such an understanding in integral for making high quality Ohmic or rectifying (Schottky) contacts. Additionally, while ZnO is intrinsically n-type, its source remains controversial and p-type doping remains a challenge.

This work will focus on the role of surface adsorbates and chemical reactions, surface morphology, and near surface defects on the optical efficiency and the formation
of ohmic and Schottky contacts. Additionally we will explore the role of native point defects in controlling both high $n$- and $p$-type doping.

1.2 Crystal Structure

Most of the II-VI binary compound semiconductors crystallize in either cubic, zinc blend, or hexagonal wurtzite structure. In ZnO, each anion (O) is surrounded by four cations (Zn) forming the corners of a tetrahedron, and vice versa. With this, the iconicity of ZnO is both covalent and ionic. The stacking sequence of close-packed diatomic planes determines what is zinc blend (AaBbCcAaBbCc…) and wurtzite (AaBbAaBb…). And, while ZnO can be found in several allotropes including rock salt (NaCl structure) and zinc blend, under ambient conditions, the thermodynamically stable phase is wurtzite (hexagonal). The wurtzite structure, shown in Figure 1.2, has a hexagonal unit cell with two lattice parameters, $a$ and $c$, with the ration of $c/a = \sqrt[3]{8/3} = 1.633$.7
Figure 1.2: The wurtzite crystal structure of ZnO. Also shown is the polarity of ZnO along the c-axis. Note the unbounded electrons on the O-polar (000-1) surface.
The most commonly used and studied surfaces for ZnO are along the (0001) basal planes (c-axis). In the (0001) crystal direction there are alternating layers of Zn and O atoms that terminate in both polar-Zn or polar-O surfaces. The sp$^3$ hybridized orbitals lead to the strong polarization and lack of inversion symmetry in the (0001) direction. Many of ZnO’s unique properties are a result of its polarity, including for example; etching rates, spontaneous polarization, defect generation and segregation, and piezoelectricity. The Zn-polar surface tends to be more stable as its orbitals hybridize into the plane. Conversely, the O-polar surface has dangled oxygen bonds extending out from its interface making it more reactive. Polar surfaces may be distinguished either by their differing etching rates or luminescence decay. For example, O-polar surfaces have increased etching rates and exponential quenching of near-band-edge (NBE) luminescence due to surface adsorbates whereas the Zn-polar surface shows stable NBE luminescence with extended exposure times. A strong understanding of these characteristics is important when considering the chemical reactions that may take place at the metal/ZnO interface. Some metals form a eutectic with Zn while some metals may pull oxygen from the ZnO sublattice to form oxides and blocking interfacial layers. Both instances result in defect generation that can have strong affects on the rectifying behavior of Schottky contacts on ZnO.
Figure 1.3: Energy Gap vs. Bond Length for many common semiconductor materials. Here it can be seen that ZnO is lattice matched to GaN. Engineering the band gap with MgO allows for ternary compounds from 3.3 eV to 8.0 eV.

Band gap engineering in ZnO is crucial for next generation opto- and microelectronics. As seen in Figure 1.3, ZnO is lattice matched with GaN and makes a ternary compound Mg$_x$Zn$_{1-x}$O with a band gap that can be tailored to the range of 3.3 eV to almost 8.0 eV making the compound ideal for quantum well structures.
1.3 ZnO Growth Methods:

Observations of room temperature optically pumped lasing in ZnO in high quality MBE grown epilayers and its potential for future UV light emitters has brought considerable attention to ZnO crystal growth. The pursuit of the highest quality bulk material is motivated by the potential advantages of homoepitaxy. While growth of ZnO layers on sapphire is conventional, high dislocation densities caused by the large lattice mismatch between sapphire (18.4% in-plane) and ZnO would degrade device performance. In addition to the performance advantages of homoepitaxy, high quality ZnO substrates could also be used for heteroepitaxial growth of GaN layers. Both ZnO and GaN are closely lattice matched with only a 1.8% lattice mismatch. The work presented here contains many collaborations between a number of the leading vendors of ZnO substrates including Tokyo Denpa Co., LTD., Cermet Inc., and Zn Technologies which allows not only for a general study of the affects of growth methods on defects and impurities but also the affects of various surface treatments. Surface preparation is an integral step in developing device quality material, and is often overlooked by researchers. Each vendor has developed and maintained advanced proprietary surface polishing and chemomechanical polishing techniques. These collaborations have revealed many interesting growth and process specific characteristics that manifest in both the electrical and optical properties of ZnO.

While ZnO has been successfully grown on sapphire (Al₂O₃), glass, and quartz (SiO₂) substrates with high quality using pulsed-laser deposition (PLD), molecular-beam epitaxy (MBE), and chemical-vapor phase (CVD) methods there are three primary methods for
producing high quality bulk single crystal substrates; Hydrothermal (HYD), vapor-phase (VP), and Melt Grown (MLT). Each method has both advantages and disadvantages that will be addressed in turn.

**Melt Grown (MLT) ZnO:**

The melt growth method consists of the controlled deposition of atoms onto a single crystal seed from molten raw materials. This method exploits the liquid-to-solid phase transition caused by a temperature gradient across the system. The two most common methods of melt growth are the Czochralski and Bridgman methods. In the Czochralski method a seed crystal is mounted to a rod and dipped into the melt. The seed crystal is gradually pulled upward out of the melt while being rotated. By controlling the temperature gradient, rate of pull, and rate of rotation large single crystal ingots can be grown. With the Bridgman method, raw material is heated in a crucible to above its melting point. This is followed by a slow cooling from one end of the vessel where a seed crystal is located. The temperature gradient from one end of the crucible to the other drives the growth from the seed. Single crystal material is formed along the length of the vessel. The primary motivation behind melt growth is its cost effectiveness due to high growth rates and growth of high purity material.\(^\text{12}\)
Cermet Inc. has produced high quality single crystal ZnO substrates by employing a pressurized melt growth approach. As seen in Figure 1.4, ZnO is melted in a water-cooled crucible to above 1450 °C at atmospheric pressures using a high pressure induction melting apparatus. An RF source induces fields supplied by inductive coils surrounding the source material causing eddy currents that produce joule heating until a molten phase is achieved. The water-cooled crucible allows a thin diffusion barrier to form minimizing contamination from the crucible. The melt growth process is carried out in a controlled gas atmosphere ranging from 1 atm to over 100 atm. This discourages the evolution of volatile components and chemical decomposition. An overpressure of oxygen is used to maintain stoichiometry and avoid chemical decomposition. The Cermet
samples show high unintentional $n$-type conductivity, with carrier concentrations $\sim 10^{17}$ cm$^{-3}$. With this method Cermet Inc. is able to produce high quality, high purity, ZnO crystal substrates up to 2 inches in diameter.\(^\text{13}\)

**Vapor Phase (VP) Grown ZnO:**

As the name suggests, vapor phase involves growth of material where its constituent components are in their vapor phase. In vapor phase growth, pure ZnO powder is used as the ZnO source. It is placed in a furnace that is sectioned into several zones that are held at different temperatures. The ZnO powder is placed in the “hot zone” of a the furnace that is kept at $\sim 1150$ °C. The constituent material is transported from the “hot zone” end of the furnace to the cooler end, known as the “growth zone”. Due to the low vapor pressure of Zn and O at these temperatures, and H$_2$ carrier gas is used. In the hot zone, ZnO decomposes according to the reaction

$$\text{ZnO (solid) + H}_2\text{(gas)} \rightarrow \text{Zn (gas)} + \text{H}_2\text{O (gas)}$$

In the growth zone, this process is reversed and growth is assisted by a single crystal seed. A small amount of water vapor is used in the growth process to add oxygen and maintain stoichiometry. The typical growth time for a 2 inch diameter, 1 cm tall crystal is $\sim 150 – 175$ hours which translates into a growth rate of roughly 1 mm/day. With the addition of H$_2$O and H$_2$ carrier gas, VP material often contains a high concentration of hydrogen impurities which may strongly effect the electrical properties.\(^\text{12}\)
Hydrothermal Grown (HYD) ZnO:

![Diagram](image)

Figure 1.5: (left) Schematic representation of Hydrothermal Growth vessel for ZnO. Both the dissolution and crystal growth zone are labeled (right) High crystalline quality ZnO substrates grown by Tokyo Denpa Co, LTD. up to 2 inches in diameter.¹⁵

In the hydrothermal growth method, growth takes place in a platinum lined autoclave held at relatively low growth temperatures of 300-400 °C. As seen in Figure 1.5, the pressurized vessel consists of two sections referred to as the “dissolution zone” and “crystal growth zone”. The dissolution zone is a high temperature, high pressure region where ZnO is dissolved in a KOH/LiOH solution. The crystal growth zone is a reduced temperatures region where ZnO constituents, transported by convection from the high temperature region, precipitate in the low temperature growth region. With this method, Tokyo Denpa is currently able to grow high purity high crystalline quality ZnO
substrates up to 2 inches in diameter \(^{14}\). When compared with other growth methods, the primary advantage of hydrothermal growth are the low growth temperatures. However, with growth rates of \(~ 0.03\) inches/day hydrothermal growth is slow when compared with methods such as melt grown. Moreover, hydrothermally grown material typically suffers from Li and K impurities introduced during the growth process that may strongly affect electrical properties. Typical Li concentrations are \(> 10^{16} \text{ cm}^{-3}\) and result in low electron concentrations and high resistivities.\(^{15}\)

It is important to note that all bulk single crystal ZnO is intrinsically \(n\)-type, regardless of the growth method. The cause of this unintentional \(n\)-type conductivity has been controversial and a widely discussed topic for many years. While this behavior is often attributed to native point defects and/or impurities, researchers have yet to reach a consensus. Such strong debate highlights the importance of studies meant to determine the fundamental role of native defects and impurities in ZnO.

1.4 Defects in ZnO:

Understanding the role of native point defects in ZnO is an integral step in controlling the doping and electrical properties necessary to develop next generation devices. As with any semiconductor, defects can have strong affects on the electrical properties, optical properties, as well as interface chemical reactions and doping. By definition, native defects are defects that involve the constituent atoms only. Therefore, in ZnO, native point defects are only those involving Zn and/or O atoms and include antisites (Zn atoms occupying O lattice sites or vice versa), interstitials (Zn or O atoms
occupying space between lattice sites), vacancies (missing Zn or O atoms), or their complexes.

Over the last decade, Van de Walle, *et al.*\textsuperscript{16} have been researching the formation of native point defects using first-principles calculations using density functional theory (DFT) within the local density approximation (LDA) as well as the LDA+U approach for overcoming the “band-gap problem” with DFT methods.\textsuperscript{17} It is important to note that DFT calculations of basic ZnO properties such as formation energies and defect energy-level relative to band edges can vary considerably with different approximations. Figure 1.5 shows the calculated formation energy as a function of Fermi level (\(E_F\)) position for each of the native point defects in ZnO using the LDA+U formulism. A low formation energy indicates a high equilibrium concentration of the defect whereas a high formation energy implies that the defect is unlikely to form. From this work it may be concluded that the most energetically favorable native point defects in ZnO are the zinc vacancy (\(V_{Zn}\)) and the oxygen vacancy (\(V_O\)). The \(V_{Zn}\) has been shown to be an acceptor type defect, capable of accepting up to two electrons (\(V_{Zn}^{-2}\)) while the \(V_O\) has been shown to be a donor type defect able to contribute up to two electrons (\(V_O^{+2}\)). Generally, native point defects act to compensate the dominant acceptor or donor dopants. As such, donor defects are easier to form in \(p\)-type material while acceptor defects have lower formation energies in \(n\)-type material. It’s important to note, however, that Zn- vs. O-rich environmental growth conditions also effect the formation energies of these native defects. This behavior is clearly seen in Figure 1.6 where, under both O- and Zn-rich conditions, the \(V_{Zn}\) formation energy is lowest as \(E_F\) approaches the conduction-band-
minimum (CBM). Conversely, as the $E_F$ approaches the valence-band-maximum (VBM) the formation energy of $V_{Zn}$ increases. As should be expected, under Zn-rich conditions, the $V_{Zn}$ is less likely to form given most $E_F$ positions. Similarly, under O-rich conditions the $V_O$ is less likely to form for all $E_F$ except those very close to VBM.

![Figure 1.6: Formation energies as a function of Fermi level position for native point defects in ZnO. The zero of the Fermi level corresponds to the valance-band maximum. Changes in slope refer to changes in charge state.][16]

While first-principles calculations have been useful in determining both the formation energy and energy position of native defects in ZnO, experimentally the
identification of native point defects is still very much controversial. In un-doped ZnO, the well-known “green band” (GB) emission at around 2.5 eV typically dominates the defect-related luminescence. Early studies attributed the GB emission to Cu impurities,\textsuperscript{18} with some recent work supporting this designation.\textsuperscript{19} However, strong correlations between the intensity of the GB emission and V\textsubscript{O} concentrations obtained under different annealing conditions or oxidation have related the 2.5 eV feature to V\textsubscript{O}.\textsuperscript{20,21} Further studies by Vanheusden \textit{et al.}\textsuperscript{22} that include optical absorption, photoluminescence (PL), and electron paramagnetic resonance (EPR) indicate a correlation between the GB emission and V\textsubscript{O} defects as well. In addition, depth-resolved cathodoluminescence spectroscopy experiments performed by Brillson \textit{et al.}\textsuperscript{23} also indicate a correlation between GB emission and V\textsubscript{O} defects. As the dominant donor in ZnO, it was originally suspected that V\textsubscript{O} may be the cause of unintentional \textit{n}-type conductivity in ZnO. However, both theoretical calculations and experimental results demonstrate that the V\textsubscript{O} acts as a deep donor, with a defect energy-level near mid gap at \textasciitilde 2.5 eV above the VBM. While there has been widespread acceptance of the V\textsubscript{O} model explaining the GB emission, the topic is still very controversial with a number of alternative models suggesting that other native point defects or complexes may play a role.
Figure 1.7: DRCLS defect emission intensities and PAS zinc vacancy densities versus depth. For both Li-implanted ZnO (a) flash annealed at 1200 °C and (b) furnace annealed at 800 °C for 1-hr, \( I(2.0 \text{ eV})/I(\text{NBE}) \) (black squares) correlates with zinc vacancies (blue dots) while \( I(2.4 \text{ eV})/I(\text{NBE}) \) (red hexagons) does not.

Another dominant emission feature often seen in un-doped ZnO is the “red” optical emission in the range of 1.8–2.1 eV. Recently, Dong et al.\textsuperscript{24} were able to use a combination of positron annihilation spectroscopy (PAS), DRCLS, and surface photovoltage spectroscopy (SPS) to correlate 1.6 – 2.1 eV optical emission with isolated and clustered \( V_{\text{Zn}} \) defects in Li-doped ZnO. The energy-level position of isolated vacancies resides at the lower end of this energy range (~1.6 eV) while the energy-level
of vacancy clusters is 1.9 - 2.1 eV below the conduction band. While PAS is not directly sensitive to $V_O$, as Figure 1.7 shows, ~2.0 eV DRCLS emission correlates with PAS $V_{Zn}$ profiles whereas ~2.5 eV DRCLS emission does not, indicating that emission features typically associated with $V_O$ (i.e. GB emission) is not related to $V_{Zn}$ defects. Just recently K.E. Knutsen et al.\textsuperscript{25} were able to unambiguously associate the characteristic “red” PL band at ~ 1.75 eV with an optical transition involving $V_{Zn}$-related deep acceptors. Theory predicts an energy level for the $V_{Zn}^{2-}$ defect level ~2.3 eV below the CBM, which is consistent with experimental observations. The $V_{Zn}$ acts as an acceptor, capable of accepting up to two electrons and has the lowest formation energy of native point defects in $n$-type ZnO.

The $Zn_i$ defects acts as shallow donors in ZnO. They have a high formation energy in $n$-type ZnO and are fast diffusers with a low migration barrier of ~0.57 eV. They are not stable at room temperature and anneal out at temperatures as low as 170 K\textsuperscript{15}. In partial summary, Figure 1.8 shows generally accepted energy levels within the band gap of most native point defects in ZnO.
While ZnO has been actively studied for nearly over 60 years, the difficulty of $p$-type doping and the role of compensating defects remains an issue. The $V_O$, $V_O^-$-related complexes, $Zn_i$ and their complexes, and residual impurities such as hydrogen and aluminum are all believed to be donors while $V_{Zn}$ and their complexes believed to be acceptors. Although their impact on carrier compensation is recognized, the physical nature of the donors and acceptors dominating carrier densities in ZnO is unresolved. Thus, it remains an important challenge to correlate commonly observed emission features such as the 1.8 - 2.1 eV “red” and 2.3 - 2.5 eV “green” luminescence to native defects.
1.5 Impurities in ZnO:

While hydrogen is amphoteric in most semiconductors, in ZnO it behaves as a donor only. Hydrogen is difficult to remove from growth and processing environments, therefore its incorporation in ZnO is an important factor. Hydrogen can contribute to the overall $n$-type conductivity in ZnO by acting as a shallow donor and/or passivating compensating acceptor type defects. For this reason, hydrogen is often linked to the characteristic $n$-type conductivity in ZnO. Passivation of $V_{Zn}$-related acceptors by forming neutral complexes is predicted by theory. Passivation of $V_{Zn}$ has been confirmed experimentally by PL measurements$^{26}$, IR absorption$^{27}$, and PAS$^{28}$. The shallow donor nature of hydrogen in ZnO is predicted by first-principles calculations$^{29}$ and has been confirmed experimentally.$^{30}$ Hydrogen has been shown to form two types of donors in ZnO: (1) substitutional hydrogen ($H_O$), where hydrogen is bound with an oxygen vacancy and (2) interstitial hydrogen ($H_i$), where hydrogen incorporates at the bond-centered interstitial site. Interstitial hydrogen is unstable in ZnO with a migration energy of $\sim 0.4$ eV. Substitutional hydrogen, however, is stable in ZnO with a migration energy of $1.7$ eV.$^{31}$ Both $H_O$ and $H_i$ have low formation energies in ZnO, indicating that they may form in significant concentrations.$^{15}$ To achieve $p$-type conductivity and control the electrical properties for ZnO devices, it is important to understand the incorporation and activation of hydrogen.

Lithium is another important impurity often found in large concentrations in ZnO. Lithium may behave as both a donor or an acceptor in ZnO, depending on where it incorporates into the lattice. Interstitial lithium ($Li_i$) acts a donor while substitutional
lithium (Li$_{Zn}$), where lithium occupies a zinc vacancy site, acts as an acceptor. Like hydrogen, lithium is difficult to remove from certain growth environments. For example, HT-grown ZnO wafers are often highly resistive which has been attributed to high Li concentrations inherent to the HT-growth process.
CHAPTER 2  EXPERIMENTAL METHODS

2.1 Ultra High Vacuum:

The study of surfaces and interfaces requires equipment needed to prepare and maintain clean surfaces. This is achieved through a collection of pumps that act together to keep ambient pressures low enough such that impinging molecules do not adsorb onto surfaces in considerable numbers. Equipment that is typically used to achieve such conditions consist of stainless steel chambers, pumps to remove gaseous contaminants and air, pressure gauges to monitor changes in pressure, quartz viewports to monitor internal operations, manipulators to move samples from one location to another within the chamber environment, and analysis tools to measure material properties under various conditions. These stainless steel chambers are sealed and joined together with bolts and copper gaskets that deform around “knife edges” machined into each flange that keep gas leakage minimal. A combination of pumps acting in parallel and in series are needed to reach ultra high vacuum (UHV) which is defined as pressures at or below $10^{-10}$ Torr. Often, these pumps operate in isolated regions of a chamber that are at different pressures and separated by valves. Each region and pump therefore acts as a “stage” in achieving UHV conditions. These pumps include roughing pumps (max $10^{-3}$ Torr), turbo molecular pumps (max $10^{-9}$ Torr), ion pumps (max $10^{-10}$ Torr), and cryopumps (max $10^{-10}$ Torr).
Roughing pumps are used to initially evacuate the chambers. They are necessary not only as the initial stage in reaching UHV, but because high vacuum pumps (i.e. turbo molecular pumps) do not operate efficiently at atmospheric pressures. The most common roughing pumps are the rotary vane and scroll pumps. Some considerations need to be made when choosing the type of roughing pump to use with a UHV system. For example, rotary vane pumps use lubricating oils which may “backstream”, or flow into the vacuum chamber, in gas form. This is a significant issue when trying to maintain surfaces void of hydrogen or carbon adsorbates. For this reason, oil free pumps, such as the scroll pump, are ideal. A rotary vane pump is a positive-displacement pump that consists of vanes mounted to a rotor that rotates inside a cavity generating vacuum. Turbo molecular pumps are essentially turbine engines that push air through a series of vanes rotating at 15-75 kRPM. Cryopumps produce vacuum by condensing molecules and vapor onto a cooled surface. The method involves the adsorption of gases onto a condenser coil connected to a source of cryogenic gas. Ion pumps ionize gas within the chambers and uses a strong electric potential, typically 5 kV, which allows the ions to accelerate into and be captured by Ti cathode plates. The ionized gas molecules either bond with the Ti layer and are buried or they knock off additional Ti which can bond with other gas ions.

Typical operating procedures begin by loading a specimen into and “intro chamber” which is then pumped to $10^{-3}$ Torr by a roughing pump. Once the roughing pump has maximized its vacuum a turbo molecular pump may be initiated and the intro chamber can be taken to $10^{-9}$ Torr. Once acceptable vacuum has been confirmed, by read outs from a convectron or ion gauge, the specimen can then be moved to the analysis
chamber. Analysis chambers, or “main chambers” are typically equipped with either a turbo molecular pump, ion pump, cyro-pump, or some combination of all three. Typically a turbo molecular pump is used to reach or maintain $10^{-9}$ Torr, where it is then safe to operate ion and cryopumps efficiently. At this point measurements may begin.

2.2 Cathodoluminescence Spectroscopy (CLS):

The interactions of high energy (keV) electrons with semiconductor materials has become a valuable method of characterization. Cathodoluminescence is the emission of light as a result of electron excitation. CLS is similar to photoluminescence spectroscopy (PLS) except that electrons produce the optical transitions instead of photons. While both techniques involve the creation of electron-hole pairs, there subsequent recombination and optical emission, it is this difference in excitation source that gives CLS an distinct advantage over PLS.

The advantages of CLS include: orders-of-magnitude higher free carrier generation rates, the ability to excite electron-hole pairs in wide band gap semiconductors and insulators, true surface sensitivity at low beam energies, a tunable excitation depth allowing for both bulk and surface sensitivities, variable incident beam energies allowing for nanoscale depth resolution, tunable beam sizes allowing for nanoscale spatial resolution, and the ability to probe interfaces below the free surface and through metal over layers. PLS is most limited by its lack of depth information and low electron-hole pair generation when compared to CLS. In PLS, both the excitation depth and maximum excitation energy are limited by the photon energy of the laser source. As a result, photon
excitation occurs at a single energy and a single absorption depth and most conventional laser sources have photon energies that limit their use for wide band gap semiconductors such as MgZnO (3.3-8 eV) or insulators such as Al₂O₃ (8.8 eV).

Figure 2.1: Schematic illustration of processes generated by a secondary electron cascade in a solid.

A wide variety of processes occur when a focused electron beam irradiates a solid. Figure 2.1 illustrates these various processes that occur due to an electron beam...
focused to 10-100 Å on a solid surface. The electron beam irradiation produces a pear-shaped volume where in the following are generated: (i) Auger electron generation within the first few Å of the free surface, (ii) secondary electrons due to ionization of impacted atoms ranging from the first few nanometers to higher depths depending on the incident electron beam energy, (iii) backscattered electrons at lower depths due to random collisions of electrons that have lost significant kinetic energy, (iv) X-rays characteristic of specific atomic transitions, (v) a continuum of X-ray energies resulting from secondary X-ray excitation, and (vi) optical emission (fluorescent X-rays) due to low energy electrons initially excited by X-rays. The width of the generation volume, and thus the resolution of CLS, is determined by the electron beam size, the size of the generation volume, and the minority-carrier diffusion length. The minority carrier diffusion lengths of semiconductors is typically small making CLS an ideal characterization tool with nanoscale resolution in all dimensions.
The cascade of generated electrons makes CLS a powerful technique for characterizing the radiative defect states in semiconductor materials. As previously mentioned, the large free carrier generation in CLS produces a cascade of electrons that are free to recombine with holes through one or more available channels. Figure 2.2 shows schematically the various channels that exist: (1) intra-band transitions due to electrons excited to well above the conduction band edge falling down as thermal equilibrium is reached typically resulting in the emission of a phonon, (2) band-to-band transitions, (3) excitonic transitions including free, donor bound, and acceptor bound excitons, (4), (5), (6) transitions involving defect states, and (7) transitions due to radiative de-excitation of centers. Recombination of electron-hole pairs may also occur through nonradiative processes but these are difficult to characterize.32
One of the fundamental advantages of CLS over similar methods, such as PLS, is that while a single photon can generate one electron-hole pair (EHP), a single 20 keV electron can generate thousands of electron-hole pairs. In CLS, the local generation rate of EHPs is given by the following relation...

\[
G = \frac{V_b I_b (1 - \gamma)}{e E_i}
\]

where \( V_b \) is the electron-beam voltage, \( I_b \) is the beam current, \( e \) is the electronic charge, \( \gamma \) represents the fractional electron beam energy loss due to backscattered electrons, and \( E_i \) is the ionization energy which is the minimum energy required to generate an EHP. The ionization energy \( E_i \) is related to the band gap of the semiconductor by the following relationship...

\[
E_i = 2.8 E_g + M
\]

where \( E_i \) is the ionization energy, \( E_g \) is the band gap of the semiconductor, and \( 0 < M < 1 \) eV is a material property, independent of the electron-beam energy.\textsuperscript{33} It is important to keep generation rates constant to accurately compare data from different depths in a material. For this reason, it is important to keep constant power, i.e. the product of \( V_b I_b \) constant.
One of the more powerful features of CLS is the ability to probe at different depths by varying the energy of the incident electron beam. As such, it is important to understand the series of successive elastic and inelastic scattering events that incident electrons undergo once injected into the semiconductor. The electron kinetic energy $E$ changes along a path $s$ can be determined using the Bohr-Bethe energy loss formula...

$$-\frac{dE}{ds} = (2\pi N_A e^4) \left( \frac{Z\rho}{A} \right) \left( \frac{1}{E} \ln \frac{aE}{l} \right)$$
where \( N_A \) is Avogadro’s number, \( Z \) is the atomic number, \( \rho \) is the density, \( A \) is the atomic weight, \( I \) is the mean excitation loss energy, equal to \( (9.76 + 58.8 \, Z^{1.19}) \, Z \, (\text{eV}) \) and \( a = 1.1658 \) is a material-independent constant. The resultant energy loss profile has a maximum energy loss rate at a depth \( U_0 \) and a maximum range \( R_B \), known as the Bohr-Bethe range. Figure 2.3 illustrates how \( U_0 \) and \( R_B \) vary with incident beam energy \( E_B \). The Bohr-Bethe range can be determined by...

\[
R_B = \int_E^{\infty} \frac{dE}{d(\rho s)} = \int_0^{\xi(E_B)} \frac{\xi \, d\xi}{\ln(\xi)}
\]

where \( \xi = aE/I \) and \( E_B = \) incident beam energy. From this one can calculate the Bohr-Bethe range and approximate it as…

\[
R_B^{E-H} = \frac{0.0398}{\rho} E_B^{1.75} (\mu \text{m})
\]

for incident electron energy ranges of 5 - 25 keV and atomic numbers 10 < \( Z < 15 \). A useful Everhart-Hoff approximation that acts as a “universal” fit to experimental data is...

\[
R_B = C \xi^a
\]
where \( C \) is a material-dependant constant = \( 9.40 \times 10^{-12} \, I^2 \, (A/Z) \, c' / \rho \), both \( a = 1.29 \) and the material independent constant \( c' = 1.48 \) are valid for the range of \( \xi < 10 \). Kanaya and Okayama have also proposed a general expression for determining the Bohr-Bethe range that also agrees well with experimental results and includes a wider range of atomic numbers. The range according to Kanaya and Okayama is given by:

\[
R_B^{K-O} = \frac{0.0276}{\rho Z^{0.889}} E_B^{1.67} (\mu m)
\]

These expressions are only useful above keV electron beam energies for solids with uniform composition. Therefore, it can be challenging to accurately determine penetration depths at sub-keV energies where precession is necessary. While many alternative models have been proposed, they often yield significantly different results even for the same material.

A more accurate way to model the rate of EHP production versus depth is to employ Monte-Carlo simulations such as CASINO. The CASINO program is designed to simulate the random collisions of the secondary electrons generated by a large amount of incident electrons. The program is specifically designed to simulate the electron trajectory in solids at energies equivalent to those used in the CL method. The CASINO program is capable of modeling the production of X-rays, backscattered electrons, and lateral beam widening. Beyond its ease of use, the program also allows for simulations through multiple layers with different densities and atomic weights, which together with incident beam energies and primary loss mechanisms will determine the scattering cross-
sections. Figure 2.4 shows a CAINO Monte-Carlo simulation for ZnO. Here, the depth of peak excitation ranges from ~7 – 60 nm for incident beam energies of 1-4 keV, respectively. The FWHM of the excitation curves at low probe energies is small indicating highly localized EHP production at the near surface. Such a simulation stresses the capability of CL to not only measure bulk properties, but also the near surface properties of a semiconductor with high resolution. Experimental results provide strong evidence that CASINO simulations can provide remarkably precise depths of peak excitation values for CLS.

Figure 2.4: Energy loss versus depth for low $E_B$ in ZnO.
Several limitations for CL characterization of semiconductors also exist. CLS intensities are quite high for direct band gap materials, however, materials with indirect band gaps often show low CL signal making data taking a challenge. Other materials may have large concentrations of non-radiative defects that make CL characterization challenging. Also, prolonged exposure to high concentrations of incident high energy electrons could potentially cause damage in some materials. CLS is not a quantitative technique and cannot determine absolute defect densities. However, by using a complement of techniques such as positron annihilation spectroscopy (PAS), capacitive methods such as deep level transient spectroscopy (DLTS), and/or carrier lifetime measurements such as surface photovoltage spectroscopy (SPS) one can determine both the defect identity, its concentration, and energy position within the band gap with very good accuracy. ZnO is an ideal material for CL characterization because it is a direct band gap semiconductor and is highly tolerant to radiation.

**Cathodoluminescence Instrumentation:**
Figure 2.5: Cross sectional schematic of low energy CLS equipment.

Within the Electronic Materials and Nanostructures Laboratory (EMNLab) at The Ohio State University we have two unique instrumental configurations used to perform depth resolved cathodoluminescence spectroscopy (DRCLS). Figure 2.5 shows the schematic of a ultrahigh vacuum (UHV) chamber in cross-section, with a 45° glancing incident electron gun and beam that impinge upon a sample attached to a manipulator positioned at the focal point of the electron gun. The impinging electrons produce radiative recombination that is collected by a UV-IR transmitting light lens and passed through a sapphire window into a monochromometer and finally a CCD detector provides an electrical signal proportional to the energy-resolved light intensity. The CCD pixel size
ultimately determines the resolution of CL spectra in this configuration but the following bandpass relationship applies for the monochromater...

\[ BP = W \times R_d \]

where \( BP \) is the bandpass, \( W \) is the slit width, \( R_d = d/(f \times m) \) where \( d \) is the grating distance, \( f \) is the distance from one grating slit center to the next, and \( m \) is an integer representing the propagation-mode of interest. So, for the ZnO near-band-edge (NBE) emission region of \( \sim 370 \) nm, using a slit width of \( 1 \) mm results in an \( R_d \) of \( 3.33 \) nm. So, the range of \( 366.7 \) nm to \( 373.3 \) nm has a resolution of \( \sim 60 \) meV. The energy of incident electrons ranges from only a few hundred volts to \( 5 \) keV with currents of a few microamperes and a beam spot diameter of \( \sim 0.5 \) mm at the focal point. The sample stage can be cooled cryogenically by a gas He condenser unit that is capable of cooling the sample stage to as low as \( 80 \) K. The base pressure inside the chamber is less than \( 10^{-10} \) Torr minimizing the effects of residual gases and contamination.
For experiments that necessitate higher prober energies than those described above, the scanning electron microscope (SEM) may be employed. Figure 2.6 shows the cross sectional view of a UHV field emission JEOL 7800F SEM. A focusing column with typical $E_B$ ranging from > 1 keV to 25 keV directs an electron beam through a hole in a parabolic mirror that sits above the sample holder and stage configuration. The mirror captures the luminescence and directs it through a UV-IR window through an Oxford MonoCL system to a photomultiplier tube where the intensity of the
monochromatized light is measured. In addition, the electrons emitted from the sample
are collected by a hemispherical analyzer and used for Auger electron spectroscopy
(AES) and secondary electron imaging. The base pressure inside the chamber is less than
$10^{-10}$ Torr allowing for measurements of clean and controlled surfaces. The SEM offers a
number of stage configurations; liquid helium cooled stage capable of reaching
temperatures as low at 10 K, an electron beam-induced current (EBIC) stage for in-situ
electrical manipulation of samples, and a liquid nitrogen cooled stage capable of reaching
80 K. The SEM also offers finer control over the electron beam spot size, in addition to
being capable of higher beam voltages and lower beam currents. For example, the SEM
electron beam can be focused up to 5 nm, depending on the beam parameters, offering
remarkably high lateral spatial resolution for CL measurements. Table 1 outlines many of
the beam parameters and their corresponding spot sizes.

Table 1.1: Calculated beam sizes for given beam voltages ($E_B$) and beam currents ($I_B$).

<table>
<thead>
<tr>
<th>Beam Voltage ($E_B$)</th>
<th>10 pA</th>
<th>1 nA</th>
<th>10 nA</th>
<th>50 nA</th>
<th>100 nA</th>
<th>1 mA</th>
</tr>
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<tr>
<td>25 keV</td>
<td>4 nm</td>
<td>6 nm</td>
<td>10 nm</td>
<td></td>
<td>30 nm</td>
<td>80 nm</td>
</tr>
<tr>
<td>10 keV</td>
<td>8 nm</td>
<td>10 nm</td>
<td>20 nm</td>
<td></td>
<td>60 nm</td>
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</tr>
<tr>
<td>5 keV</td>
<td>14 nm</td>
<td>15 nm</td>
<td>43 nm</td>
<td>140 nm</td>
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</tr>
<tr>
<td>2 keV</td>
<td>16 nm</td>
<td>20 nm</td>
<td>52 nm</td>
<td></td>
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</tr>
</tbody>
</table>
The highly tunable nature of the SEM electron beam allows for highly localized excitation volumes making CLS measurements of specific locations across the surface and at specific depths at these locations. This makes CLS with SEM a powerful tool for probing individual layers and their interfaces.

2.3 Scanning Probe Microscopy (SPM):

The Scanning Probe Microscopy (SPM) is a branch of microscopy that utilizes a very small physical probe that is scanned across a material surface with the purpose of extracting information related to a large assortment of material properties. The SPM excels due to resolution capabilities that are order of magnitude higher than most other forms of microscopy. At its most fundamental, a SPM operates by lowering a physical probe, of varying dimensions and compositions, down to the surface of a material and scanning it across the surface. As the probe approaches the surface, it will interact with surface and/or subsurface atoms in a variety of ways. These probe-sample interactions include topographical, electrical, and magnetic information that may serve to describe the material of interest. The EMNLab at The Ohio State University utilizes a Park Systems XE-70 Scanning Probe Microscope with Au/Cr coated Si cantilevers. The XE-70 SPM is capable of measuring topography using atomic force microscopy (AFM), contact potential difference using Kelvin probe force microscopy (KPFM), as well as various semiconductor electrical properties using a modification to the KPFM mode.
known as surface photovoltage spectroscopy (SPS). Each of these modes will be described and discussed in turn.

2.4 Atomic Force Microscopy (AFM):

Figure 2.7: Atomic force microscopy (AFM) mode operation for Park System XE-70 Scanning Probe Microscope.

Atomic force microscopy (AFM) uses a micro-machined cantilever with a sharp tip to measure the surface of a material. Depending on the distance between the tip and
surface atoms there exists either an attractive or repulsive force that may be utilized to measure a samples topography. Figure 2.7 shows a schematic representation of non-contact mode AFM for the Park Systems XE-70 SPM. Essentially, the changes in surface morphology cause the cantilever to deflect. A laser shining on the backside of the cantilever reflects onto a mirror which directs the laser signal onto a position sensitive photo detector (PSPD). The tube shaped piezo-electric scanner beneath the sample moves the sample in the X-Y directions and in the Z-direction. It scans the sample line by line while the PSPD is used to establish a feedback loop which controls the vertical movement of the scanner as the cantilever is raster scanned across the surface. AFM is a useful tool for characterizing a wide array of materials including conductors, insulators, and even liquids. Furthermore, the small tip-cantilever configuration makes it ideal for studying properties of device structures with nanoscale dimensions.

The XE-70 SPM is capable of measuring in full non-contact (NC-AFM) mode using a feedback loop coupled with an independent Z-scanner. In AFM there are two major forces at very small distances: the static electric repulsive force and attractive van der Waals force. When the tip-sample distances get very small, the repulsive forces between them dominates. Typical contact AFM modes utilize this repulsive Coulomb interactions to measure surface topography. However, at larger tip-sample distances the attractive van der Waals force becomes dominant. It is in this regime where NC-AFM operates. Since forces between tip-sample are small, NC-AFM detects changes in phase or the vibrational amplitude of the cantilever induced by the attractive force while the cantilever is mechanically oscillated near its resonant frequency to measure surface
topography. More specifically, in NC-AFM, a piezoelectric bimorph is used to vibrate the cantilever near the cantilever’s intrinsic resonant frequency \( f_0 \), usually between 100 kHz and 400 kHz, with an amplitude of a few nanometers. The resonant vibration has a corresponding spring constant \( k_0 \), described by the following equations…

\[
f_0 = \sqrt{\frac{k_0}{m}} \quad \rightarrow \quad f_{\text{eff}} = \sqrt{\frac{k_{\text{eff}}}{m}}
\]

As the tip-sample distance decreases, the van der Waals force changes the amplitude and phase of the cantilever’s resonance, resulting in a new effective resonant frequency \( f_{\text{eff}} \) and effective spring constant \( k_{\text{eff}} \). As the tip-sample distance decreases, \( k_{\text{eff}} \) decreases and \( f_{\text{eff}} \) becomes smaller than \( f_0 \). Changes in the amplitude reflect changes in tip-sample distance. By measuring these changes in amplitude at the resonant frequency of the cantilever, the NC-AFM feedback loop compensates for the changes in tip-sample distance by controlling the Z-scanner movement. So, by maintaining constant amplitude and tip-sample distance, the NC-AFM mode can measure surface topography.

### 2.5 Kelvin Probe Force Microscopy (KPFM):

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Figure 2.8: Kelvin probe force microscopy (KPFM) mode operation for Park System XE-70 Scanning Probe Microscope.

The XE-70 SPM also has enhanced electro static force microscopy (e-EMF) modes with the scanning KPFM mode being the most utilized. In e-EMF, an external lock-in amplifier is connected with the XE-70 to apply an AC bias of frequency $w$, in addition to an applied DC bias, to the tip. The external lock-in also serves to separate the frequency component from the output signal. Figure 2.8 shows a schematic representation of KPFM mode for the Park Systems XE-70 SPM. In KPFM, the DC bias is controlled by feedback loop to zero the $w$ term in the applied bias. A force between the
tip-sample is generated when the tip and sample come into electrical contact. As shown in Figure 2.9, when a metallic tip comes into electrical contact with a semiconductor surface, their Fermi levels align producing a shift in the semiconductor vacuum level, which results in a force proportional to this change known as the contact potential difference (CPD).

Figure 2.9: (a) As the tip-sample distance decreases the two come into electrical contact. (b) After reaching electrical contact the two Fermi levels align resulting in a shift of vacuum level and resulting in $V_{\text{CPD}}$. (c) Lock-in amplifier applies DC bias to nullify $V_{\text{CBD}}$.

The DC bias that zeros the force is a measure of the surface potential. The difference is in the way the signal from the lock-in amplifier is processed. The signal from the lock-in may be expressed by the following equation…
\[ 2 \times \frac{C}{d} \times (V_{DC} - V_S) \times V_{AC} \sin \omega t \]

where \( V_{DC} \) is the DC bias, \( V_S \) is the surface potential, \( V_{AC} \) is the applied AC bias, \( C \) is the capacitance of the tip-sample system, and \( d \) is the tip sample distance. The \( w \) signal itself can be used to measure the surface potential. The amplitude of the \( w \) signal is zero when \( V_{DC} = V_S \) or when the DC offset matches the surface potential of the sample. A feedback loop can vary the DC offset bias such that the output of the lock-in amplifier that measures the \( w \) signal is zero. This becomes the measure of surface potential and an image can then be created from the variation in the DC offset bias.

### 2.6 Surface Photovoltage Spectroscopy (SPS)

Surface photovoltage spectroscopy (SPS) involves measuring the potential of a semiconductor surface as a function of incident photon energy. SPS features reveal the presence of filled and/or unfilled states within the semiconductor band gap. Similar to KPFM, SPS measures the changes in CPD at the surface. However, the SPS technique involves shining monochromatic light on a surface to generate photoinduced population or depopulation of charge states within the band gap. The population or depopulation of charge states at the surface produces band bending within the surface space charge region of the semiconductor, resulting in changes of the CPD that are then measured with KPFM.\(^{41}\)
Figure 2.10: (a) Contact potential difference (CPD) as a function of incident photon energy $h\nu$ for an $n$-type semiconductor. (b) Photoinduced depopulation ($E_1$) from trap state ($E_T$) to the conduction band (CB), resulting in an increase in CPD and corresponding positive change in slope denoting an $n$-type transition. (c) Photoinduced population ($E_2$) of trap state ($E_T$) from the valance band (VB), resulting in an decrease in CPD and corresponding negative change in slope denoting an $p$-type transition. (d) Photoinduced band gap transition where an electron is promoted from VB to CB producing an increase in CPD and corresponding increase in slope.
By using the KPFM functionality of our XE-70 SPM we are able to measure surface states with nanometer scale lateral resolution. The system configuration consists of an optical fiber that directs monochromatized light between the tip and the surface. By focusing monochromatic light at the KPFM tip we are able to obtain nano-SPS spectra from surface areas localized to less than a few tens of nanometers laterally and within the outer ~15 nm of the surface. The fiber optic core produces a ~5 mm spot size under the tip. Figure 2.10 shows the possible transition due to photinduced population and depopulation and their corresponding affect on the surface photovoltage spectra for an $n$-type semiconductor, such as ZnO. As shown in Figure 2.10 (a), measurements of the CPD between the surface and tip as a function of incident photon energy $h\nu$ produces the surface photovoltage spectra. For an $n$-type semiconductor, a positive slope in SPS corresponds to either photoinduced band to band (Figure 2.10 (d)) transitions or depopulation of trap states ($E_T$) towards $E_C$ (Figure 2.10 (b)). Alternatively, a negative slope in SPS corresponds to photoinduced population of trap states ($E_T$) from $V_B$ (Figure 2.10 (c)). In practice only the onset of these transitions are well defined, as indicated by the arrows in Figure 2.10. With this technique we are able to characterize the distribution of electrically active defects lateral across a surface with nm scale resolution as well as assign an energy position and type ($n$- or $p$-) to each defect. This technique can be extended further to perform time-dependant SPS (tSPS) measurements in which the slope of the change in CPD can be used to determine the density of surface states.
2.7 X-ray Photoemission Spectroscopy (XPS):

X-ray photoemission spectroscopy (XPS) is a highly surface sensitive technique used to characterize the atomic composition of a material, chemical states of constituent atoms, as well as the surface electronic structure. XPS works, in principle, by utilizing the photoelectric effect. As shows schematically in Figure 2.11, a photon of energy $h\nu$ penetrates the surface of a material and is absorbed by an electron with binding energy $E_B$.

Figure 2.11: Schematic view of photo ionized electron $E_1$.\textsuperscript{49}
This electron is emitted into the vacuum with a kinetic energy characteristic of either
the core levels or valance band states within the material. The kinetic energy can be
determined by the following expression...

\[ E_{\text{kin}} = h\nu - E_B - (E_{\text{vac}} - E_{\text{Fermi}}) \]

where \( E_B \) is the characteristic binding energy of the photoelectron, \( E_{\text{vac}} \) is the vacuum
level of the semiconductor, and \( E_{\text{Fermi}} \) is the Fermi level of the electron spectrometer. The
Fermi level of the system is determined to be the point where the electron emission is
zero and is independent of material. The work-function used to determine the binding
energies of emitted electrons is the work function of the system itself. As such, the Fermi
level of the system will appear as a constant kinetic energy across photoemission
spectra.\(^{43}\) The Fermi level of the analyzer can be determined experimentally by taking the
80%/20% midpoint of a linear extrapolation of the valance band spectrum of a well-
defined metal such as Au.

A typical XPS energy distribution curve (EDC) for ZnO is shown in Figure 2.13. The EDC is obtained experimentally by collecting the photoemitted electrons and
analyzing their energies at a fixed \( h\nu \) with fixed electron monochromator resolution. The
EDC measured experimentally are directly proportional to the rate of photoexcitation and
therefore the density of states (DOS). So, the EDC represents a photoexcited replica of
the density of occupied states distributed below the vacuum level. Figure 2.13 shows
lines with binding energy characteristic of the major core level electrons associated with
Zn (Zn2s, Zn2p1, Zn2p3, Zn3s, Zn3p, Zn3d) and O (O1s, O2s) atoms. In addition to core electron and valence band DOS, characteristic Auger electrons are also visible. Note that secondary electrons which have undergone scattering processes on their way towards vacuum are detected at lower binding energies and form the continuous background that can also be seen in the figure.

Figure 2.12: Typical survey spectra for clean ZnO.

While X-rays can penetrate deep into a sample surface, photoelectrons can only travel a short distance before their energy is modified due to scattering. Only electrons that escape at their original energy contribute to the XPS photoemission curve. As a result, XPS is a very surface sensitive technique with an average depth of analysis of ~50
Å. Figure 2.13 shows the work of Seah and Dench\textsuperscript{44}, where they have determined the electron scattering lengths in a solid. From this curve it can be seen that electrons only from the first few nanometers of the surface escape elastically.

Figure 2.13: Electron scattering lengths in a solid. From this curve it can be seen that electrons only from the first few nanometers of the surface escape elastically.\textsuperscript{49}

The MBE Oxide Laboratory in the physics department at The Ohio State University houses the PHI 5000 VersaProbe XPS system. The system is enclosed in a true UHV analytical chamber to prevent sample contamination and provide unambiguous
elemental and chemical analysis of surfaces. An electron beam is scanned upon an Al anode for monochromatic X-ray generation with energy 1486.6 eV (Al K\(_{\alpha}\)). The energy resolution of the electron analyzer is ~ 0.046 eV as determined using the width of the 80/20% of the Fermi edge in the valance band emission of Au.

2.8 Ultra-violet Photoemission Spectroscopy (UPS):

While XPS is highly capable of measure the valance band states of a material, the large linewidths (830 meV for Al K\(_{\alpha}\) X-rays) of higher photon energy sources limit the energy resolution of the technique. Such line widths produce corresponding broadening of spectral features so that the electronic structure or chemical shifts of >1 V are difficult to resolve. Ultraviolet photoemission spectroscopy (UPS) uses rare gas discharge lamps to produce photons energies of 20 - 40 eV. He gas is commonly used to generate photons at 21.2 eV (HeI) and 40.8 eV (HeII) to probe valance and shallow core levels with surface sensitivity. There are advantages of UPS as compared to XPS for measuring valence band states. Foremost, the energy resolution of UPS is higher than that of XPS due to the narrower line widths (3 and17 meV for HeI and HeII) of rare gas discharge lines. Even more, UPS can measure the valence band position, Fermi level position, the work function, and changes in width of EDC (\(\Delta\text{EDC}\)) due to surface dipoles all with very high surface sensitivity and energy resolution.

The width of EDC (\(\Delta\text{EDC}\)), or the difference between the highest and lowest photoelectron energies, equals \(h\nu-E_V\) since electrons with the highest valance band energy are excited to the highest kinetic energy. Since \(E_V\) is defined relative to the
vacuum level and is equal to the electron affinity ($\chi$) plus the band gap ($E_G$), $\Delta E_{DC}$ yields the electron affinity $\chi$ and work function (ionization potential) $\Phi_W$. By biasing the sample at a small negative bias (-9 V), the energy levels of the sample will be lifted by the biasing voltage, as compared to the electron analyzer. A change in the sample work function will then show as a change in the secondary electron cut-off of the photoemission spectra. The work function of a sample may then be determined by the following expression…

$$\Phi_W = h\nu - (E_{\text{cut-off}} - E_{\text{Fermi}})$$

where $h\nu$ is the incident photon energy, $E_{\text{cut-off}}$ is the binding energy of the secondary electron cut-off of the photoemission spectrum, and $E_{\text{Fermi}}$ is the Fermi level of the electron spectrometer.

2.9 Remote Plasma Processing:

A plasma is a collection of freely moving charged particles consisting of electrons, ions, neutral atoms, and radicals. The system of particles is on average electrically neutral, or “quasi-neutral”. Applications for plasma processing of semiconductors include various deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD)\textsuperscript{45} and film removal by plasma etching.\textsuperscript{46} Also, plasmas contain reactive species that impinge on the surface and react with complex organic molecules. For this reason, a primary function of plasma processing is to remove surface
contamination. Reactive species incident to sample surfaces include reactive neutral atoms and molecules, electrons, reactive ions, and photons in the IR, UV, and visible spectrum. The breakdown of organics and solids into gases such as CO, H₂O, CO₂, O₂, and H₂ create significant vapor pressures that can then be removed by vacuum pumps. Plasma processing is useful for cleaning, etching, and functionalizing the surfaces of semiconductors in order to increase device performance and stability.

Semiconductor processing applications are generally concerned with low pressure (< 1 Torr) plasmas. The requirements for semiconductor processing plasmas include high densities of ions, electrons and radicals, excellent uniformity over chamber distances, as well as low and controllable ion energies. Plasmas can be created by AC and DC sources either with capacitive or inductive methods. Traditional inductive geometries include cylindrical coil and planar coil geometries. For inductively coupled plasma (ICP) sources, the plasma chamber is surrounded by a coil. An rf power supply generates rf currents through the coil. The rf currents in the coil generate an rf magnetic flux, which penetrates the plasma region of the chamber. The time-varying magnetic flux (B) follows Faraday’s law,

\[ \nabla \times E = -\frac{\partial B}{\partial t} \]

inducing a solenoidal rf electric field (E) that accelerates the free electrons and sustains the plasma discharge. Inductive sources have many advantages over other types of high-
density sources, including the simplicity of concept, simple design, exclusion of DC magnetic fields, and rf rather than microwave source power.\textsuperscript{48}  

ICPs can be classified into local thermodynamic equilibrium (LTE) and non-LTE plasmas. The sorting is typically related to the pressure of the plasma. For example, high gas pressures imply many collisions in the plasma leading to an efficient energy exchange between the plasma species, resulting in uniform temperatures. Conversely, low gas pressures imply few collisions in the plasma leading to a non-uniform distribution of temperatures within the plasma. Non-LTE plasmas are typically used for applications where heat is not needed. For non-LTE plasmas the heavy particle temperature is low, but the temperatures of electrons are much higher because they are more easily accelerated by the applied field. The high electron temperatures produce many inelastic electron collisions which serve to sustain the plasma and result in a chemically-rich environment. For this reason, the electrons are considered to be the active component of the plasma, rather than the ions. Therefore, it is the electrons that are responsible for the mechanism that allows plasmas to etch, clean, and functionalize surfaces. For semiconducting processing applications it is important to understand the thermal limits of a sample or device as it may be necessary to eliminate high energy electrons and ions to reduce damage. One way to limit high energy electron and ion-induced damage is to process samples and devices away from the plasma discharge region. This technique is often referred to as “indirect” or “remote” plasma processing.

Remote plasmas were developed to limit sample exposure to regions of intense fields, excessively energetic plasma species, and high temperatures. The indirect region
of the plasma is where electron-ion recombination occurs, but where non-equilibrium of recombination outweighs generation. In this region, ion velocities are reduced limiting the extent of surface damage and allowing processing to be done near room temperature. The gentle nature of remote inductively coupled plasma (RICP) lends itself to many practical applications, such as the removal of oxides and surface contaminants without significant morphological changes.

Figure 2.14: RICP configuration consisting of a fused silica feed gas tube wrapped with a copper coil. The chamber can be evacuated to a base pressure of < 1 x 10⁻⁸ Torr using a 150 liter/s turbomolecular pump. A pneumatic butterfly valve separates the main chamber from the turbomolecular pump. It is adjusted to restrict vacuum pumping in order to reach the pressure of ~ 10 mTorr needed to maintain stable RICP
Figure 2.14 shows the typical configuration of a RICP system in the Oxide MBE Laboratory at The Ohio State University. The design is based on those originally proposed by Lucovsky et al.\textsuperscript{45} The system consists of a fused silica feed gas tube wrapped with a copper coil (cylindrical coil). The copper coil connects to an rf power supply through a match network. The chamber can be evacuated to a base pressure of $< 1 \times 10^{-8}$ Torr using a 150 liter/s turbomolecular pump. A pneumatic butterfly valve separates the main chamber from the turbomolecular pump. It is adjusted to restrict vacuum pumping in order to reach a pressure of $\sim 10$ mTorr needed to maintain stable RICP. The sample stage is located $\sim 20$ cm downstream from the plasma-generating coil. The stage itself is integrated with the transfer rod to assist with sample positioning.

Previous work has shown the value of RICP processing of ZnO semiconductor. The work by Strzhemechny et al.\textsuperscript{49,50} demonstrated that remote hydrogen plasma treatment is an effective tool for controlling transport and optoelectronic properties in ZnO by introducing shallow donors and hydrogen-related impurities. In addition, the work by Mosbacker et al.\textsuperscript{52} shows how integral remote oxygen plasma (ROP) cleaning of surfaces to remove contamination layers is in preparing functional surfaces for ohmic and Schottky contacts. Their work showed that extended ($> 1$ hr) room temperature ROP plasma treatments consistently transforms ohmic Au contacts to rectifying contacts on ZnO. They attribute this ohmic-to-Schottky conversion to the removal of OH-induced accumulation. Their work further showed that extended ROP treatments decreases $V_O$-R “green-band” emission by up to 50%, suggesting passivation or removal, resulting in a
decreased depletion width limiting tunneling and hopping transport in Au contacts. A more detailed introduction to basic Schottky barrier formation will follow in subsequent chapters.
CHAPTER 3    SCHOTTKY AND OHMIC CONTACTS:

3.1 Introduction:

Schottky contacts play an integral role in modern electronic devices. Transparent thin film transistors, light emitting diodes and lasers, photodetectors, high electron mobility transistors, electronic nanostructures, and spintronic devices all require metal contacts. A Schottky diode is a simple rectifying device that exploits the potential barrier formed at some metal/semiconductor junctions. This “simple” device has many advantages over a $p$-$n$ junction, including lower junction voltage and decreased depletion width in the metal. They are also advantageous because majority carriers control the diode operation, simplifying the fabrication process. Owing to their majority carrier operation, Schottky diodes do not rely on minority carrier diffusion and recombination. Therefore, they can achieve greater switching speeds than $p$-$n$ junction diodes making them ideal for power converters and RF detectors. Schottky diodes are best for applications where ideal diodes are desired. An ohmic contact is a non-rectifying metal/semiconductor junction. Low resistance, stable ohmic contacts are critical for performance and reliability of many electronic devices. Both ohmic and Schottky barrier formation depends on a number of material properties, including the metal and semiconductor work functions, the band gap of the semiconductor, semiconductor carrier densities, and surface chemical composition. Hence, it is crucial to understand of how
electronic properties depend on surfaces and metal/semiconductor interfaces and the processes involved during contact formation.
3.2 Introduction to Schottky Theory:

Figure 3.1: Basic model for barrier formation between a metal and an n-type semiconductor where $\Phi_M > \Phi_{SC}$ (a) before electrical contact and (b) following alignment of Fermi levels.
A Schottky diode is a metal-semiconductor contact that shows rectifying electrical behavior. Observations of rectification at semiconductor interfaces was reported as far back as the 1870’s. Schottky barrier studies of metals on ZnO surfaces originated in the mid-1960’s in large part as an effort to understand the relationship between surface states and Fermi level position. Figure 3.1 illustrates the basic model for barrier formation between a metal and an n-type semiconductor where the metal work function is greater than the work function of the semiconductor ($\Phi_M > \Phi_{SC}$). As shown in Figure 3.1 (a), before contact, the energy bands of the metal and semiconductor show different Fermi level positions. Following contact of a high work function metal to an n-type semiconductor, electrons flow from the semiconductor to the metal, depleting the surface of electrons. After sufficient charge transfer, the two Fermi levels $E^M_F$ and $E^{SC}_F$ are aligned as shown in Figure 3.1 (b). The alignment forms a surface space charge layer with a voltage drop $qV_B$, equal to the contact potential difference between the metal and semiconductor bulk region. The width of the depletion region layer ($w$) is given by the following expression…

$$w = \left(\frac{\varepsilon_S (V - V_0)}{2\pi N_q}\right)^{1/2}$$

where $\varepsilon_S$ is the static dielectric constant of the semiconductor, $N_q$ is the bulk concentration of ionized impurities within the surface space charge region, and $(V-V_0)$ represents the change in contact potential of the semiconductor surface. This relationship
represents the parabolic band bending region at the metal/semiconductor junction. In the ideal case depicted here, the barrier height depends on the difference between the metal and semiconductor work functions…

\[ \Phi_{SB} = \Phi_M - \Phi_{SC} \]

Unfortunately, the ideal description presented above fails to describe the behavior at most metal/semiconductor junctions. In fact, in many cases the barrier height shows only a weak dependence on the metal work function.

Bardeen was among the first to interpret the failure of this simple equation. In 1947, Bardeen\textsuperscript{51} proposed that localized surface states could accumulate at the metal/semiconductor interface. Such an accumulation layer could effectively modify the contact potential difference between the metal and semiconductor, altering the predicted barrier height dramatically. As shown in Figure 3.2 (a), for an \emph{n}-type semiconductor, the presence of acceptor like surface states produces an upward band bending at the semiconductor-vacuum interface, as the Fermi level moves towards the energy level of the surface state (\(E_{SS}\)). If the density of surface states is high enough, the Fermi level remains “pinned” at \(E_{SS}\) and will not move as a result of metal contact, as seen in Figure 3.2 (b). Here, charge transfers to the metal primarily from a dipole region generated by the high density of surface states and \emph{not} from the surface space charge layer of the semiconductor. Hence, the barrier height instead may be modeled as…
\[ \Phi_{SB} = qV_B + E_C - E_F = \Phi_M - \chi_{SC} - \Delta \chi \]

where \( \Delta \chi \) depends on the surface state energy position (\( E_{SS} \)) within the semiconductor band gap. This results in a barrier height that is weakly dependant on the metal work function.\(^{41}\)
Figure 3.2: Barrier formation between a metal and an n-type semiconductor with surface state induced band bending (a) before contact. Following contact, interface traps pin $E_F$, resulting in an interface dipole.
3.3 Role of Surface and Interface Quality:

Adsorbed layers of contaminants can have a significant effect on the density of surface states. In ZnO, hydrogen and carbon adsorbates have been shown to produce high surface state charge densities that have significant effects on the Fermi level position and subsequent metal/ZnO contacts. In fact, gas adsorption is analogous to barrier formation since it involves charge transfer at the semiconductor interface that alters the carrier density in the surface space charge region. For example, when oxygen adsorbs onto ZnO surfaces, electron charges transfer from the ZnO to the O atoms. This results in a negatively charged surface and positively charged donors within the surface space charge region that produce an $n$-type upward band bending at the surface. These effects create a depleted surface and surface barrier ($qV_B$). Conversely, when hydrogen adsorbs onto ZnO surfaces, electrons transfer from the hydrogen to the ZnO. This results in positively charged surface and negatively charged acceptors within the surface space charge region that produce a $p$-type downward band bending at the surface. These effects move the conduction band edge below $E_F$, inducing an accumulation of electrons at the surface. The sensitivity of ZnO to surface oxygen and hydrogen emphasizes the role of adsorbates in Schottky barrier formation.

Remote Oxygen Plasma (ROP):

The control and removal of surface adsorbates in order to produce high quality, ordered interfaces, is vital for any semiconductor device system. While annealing at high
temperatures (600 – 700 °C) in pure oxygen has been shown to remove all surface adsorbates, it also results in a thermal decomposition of the ZnO surface. Fortunately, remote oxygen plasma (ROP) treatments, consisting of 20% O₂ with 80% He, have been shown to remove surface adsorbates with minimal surface damage. As mentioned in the previous section, hydrogen can adsorb onto ZnO surfaces giving up electrons that create states and increase carrier concentrations in the space charge region through the following process…

\[ \text{H} + \text{O}^{2-} \rightarrow \text{OH}^- + e^- \]

Such an accumulation layer would serve to increase the tunneling through barriers in rectifying contacts. Ultraviolet photoemission spectroscopy (UPS) experiments by Coppa et al.³ show the effects of such a degenerate layer. Figure 3.3 (a) shows a band-diagram representations derived from UPS spectra of Zn-polar (0001) ZnO surfaces at various stages of remote oxygen plasma (ROP) treatment at 525 °C. Figure 3.3 (a) shows surface band bending due to OH induced accumulation where the \( E_F \) sits well above the conduction band minimum. Subsequent (ROP) processing (b) and further ROP processing (c) removes OH, depleting the surface of donors, causing upward band bending at the very near surface.
Figure 3.3: UPS of Zn-polar ZnO surfaces at various stages of treatment. (a) as-received, (b) moderate treatment with 20-W 20% O/80% He remote plasma, (c) extensive remote plasma processing.\(^{57}\)

The work by Mosbacker \textit{et al.}\(^{52}\) further highlights the importance of surface preparation in fabrication rectifying contacts on ZnO surfaces. XPS measurements show that extended (1 hr. or longer) room-temperature surface treatments of ZnO with 20% O/80% He remote plasma completely removes surface hydrocarbon and nearly all OH.
AFM topography scans of ROP treated ZnO surfaces showed no significant surface damage due to ROP. Yet, extended ROP treatment consistently transforms ohmic Au contacts to ZnO into rectifying barriers with heights ranging from 0.5-0.6 eV. They concluded that Au-ZnO ohmic contacts result not only from OH-induced surface accumulation but also tunneling due to increased donor concentrations in the surface space charge region. Removal of OH eliminates this accumulation layer and lowers the Fermi level back into the ZnO band gap.

3.4 Schottky Barrier Measurement Techniques:

There are 3 basic mechanisms through which current can flow through a metal-semiconductor interface: 1) thermionic emission, 2) recombination or generation, and 3) field emission (tunneling). Thermionic emission over the barrier is the dominant mechanism in an ideal Schottky diode. Here, the electron current is created from diffusion, drift, and emission over the barrier. The most straightforward method for measuring contact rectification is by the current-voltage (I-V) technique. For thermionic emission the forward current at an applied voltage through a metal-semiconductor interface is given by…

\[ I = A^{\text{**}} T^2 \exp \left( -\frac{q \Phi_B}{k_B T} \right) \left[ \exp \left( -\frac{q V}{nk_B T} \right) - 1 \right] \]

where \( A^{\text{**}} \) is the Richardson’s constant, \( k_B \) is Boltzmann’s constant, \( T \) is temperature and \( \Phi_B \) is the barrier height of the semiconductor, \( V \) is the applied voltage and \( n \) is known as
the “ideality factor”. From this equation, the forward current density extrapolated logarithmically to zero applied forward bias has an intercept at…

\[ I_S = A^{*} T^2 \exp \left( -\frac{q \Phi_B}{k_B T} \right) \]

Therefore, the barrier height can be extrapolated from a plot of \( \ln I \) vs. applied voltage \( V \) as shown in Figure 3.4. The slope of the \( \ln I \) vs. \( V \) curve also gives the ideality factor \( n \) of the contact, which is defined by…

\[ n = \left( \frac{q}{k_B T} \right) \left( \frac{\partial V}{\partial (\ln I)} \right) \]

The “ideality factor” is a measure of how close a diode is to ideal \( (n=1) \), and therefore acts as a measure of diode quality. There are a number of physical mechanisms that can contribute to ideality factors \( n > 1 \) including intermediate dielectric layers, electron-hole recombination, and interface surface traps can also increase ideality factors.
The barrier height may also be affected by what is known as the image force lowering effect. Image force lowering occurs when a tunneling free electron enters the conduction band of the semiconductor. This induces a positive image charge on the metal surface that creates an attractive force between the image charge and the electron. The electron potential energy due to the image force will add to the electron potential energy
due to the depletion field resulting in a lowering of the barrier height by some $\Delta \Phi$, given by…

$$\Phi_{SB} = \Phi_{SB0} - \Delta \Phi = \Phi_{SB0} - \left( \frac{q^3 E}{4 \pi \varepsilon_S} \right)^{1/2} = \Phi_{SB0} - 2qE x_m$$

where…

$$x_m = \left( \frac{q}{16 \pi \varepsilon_S E} \right)^{1/2}$$

Here $E$ is an applied electric field due to the image force. The correction due to image force lowering is typically not large, but does affect the I-V characteristics away from zero bias.

When carrier densities are high, Fermi level positions can approach or surpass the conduction band edge. This can result in carrier emission through barriers by thermionic emission, field emission, or a combination of the two. In field emission, the carrier transmission occurs through tunneling through the barrier. Thermionic field emission occurs by transmission of thermally excited electrons that tunnel through the barrier. These transmission mechanisms manifest themselves by producing ideality factors much greater than unity and exhibit large reverse bias currents. The dominant transport method can be estimated by the following equations…
\[ E_{00} = \left( \frac{q^2 h}{4 \pi} \right) \left( \frac{N_D}{m^* \varepsilon_s} \right)^{1/2} \]

where \( N_D \) is the carrier density, \( m^* \) is the effective mass of the semiconductor, \( \varepsilon_s \) is the static dielectric constant of the semiconductor and \( h \) is Planck’s constant. When \( E_{00} \ll kT \), thermionic emission is dominant and if \( E_{00} \gg kT \) then field emission is dominant. When \( E_{00} \sim kT \), a combination of thermionic emission and field emission effectively characterizes the diode.\(^{53}\)

Other measurements such as capacitance-voltage (C-V) and internal photoemission (IPE) are capable of determining Schottky barrier heights. These methods, along with I-V measurement, each provide a different measure of Schottky barrier height. As such, each has their own advantages, disadvantages, and difficulties. For example, I-V is sensitive to tunneling and interface recombination and traps. C-V measurements are affected by deep level traps but less sensitive to tunneling. All three techniques are influenced by image force lowering of the barrier. Ultimately, it is best to use a complement of these techniques to accurately characterize Schottky barrier heights.

### 3.5 Metal Induced Gap States (MIGS):

While surface adsorbates and surface states can have a profound impact of Schottky barrier formation, somewhat surprisingly so can the metals themselves. Some metals form interfacial layers with semiconductors. On ZnO, for example, metals such as Ag, Pd, Ta, and Pt form oxides at the metal/ZnO interface. Often the oxygen is leached from the underlying ZnO, leaving behind oxygen vacancy related native defects. This
behavior was observed directly by Brillson et al. who found metal induced deep levels within the first few tens of nanometers beneath 30 nm Al, Ta, and Pd diodes on O-polar ZnO. As shown in Figure 3.5, DRCLS results indicate an increase in 2.5 eV, $V_{O}$-R emission for Al, Ta, as well as an increase in 2.1 eV, $V_{Zn}$-R emission for Pd diodes. Oxygen is also capable of diffusing through some metals, reaching the interface that way. In these cases, the ZnO contact is with a dielectric and not the metal. Likewise, as shown in Figure 3.6, Au diodes on ZnO have been shown to form a eutectic with Zn after annealing at high temperatures (650 °C). Similar to the described oxide formation mechanism, the Au/Zn eutectic forms by pulling Zn from the underlying lattice leaving behind zinc vacancy related native defects. Hence, one must consider the role of subsurface defects and metals reactions when fabricating ZnO Schottky barriers.
Figure 3.5: Room temperature deposition of 30 nm Au, Al, Pd, and Ta on ROP cleaned ZnO O-polar surfaces showing Al, Ta, and Pd metal induced deep levels.
Figure 3.6: DRCLS of 30 nm of Au on high defects O-polar ZnO. Intense 2.1, 2.5, and 3.0 eV emissions are dominated by 2.1 eV emission after 650 °C anneal.
CHAPTER 4  POLARITY-RELATED ASYMMETRY AT ZnO SURFACES AND METAL INTERFACES

4.1 Background and Previous Work:

As one of the most important candidates for next generation semiconductor devices, ZnO has been studied extensively in recent years. Although metal/ZnO interfaces are essential to all ZnO electronic device applications, it still remains a challenge to fabricate high quality and thermally stable ZnO contacts. Their electronic properties have only recently been explored in detail. The famous Schottky-Mott theory is seldom obeyed by metals on ZnO, i.e., their Schottky barrier heights are not proportional to their work functions. Our previous studies revealed the importance of surface and near surface effects, including surface adsorbates, near-interface native defects, interface chemical bonding, and thermally-induced interface chemical interactions at metal/ZnO contacts. Now, we are correlating polarity-related surface and near surface defects and chemical reactions with electronic properties. Surface polarity plays important role in wurtzite semiconductor devices. Significant polarity-related effects have been found in GaN-based devices. Likewise, homoepitaxial ZnO layers grown on polar surfaces have very different optical properties and impurity levels. The stabilization mechanisms of Zn(0001)- or O(000 1)-terminated faces have been a source of controversy for quite some time. Differences
between hydrothermal ZnO polar surfaces were ascribed to surface band bending induced by spontaneous polarization,\textsuperscript{68} while melt-grown ZnO exhibits only a small difference in band bending.\textsuperscript{69} However, it is still not clear which polar face should give better Schottky contacts because few comparisons between two polarities exist regarding their surface optical properties, defect concentrations, metal reactivities with various metal contacts, and Schottky barrier heights.

In this study, we probed the polarity- and metal- dependent properties of (0001) Zn- and (000\,\overline{1}) O-polar surfaces of single crystalline ZnO with very low bulk defect grown by vapor phase process and their metal contacts by using nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS) coupled with surface science and electronic transport techniques.

\textbf{4.2 Experimental Details:}

Vapor-phase grown single crystal ZnO samples from ZN Technology Inc. and polished chemomechanically on both the (0001) and (000\,\overline{1}) faces had mid-$10^{16}$ cm\textsuperscript{-3} carrier concentration and 220 cm\textsuperscript{2}/V-s Hall mobility at 300 K.\textsuperscript{70} All samples were ultrasonically cleaned in acetone, dimethysulfoxide, methanol, isopropyl alcohol, and deionized water for five minutes respectively, then nitrogen blow dried. These samples are referred as “as-received”. We used remote oxygen plasma (ROP) treatment to remove surface adsorbates and sub-surface impurities and defects such as oxygen vacancies.\textsuperscript{3,56} For the plasma cleaned samples, both Zn- and O-faces from separate halves of the same “as-received” ZnO crystal were ROP processed for 1-2 hours. Subsequent
atomic force microscopy (AFM) measurements show only negligible increase of surface roughness. In general, the Zn-face is smoother than O-face (RMS 0.2 nm vs. 0.4 nm) although both surfaces have very smooth surfaces. Both surfaces show no atomic step edges, grain boundaries, or polishing scratches, with and without ROP treatment. Arrays of metal diodes (Au, Pd and Ta, 0.4 mm diameter, 30 nm thick) were e-beam deposited in situ on two ROP-cleaned and “as-received” polar surfaces at mid-10^{-9} Torr pressures. We note the importance of in situ metal deposition on clean surfaces within the same plasma chamber. It has been recognized that ZnO surfaces are very reactive even under atmosphere. The surface adsorbates (primarily OH⁻) will form a surface conductive layer, degrade metal contacts and introduce SBD leakage. The UHV e-beam deposition was kept at a slow rate (~1 nm/min) to avoid possible metal-deposition-induced surface damage. Subsequently, we prepared Ohmic contacts on the entire backside of each ZnO piece using e-beam deposited (40nm/60nm/30nm) Ti/Ni/Au film. DRCLS, remote O₂/He plasma (ROP) processing and deep level transient spectroscopy (DLTS) are described elsewhere.³, ⁷¹

4.3 Results and Discussion:

Figures 4.1(a) and (b) show DRCL spectra for “as-received” and 2 h ROP-treated Zn- and O-faces respectively. Electron beam energies E₉ varied from 1 to 5 keV, corresponding to depths U₀ of peak electron-hole pair creation rates increasing from 10 to 100 nm, respectively. Although spectral features appear similar, the Zn face displays 4x higher band edge (NBE, at 3.45 eV) emission throughout the near-surface region. ROP
does not change the spectral features. Defect emission is always dominated by the 2.5-eV “green” emissions and no apparent new defect emission appears after 2 h ROP. Figure 4.2 shows relative defect intensity changes vs. depth. The CL intensities (I_D or I_NBE) were read from their maximum peak values. Defect intensities are normalized relative to NBE intensities. The general trend of I_D/I_NBE decrease from surface indicates more oxygen vacancy defects in the surface region. The 2.5-eV “green” defect (I_D) and 3.45-eV near band edge (I_NBE) emission intensity exhibit significant polarity-related differences. The O face has 2x higher defect intensity than the Zn face even after ROP cleaning. As-received surfaces show similar polarity effects. Figure 4.2 also shows that ROP cleaning effectively decreases the O-face I_D/I_NBE ratio, while changing the Zn-face ratio only slightly. We previously assigned the 2.5-eV peak to defects related to oxygen vacancies. The results indicate that the O-face has more oxygen vacancies than the Zn-face.
Figure 4.1: DRCL spectra for (a) as-received Zn- and O-face (b) ROP cleaned Zn- and O-face.
In cathodoluminescence measurements, we found a complex polarity- and metal-dependent luminescence evolution under low electron beam irradiation of our scanning electron microscope (SEM). Electron beams with 2 and 5 kV energy were applied to bare surfaces and metal diodes respectively, which give the same probing depth in ZnO (~24 nm). Figure 4.3 shows the time dependence of NBE emission for bare Zn- and O-face and their diodes. For Zn-face, the NBE intensity first increases slightly and then changes little after 50s exposure. However, the O-face behaves very different, with the NBE intensity decreasing sharply by a factor of 6 at the first 100s exposure. Similar polarity effects were found for hydrothermally-grown ZnO single crystal samples, where the decrease of NBE intensity was attributed to metastable bulk defect reactions. It is reasonable that O-face, with much more defects, shows the sharp decrease of NBE intensity. The time dependence of NBE intensity for metal diodes on two polar surfaces is more complicated. There are two important features: (i) For Au diode, the NBE intensity is stable on the Zn-face while on the O-face, it is stable only for ~60 s, decreasing exponentially thereafter; and (ii) For Pd diodes, the intensity increases on the Zn-face while it increases slightly and then exponentially decreases on the O-face. The mechanisms for the complicated electron-beam-irradiation-induced processes are related not only to the metastable near surface defects induced by e-beam but also to the metal/ZnO interface chemistry, which are still under investigation. Nevertheless, the different behavior of Zn- and O-face shows the polarity effects and serves as a signature for two polar surfaces. We note that the DRCL spectra in Figures 4.1 and 4.2 were
recorded by a CCD detector with 0.2 seconds e-beam exposure, where the mentioned time-dependence is negligible.

![Graph showing relative defect intensity changes vs. depth for (0001) Zn and (000) O faces.](image)

**Figure 4.2:** Relative defect intensity changes vs. depth for (0001) Zn and (000) O faces.

The higher $I_D$ of 2.5 eV defects in cathodoluminescence spectroscopy, previously associated with O vacancies,\textsuperscript{23,54} induces different transport behavior on the O- vs. Zn-face-metal diodes. All the metal diodes (Au, Pd and Ta) deposited on “as received” surfaces are Ohmic and there is an Ohmic to rectifying transition for Au and Pd diodes on ROP surfaces. However, electrical properties show both metal- and polarity-dependence.
First, resistivity of two Au Ohmic contacts on the Zn-face increases monotonically while that on O-face decreases slightly as temperature decreases from 300 K to 100 K, as shown in Figure 4.4. This indicates more near-surface defects at the O face than at the Zn face, consistent with the DRCLS results. Since gold contacts on as-received O-faces are Ohmic, decrease of resistance with decreasing temperature is due to the increase of mobility of bulk ZnO, assuming constant carrier concentration. The effects of vacuum activated layers, observed on high-resistive ZnO crystals,\textsuperscript{73, 74} may not play the dominant role here. However, gold contacts on Zn-face are not good Ohmic although the resistance is still low. Actually, the measured gold diodes can be viewed as two back-to-back poor Schottky diodes. Thus, we see the increase of resistance with decreasing temperature. In addition, subsequent ROP treatment \textit{through} the diodes changes only the Au diodes on the Zn face from Ohmic to rectifying, indicating different chemistry for oxygen plasma on the two polar surfaces.
Figure 4.3: CL time dependence of NBE emissions for Zn- and O-face and their metal diodes.
Figure 4.4: Temperature-dependent contact resistance for two gold diodes on the Zn- and O-face.
Figure 4.5: Typical I-V characteristics at 300K for Au and Pd SBDs on ROP treated Zn- and O-faces.

For Au and Pd Schottky barrier diodes (SBDs) on ROP-treated surfaces, typical I-V characteristics at 300K in Figure 4.5 show not only metal sensitivity but also a polarity dependence. In general, Au/Zn-face SBDs have 10x lower leakage current and higher rectification than Au/O-face SBDs. Pd SBDs always have larger currents than Au SBDs in the entire bias region, with Pd on the Zn face the highest. Assuming that thermionic emission (TE) dominates forward current, then for $V>3\ kT/q$, the current is

$$I = I_s \left\{ \exp \left[ \frac{q(V - IR_s)}{nkT} \right] - 1 \right\}, \text{ with } I_s = AA'T^2 \exp \left( -\frac{q\Phi_{SB}^W}{kT} \right)$$
the saturation current, \( R_S \) the series resistance, \( n \) the ideality factor, \( A \) the diode area \((1.25 \times 10^{-3} \text{ cm}^2)\), \( A^* \) the effective Richardson constant \((32 \text{ A cm}^{-2} \text{ K}^{-2})\), and \( \Phi_{SB}^{IV} \) the zero-biased SBH. Ideality factor \( n \) and effective barrier heights from a TE model are summarized in Table 4.1. Au SBDs have larger Schottky barrier height than Pd SBDs, notwithstanding the same work function values.\(^7\)\(^5\) Furthermore, the very different SBD behavior for the same metal, either Au or Pd, on the Zn- or O-face indicates strong polarity effects. Note that the TE model alone cannot account for the large reverse currents, especially for Pd SBDs, where defect-assisted tunneling and/or hopping may play a role. Therefore, the barrier height evaluated from I-V for Pd SBDs may not be as accurate as that for Au SBDs. The nonideal characteristic of Au and Pd diodes may also be attributed to the inhomogeneous Schottky barriers.\(^7\)\(^6\)\(^7\)\(^7\)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Schottky metal</th>
<th>Ideality ( n )</th>
<th>( \Phi_{SB}^{IV} ) (eV)</th>
<th>( \Phi_{SB}^{CV} ) (eV)</th>
<th>( N_D^*N_A ) (( \times 10^{17} \text{cm}^{-3} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001) Zn</td>
<td>Au</td>
<td>1.2</td>
<td>0.81</td>
<td>1.20</td>
<td>0.7~1.0</td>
</tr>
<tr>
<td>(0001) Zn</td>
<td>Pd</td>
<td>1.3</td>
<td>0.53</td>
<td>0.73</td>
<td>0.8~1.0</td>
</tr>
<tr>
<td>(000 ( \bar{T} )) O</td>
<td>Au</td>
<td>1.3</td>
<td>0.77</td>
<td>1.07</td>
<td>1.1</td>
</tr>
<tr>
<td>(000 ( \bar{T} )) O</td>
<td>Pd</td>
<td>1.2</td>
<td>0.61</td>
<td>0.68</td>
<td>1.1</td>
</tr>
</tbody>
</table>

We have carried out C\(^2\)-V measurements at 1 MHz, 100 KHz, and 10 KHz.
Figure 4.6 shows the room temperature $C^2$-V characteristics at 1 MHz for the same Au- and Pd-SBDs. The frequency-dependence is negligible. Due to the small series resistance ($Rs, \sim 50 \Omega$) for both Au and Pd SBDs, the criterion $Rs << (\alpha C)^{-1}$ for the accurate determination of depletion capacitance can be satisfied at all frequencies. $\Phi^{CV}_{SB}$ values were calculated from

$$\Phi^{CV}_{SB} = V_i + V_0 + kT/q \text{ with } Vi \text{ the intercept and } V_0 = \frac{kT}{q}\ln\left(\frac{N_c}{N_D}\right).$$

Note that $C^2$-V characteristics are linear only for O-face SBDs and they bend down for SBDs on the Zn-face when approaching zero bias, which indicates the carrier inhomogeneity for Zn-face with depth. Table 4.1 shows $\Phi^{CV}_{SB}$ values for the SBDs extracted by linear-fitting, which confirms the better rectifying behavior of Au than Pd SBDs. The evaluated $\Phi^{CV}_{SB}$ values are larger than $\Phi^{IV}_{SB}$, especially for Au diodes, indicating the lateral inhomogeneity. The associated carrier density profiles as shown in Figure 4.7 are strongly polarity- and metal- dependent. There are two important features: (i) net carrier concentrations ($N_d - N_a = N_{eff}$) are constant for both the Au and Pd SBDs on the O-face in the near surface region (90-170 nm), whereas they gradually decrease by about 30% in the same region for Au and Pd on the Zn-polar surface; and (ii) $N_d$ increases sharply for the Pd SBDs on both polar surfaces at the shallowest depths profiled by C-V. Similar decrease of surface carrier concentration was also found for Pt diodes on sulfide treated ZnO O faces and for Pd on hydrogen peroxide treated ZnO O faces. But
this is the first report of the polarity-dependence for ROP cleaned surfaces. Note that due to higher currents at zero bias on Pd/ZnO diodes, as compared to Au/ZnO diodes, larger conductance is involved in the capacitance measurement, which may contribute to the sharp increase of carrier concentration at near-surface region. Nevertheless, large conductance and sharp increase of $N_d$ indicate a surface conductive layer at Pd/ZnO interfaces.

Figure 4.6: Typical $1/C^2$-V curves at 300K for Au- and Pd-SBDs on ROP treated Zn- and O-faces.
The observed decrease of carrier concentration at the near surface region of Zn-face is closely related to oxygen plasma treatment, which further decreases towards the surface with increasing ROP time, while that at the O-face is independent of ROP time. The oxygen plasma is much more likely to react with the Zn-face than with the O-face. Because there is no obvious new defect CL emission other than the 2.5-eV emission (due to oxygen vacancy) after up to 2h ROP, the possibility of Zn vacancy formation (as deep acceptor) can be excluded, since Zn vacancy-related defects should have an emission
peak around 2.1 eV if present.\textsuperscript{23} Hydrogen removal from surface regions can also decrease the carrier profile by decreasing donor density or activating acceptor impurities. Conversely, a previous study found that remote hydrogen plasma treatment increased surface electron concentration in single crystal ZnO.\textsuperscript{50} Consistent with hydrogen removal, recent 4.2 K PL shows that ROP reduces the $I_4$ line at 3.368 eV assigned to hydrogen donor bound exciton on the Zn-face but much less on the O-face for the same samples.\textsuperscript{80} First principles calculations provide further evidence that it is much easier for hydrogen to diffuse out of the Zn face.\textsuperscript{81} However, there is no asymmetry for oxygen diffusion within ZnO.\textsuperscript{82} Therefore, we propose several points about the polarity-related ROP effects: (i) ROP cleans both surfaces by removing surface adsorbates; (ii) ROP effectively removes hydrogen from the Zn face and dissociates $V_O$-H complexes within the near surface region; (iii) ROP decreases $V_O$ density on the O face, which was shown by the decrease of CL defect emission, but have no effect on the carrier profile as $V_O$ is a deep level; and (iv) ROP can also decreases $V_O$ density on the Zn face, although the decrease in free carrier density is dominated by the dissociation of $V_O$-H complexes.

Thus, while ROP removes O vacancies and H from both surfaces, the higher O vacancy concentration and lower H removal rate at the O surface results in to higher near-surface carrier concentrations at the O face.

ZnO has strong spontaneous polarization along $<0001>$ direction, which can induce electron accumulation/depletion on the ideal O/Zn faces and make $n$-type SBDs easier to form on the Zn face.\textsuperscript{17,83} However, metal diodes on as-received Zn and O faces are ohmic which indicates electron accumulation on both surfaces due to surface
adsorbates. ROP can effectively remove surface adsorbates. But ideal Zn face is hard to stabilize in O-rich atmosphere.\(^{16}\) Therefore, we argue that spontaneous polarization is not the dominant role that decides the polarity effects found here.

With increasing ROP time from 1h to 2h, the SBDs’ rectification increases, regardless of the surface polarity. But the polarity dependence and metal sensitivity are still significant. Our DLTS reveals the evolution of defect traps with ROP time. E3 is the dominant trap for all SBDs. It is closely related to ROP, increasing with ROP exposure time on both surfaces but only shifting in energy on the Zn face. One surface trap Es was only found for Pd SBD on 1-hr ROP cleaned Zn-face, consistent with DRCL results.\(^{12}\) The detailed DLTS results will be reported elsewhere.\(^{30}\)

The surface conductive layer at Pd/ZnO interfaces is due to hydrogen diffusion. It is easy for hydrogen to penetrate the thin Pd film and accumulate at interfaces. Our PL data indicates that this accumulation is larger for the Zn-face. Figure 4.8 shows low temperature (80 K) PL spectra for ROP treated bare Zn-face, Pd and Au SBDs. Pd SBDs exhibit a much larger I\(_4\) peak increase, compared with Au SBDs. Pd SBDs exhibit a similar enhancement on the O-face but in smaller magnitude. Interface H\(^+\) acts as donors, forms negative interface dipole with its image charge on the metal side, and decreases Schottky barriers at Pd/ZnO interfaces. We calculated the interface Fermi level position as a function of H-related surface donor density, as shown in Figure 4.9. In Schottky limit, barrier height is given by the energy difference of metal work function (\(\Phi_M\)) and semiconductor electron affinity (\(EA\)), while in Bardeen limit the interface Fermi level is pinned close to the defect level. ZnO has an EA around 4.0~4.4 eV, depending on surface
properties. With a negative interface dipole $\Delta V$, the Schottky barrier height $\Phi_B$ is given by $\Phi_B = \Phi_M - E_A - |\Delta V|$. As shown by Figure 4.9, the Schottky barrier is reduced by ~0.4 eV with $10^{13}$ /cm$^2$ surface donor density.

Figure 4.8: 80 K PL for ZnO surfaces and Pd/Au SBDs.
Figure 4.9: Calculated interface Fermi level as a function of surface H+ donor density.
Figure 4.10: Carrier concentration profiles and calculated conduction band diagrams for Au and Pd SBDs on the Zn- and O-face.

To account for these metal- and polarity-dependent carrier concentration profiles, we propose a comprehensive model and describe the effective donor concentration $N_d^{\text{eff}}$ as...

$$N_d^{\text{eff}} = N_d^{\text{bulk}} + N_d^{\text{surf}} \exp \left( \frac{-Z}{d_1} \right) - N_a^{\text{surf}} \exp \left( \frac{-Z}{d_2} \right)$$

where $N_d^{\text{bulk}}$ is the bulk donor concentration, and $N_d^{\text{surf}}$ and $N_a^{\text{surf}}$ are surface donor and
acceptor densities decaying away from the surface with decay lengths $d_1$ and $d_2$, respectively. The sharp $N_d$ increase for Pd SBDs near the surface is due to hydrogen incorporation at the interface and it is consistent with the most leaky I-V characteristic for Pd SBDs on the Zn-face. The $N_d^{\text{surf}}$ term describes the sharp $N_d^{\text{eff}}$ increase within the outer few nanometers, due to H and perhaps to impurity segregation from the bulk. An $N_a^{\text{surf}}$ surface acceptor term with $d_2 \sim 100$ nm accounts for the Zn-face $N_d^{\text{eff}}$ subsurface decrease, possibly due to the polarity-dependent H-removal. With reasonable values assigned to the terms in above equation and by solving Poisson’s equations, the carrier profile and associated conduction band diagram are shown in Figure 4.10. The rapidly increasing $N_d^{\text{eff}}$ near the Pd/ZnO (0001) and (000T) interfaces narrows the surface space charge region and forms an ultrathin surface barrier, which also represents the negative interface dipole $\Delta V$. Thus tunneling through a hydrogen-induced interface dipole decreases the effective Schottky barrier. In addition, introduction of $N_a^{\text{surf}}$ widens the SBDs’ depletion region on the Zn vs. O-face. The revised band bending is consistent with the Table I values of $\Phi_{SB}^{CV}$ and $\Phi_{SB}^{IV}$, and accounts for the metal- and polarity-dependences.

4.4 Conclusions:

The polarity-related asymmetry in ZnO $c$-plane polar surfaces and metal diodes has been studied by DRCLS and electrical measurements. Significant optical polarity-signatures have been found for the Zn- and O-face in CL, including higher oxygen
vacancy density and faster evolution with exposure time on the O face. Au and Pd diodes on as-received and O₂/He plasma-cleaned surfaces display not only a significant metal sensitivity but also a strong polarity dependence that correlates with defect emissions, traps, and interface chemistry.
5.1 Background and Previous Work:

ZnO has attracted extensive study due to its large band gap and exciton binding energy, which have the potential to enable numerous optoelectronic applications. Despite ZnO’s long history of research and thousands of publications, many fundamental issues remain unresolved. One key issue centers on the difficulty of doping ZnO p-type, which has been attributed to the compensation of acceptors by native defect donors. Oxygen vacancies, Zn interstitial-related complexes, impurities and hydrogen have all been suggested as the origin of native donors in ZnO, while Zn vacancies and complexes were considered as acceptors. In spite of the importance of native defects as important native donors and acceptors, many of the fundamental physical properties of native defects in ZnO are unknown. For example, it is still a challenge to correlate the red and green luminescence emissions with native defects.

Our previous studies on ZnO surfaces and metal/ZnO interfaces have revealed the important role of polarity, surface adsorbates, near surface native defects, and thermally induced interface chemical interactions on the electrical and optical properties of single crystal ZnO and related devices. The 2.5 eV green luminescence predominant in most ZnO luminescent spectra has been associated with oxygen vacancies. However,
the origin of this and other deep level emissions, the role of native defects, and their
correlation with optical and electrical properties are still subjects of controversy. For
example, the origin of the green luminescence is still a matter of debate and it has also
been attributed to either impurities or Zn vacancies.\(^7\) In particular, there are few studies
on the polarity dependence of such native defects and their correlation with ZnO physical
properties. Here we use depth-resolved cathodoluminescence spectroscopy (DRCLS),\(^{103}\)
current-voltage and capacitance-voltage measurements, atomic force microscopy (AFM),
secondary ion mass spectroscopy (SIMS) and deep level transient spectroscopy (DLTS)
to probe the physical properties of surface and near surface defects at (0001) Zn-and
(000-1) O-polar surfaces of remote oxygen plasma (ROP) cleaned ZnO.

5.2 Experimental Details:

The single crystal ZnO samples we used in this study were grown by a vapor-
phase process at ZN Technology Inc. and polished chemomechanically on both the
(0001) and (000-1) faces. They have mid-10\(^{16}\) cm\(^{-3}\) carrier concentration and 220
cm\(^2\)/V*s Hall mobility at 300 K. The 5 x 5 x 0.42 mm\(^3\) pieces were cut into halves,
chemically cleaned, treated with a remote oxygen plasma (ROP), and deposited with
metal in situ for Schottky contacts in the same plasma chamber under 1 x 10\(^{-9}\) Torr base
pressure. The detailed procedures are described elsewhere.\(^9\) The ex situ CL
measurements were performed at 10 K employing a JEOL 7800F scanning electron
microprobe equipped with a hemispherical electron analyzer and Oxford CLS optical
train. Current-voltage characteristics for the metal diodes was measured at room temperatures.

5.3 Results and Discussion:

Figure 5.1: CL spectra at 2 keV for as-received, 2 h, and 4h ROP cleaned Zn face. The inset shows the CL spectra for as-received and 4hr ROP cleaned O face. ROP generates 2.1 eV emission on the Zn face, increasing with ROP time.

Figure 5.1 shows 10 K CL spectra at 2 keV for as-received and ROP-cleaned Zn and O faces. The high quality single crystal ZnO samples exhibit dominant near band edge emission (NBE) from neutral donor-bound excitons and their longitudinal optical (LO)
photon replicas, along with a broad visible emission whose intensity was three orders of magnitude lower than the NBE peak. Both as-received Zn and O surfaces show a single 2.5 eV defect emission peak that dominates the spectra. However, with ROP treatment, the Zn face shows an additional 2.1 eV emission, whose intensity increases with ROP time. In contrast, ROP treatment generates no new emission on the O-face. Instead, it decreases the intrinsic 2.5 eV emission. The 2.5 eV emission is due to defects associated with O vacancies (V\textsubscript{O}),\textsuperscript{23} which can pin the surface Fermi level as well as degrade the quality of Schottky diodes.\textsuperscript{92} Therefore, ROP cleaning improves the rectifying behavior of Schottky diodes on O-face ZnO.

The time dependence of ROP effects on the Zn face is more complex. The 2.5 eV emission first slightly decreases, then slightly increases, while the newly generated 2.1 eV emission continues to increase. These differences do not appear related to surface morphology. AFM images show that room mean square (rms) surface roughness increases only slightly for both faces, from 0.4 to 0.6 nm for O face and from 0.2 to 0.5 nm for Zn face after 4 h ROP treatment.
Figure 5.2: CL spectra at 2 keV for Zn and O faces with 4 h ROP: generation of 2.1 eV defect emission only on the Zn face. The inset shows the depth distribution of relative defect density for the Zn face.

Figure 5.2 shows the comparison of CL spectra for 4 h ROP treated Zn and O faces, CL spectra were normalized to a constant NBE emission intensity. The O face has relatively strong LO phonon replicas. This is consistent with PL spectra for similar samples and suggests different local crystal environments near the two polar surfaces.\(^\text{93}\) The broad defect emission for Zn face spectra can be decomposed into two Gaussian peaks, at 2.1 and 2.5 eV respectively, while the O face contains only one Gaussian peak
at 2.5 eV. The inset in Figure 5.2 shows the relative defect intensity (defect emission divided by NBE intensity ratio) of 2.1 and 2.5 eV emissions on the Zn face as a function of incident electron beam energy $E_B$. The electron cascade and thereby the primary excitation depth on a nanometer scale increases with $E_B$. The intrinsic 2.5 eV emission has higher density in the surface region, which is consistent with our previous results, suggesting more $V_O$–related defects in the surface region. The ROP-generated 2.1 eV emission is found to be mainly localized in the surface and near surface region ($< 100$ nm).

Significant polarity-related electrical differences were found for Au diodes on the two polar surfaces cleaned by ROP. The Au diodes deposited on both as-received surfaces are strongly ohmic. With ROP through the diodes, those diodes on the Zn face that were originally Ohmic gradually become rectifying, while those on the O face change little. We refer to these “ROP-post” diodes as “Au I.” Au diodes deposited on surfaces first cleaned by ROP are referred to as “Au II.” The duration of ROP treatment varied from 1h to 4h. All the Au II diodes were rectifying. The degree of rectification for Au II diodes on the O face increased significantly with increasing ROP time. For Au II diodes on the Zn face, the reverse current decreases by a two orders magnitude from 1h to 2h ROP. However, increasing ROP treatment to 4h does not decrease reverse currents of these Au Schottky diodes further.
To correlate the optical emissions to electrical properties, we measured CL spectra for Au I and II diodes on the Zn- and O-faces as shown in Figure 5.3(a) and 5.3(b) respectively and compared them to capacitance-voltage (C-V) profiles of the same diodes. The inset shows the corresponding carrier profiles derived from C-V data. Since Au I diodes on the O face are Ohmic, C-V measurements were not possible. Of chief importance, CL revealed that only Au II diode on the Zn face displays the ROP-generated 2.1 eV emission. All the other three diodes, Au I on the Zn face, and both Au diodes on the O face, exhibit only the intrinsic 2.5 eV emission. Corresponding to the 2.1 eV
emission, the carrier profile for Au II on the Zn face decreases approaching the surface, which directly indicates the correlation of ROP-generated 2.1 eV emission with a compensating acceptor-type defect.

The surface defects generated by ROP on the Zn face are most likely Zn vacancies \( (V_{\text{Zn}}) \). Thermodynamically, Zn vacancies have the lowest and the only negative formation energy in bulk ZnO in an oxygen rich atmosphere, compared with other possible native defects such as oxygen interstitials.\(^{16,94}\) This is especially true with the Fermi level close to the conduction band and, in our case, \( E_{\text{C}}-E_{\text{F}} = 0.1 \) eV in bulk. In order to understand the differences in polarity and why the \( V_{\text{Zn}} \) is introduced only on the Zn face, the thermodynamic stability of ZnO polar surfaces in the oxygen plasma atmosphere must be considered. Although the stabilization mechanisms of ZnO polar surfaces are still controversial,\(^{67}\) it is well known that adsorbates cover the air-exposed ZnO surfaces, e.g., C, H, or OH groups, that induce an accumulation layer and increase its conductivity.\(^3\) ROP can effectively remove the surface conductive layer without causing noticeable surface deterioration.\(^{23,52,54,90}\) However, after ROP, the stabilized Zn-ZnO termination of Zn face and O-ZnO termination of O face should be quite different based on the arguments of thermodynamic stability for polar oxide surfaces over a large oxygen and hydrogen chemical potential.\(^{95}\) Thus for the Zn-ZnO termination, hydroxyl groups are removed and roughly 1/4 of the surface Zn ions are missing to stabilize the polar surface;\(^{96}\) while for the O-ZnO termination, the most stable surface structure is that with 1/2 monolayer H coverage.\(^{97}\) Our photoluminescence (PL) results support this scenario by showing a decreased H donor bound exciton peak \( (I_4 = 3.3628 \text{ eV}) \) only on
ROP cleaned Zn face. Considering the near-surface region, ROP generates $V_{\text{Zn}}$ on the Zn face while only depressing $V_{\text{O}}$-related defects on the O face.

Our most recent study on ion-implanted ZnO combining DRCLS and positron annihilation spectroscopy (PAS) demonstrate that 2.1 emission is related to $V_{\text{Zn}}$ or clusters. $V_{\text{Zn}}$ is a deep acceptor (1.6–2.1 eV below conduction band, depending on the degree of vacancy clustering) and acts as compensating centers in $n$-ZnO, while $V_{\text{O}}$-related defects act as deep donors and have no significant impact on the CV carrier profiles. Therefore, we observed the generation of 2.1 eV emission, accompanied by a decreased carrier profile on the Zn face, while the constant carrier profiles are independent of the 2.5 eV emission for both faces.
Figure 5.4: DLTS spectra for Au SBDs on Zn- and O-surfaces with 4 h ROP. The DLTS parameters, bias $U_R$, filling pulse height $U_P$, filling pulse width $t_P$, and transient period $T_W$ are shown.

Figure 5.4 shows representative deep level transient spectroscopy (DLTS) spectra for Au II diodes on 4 h ROP-cleaned polar surfaces. E3 is the dominant trap for both surfaces. However, a shift of E3 trap to higher temperatures ($E_3'$) was found on the Zn face with ROP-treatment. In addition, the trap density of E3 trap is much higher for the Zn vs. O face and increases with increasing ROP-treatment time on both faces. The E3
trap is commonly observed for most bulk and thin film ZnO. Earlier studies suggest its association with $V_O$. However, this is still under discussion. A shift of the E3 trap to higher temperatures has also been found for oxygen-annealed ZnO which was associated with oxygen incorporation. Since $V_{Zn}$ is too deep (2.1 eV below conduction band) to be detected by DLTS, E3 should not be directly associated with $V_{Zn}$ defects. However, whether or not the E3 is related to a di-vacancy, i.e., $V_O$-$V_{Zn}$, requires further study. By virtue of its near-midgap energy, $V_{Zn}$ defects can act as compensating acceptors and decrease near surface carrier concentration. The peak temperature shift of the E3 trap corresponding to an increased binding energy may be related to the electric field-related Poole–Frenkel effect. The carrier concentration in the near-surface region on the Zn-face decreases with increasing ROP duration. This decrease in carrier concentration can lead to a lower electric-field in the depletion region, resulting in a shift of E3 to higher temperatures.

Finally, the impurity asymmetry on the polar surfaces was evaluated by SIMS. While pronounced segregation differences were reported for annealed bulk ZnO wafers, we found only trace accumulation (below 10 ppm) of Al, In, and Ga on both as-received and ROP cleaned surfaces, and no significant difference in impurity level was observed between the two polar surfaces. While impurity diffusion was found to be affected by substrate surface polarity in ZnO homoepitaxial growth, impurities have no significant contributions to the observed polarity effects on ROP cleaned surfaces.
5.4 Conclusions:

In summary, ROP treatment generates Zn vacancies on the Zn face and decreases oxygen vacancies on the O face which results in significant optical and electrical polarity-dependence. The ROP-generated $V_{Zn}$ corresponds to a 2.1 eV deep level emission and may also be attributed to decreasing carrier profiles on ROP-treated Zn-face, which results in the shift of E3 trap to a higher temperature due to an electric field related Poole–Frenkel effect. Our findings demonstrate the importance of polar effects and oxygen plasma treatment on forming surface and near-surface defects that control the physical properties of ZnO.
6.1 Background and Previous Work:

Central to all the next generation device applications of ZnO is the understanding and control of ZnO surface and interface electronic properties, yet these have until recently remained largely unexplored. Previously, we showed that surface adsorbates, hydrogen donors, and subsurface native point defects each contribute independently to interface charge transport and Schottky barrier formation. Furthermore, metal deposition and subsequent annealing induce additional native point defects extending tens of nanometers or more below the free ZnO surface that increase tunneling, recombination and hopping transport. With DRCLS we can obtain information regarding the relative densities of these native point defects, their relative energies, and their spatial locations. In addition, KPFM lets us map the work function and in turn presents information about the composition and electronic state of the local structures on the surface of a solid.

DRCL spectra show a variety of features that can be correlated with interface electronic and chemical properties. Chief among these is the Near Band Edge (NBE) emission seen at ~3.37 eV, which is composed of a number of emission peaks due to free
exciton and donor or acceptor bound excitons. At low temperatures, these bound excitons dominate the emission. DRCLS spectra of ZnO also show broad defect emission peaks around 2.1 and 2.4 eV whose intensities can vary by orders of magnitude, depending on the crystal source, growth method, and subsequent processing. Theory predicts that the two most energetically-favorable native point defects in ZnO are oxygen and zinc vacancies. The physical defects responsible for the 2.4 and 2.1 eV defects are still under debate. However, ZnO growth under Zn-rich versus O-rich conditions strongly suggests that the 2.4 eV feature is due to O vacancies ($V_O$) while emissions at 2.1 eV is due to Zn vacancies ($V_{Zn}$).

6.2 Experimental Details:

We examined a collection of both melt and hydrothermally grown single crystal ZnO substrates. The surfaces were chemically polished by their respective manufacturers. A JEOL 7800F ultrahigh vacuum (UHV) scanning electron microscope (SEM) provided spatially localized excitation of bare ZnO. A parabolic mirror connected to a photomultiplier collected the luminescence. The samples were cooled on an Oxford stage using liquid He to a temperature of 10 K. An Oxford MonoCL monochromator was used to record the spectra with a maximum resolution of 0.15 nm. All spectra were taken at constant power and shown without normalization. For incident electron beam of $E_B = 2, 5, 10, and 20$ keV, Monte Carlo simulations of the electron cascade yield depths of peak electron-hole pair production of $U_0 \approx 55, 85, 330, and 990$ nm, respectively, below the free ZnO surface. The deep level features at mid-gap energies were fit using a Gaussian
multi-peak fitting program. DRCLS showed that the ZnO substrates varied in growth technique, deep level defect density, defect emission, and near band edge (NBE) emission intensity.

Figure 6.1: Schematic diagram of the enhanced EFM (KPFM) of the Park Systems XE-70 AFM/SPM

A Park System XE-70 AFM/SPM in KPFM mode, along with a Stanford SR830 lock in amplifier and an applied DC bias feedback loop, provided efficient one pass scans that measured both the topography and surface potential simultaneously [Figure 6.1]. To prevent noise contamination, the entire SPM system sits inside an acoustic enclosure with...
The microscope sitting upon a Herzan TS-150 desktop active vibration isolation table. The scans were carried out using a Park Systems mounted Cr – Au EFM (ext) probe consisting of a 20 nm gold film on a 20 nm chrome sub layer. The resulting curvature of radius of the tip is less than 50 nm. Before taking AFM and KPFM data, each substrate was subjected to a 5 min rinse in acetone, toluene, dimethyl sulfoxide, methanol, and de-ionized water in order to remove contaminatees from their surfaces. After cleaning, each ZnO substrate was attached to a steel disk using silver paste to aid in the conduction of the DC bias through the insulating substrates. All AFM and KPFM data was taken at atmosphere and at room temperatures. It is worth noting that when taking electrical data on a semiconductor substrate, static charge can build up, caused by the application of the DC bias and the constant motion of the cantilever near the surface. We limited the number of uninterrupted scans to minimize the degrading effects of static charge on the images.

6.3 Results and Discussion:

Figure 6.2 shows the DRCLS spectra (a), topography (b), and potential maps (c) for the melt-grown single crystal ZnO substrates C14 and C15. Both samples were manufactured by the same distributor. The DRCLS spectra for both samples show uniform defect and near band edge (NBE) emission ranging from the surface into the bulk. Both samples show some of the highest NBE surface and bulk peak intensities of the collection of substrates studied. Sample C14 shows low bulk and surface defect emission while C15 shows almost no measurable defect emission. C14 exhibits deep
levels at 2.1, 2.4, and 3.0 eV. The 2.1 eV peak can arguably be attributed to a \( V_{\text{Zn}} \) while the 2.4 eV peak can arguably be attributed to a \( V_{\text{O}} \).\textsuperscript{106, 107} Both the 2.1 and 2.4 eV emissions are typically seen in most ZnO crystals. Surface topography shows circular shaped pits, roughly 2-6 nm in depth, in both C14 and C15. Sample C14 has an overall rms surface roughness of \( \sim 0.591 \) nm while C15 has an overall rms roughness of \( \sim 0.148 \) nm. In both cases, the KPFM potential maps follow the surface topography.
Figure 6.2: (a) DRCLS spectra for melt-grown single crystal ZnO substrates Cermet 14 and 15 alongside their respective (b) AFM topography and (c) KPFM potential maps. Both samples show little to no defect emission. Large potential changes around the perimeter of the surface features may be related to surface asperities.
The remaining ZnO crystals in our collection were all hydrothermally grown by a variety of distributors. Figure 6.3 shows the DRCLS results (a), topography (b), and potential maps (c) for sample M15. The DRCLS spectra show some of the highest bulk and surface NBE intensities. However, the spectra also show some of the highest bulk and surface defect densities. M15 displays deep levels at 2.1 and 2.4 eV. The DRCLS spectra show that the surface defect densities decrease and then increase into the bulk. Beyond the near-surface region, there is a gradual increase in defect emission from surface to bulk, with the 2.4 eV peak increasing slightly into the bulk. Surface topography shows a large concentration of sharply defined hexagonal pits and an overall rms roughness of \( \sim 2.027 \) nm. The KPFM potential map follows topography and shows large potential changes on the edges of hexagonal pits which may be associated with native point defects at surface asperities.
Figure 6.3: (a) DRCLS spectra for hydrothermally grown single crystal ZnO substrate MTI 15 alongside its respective (b) AFM topography and (c) KPFM potential map. DRCLS spectra show some of the highest bulk and surface NBE intensities and deep levels at 2.1 and 2.4 eV. The dashed curves represent the Gaussian deconvolution. Its KPFM potential map shows large potential changes at its surface of up to hundreds of mV.
Figure 6.4 shows the DRCLS spectra (a), topography (b), and potential maps (c) for the hydrothermally grown single crystal ZnO substrate Denpa A. The sample has the highest NBE peak intensity of all the samples in our collection. It is one of the least uniform in terms of defect emission versus depth. It exhibits some of the lowest surface defect emission of all but that emission increases strongly into the bulk. In particular, we see a jump in defect emission from the surface (20-75 nm) into the bulk (220-370 nm) with deep levels at 2.1 and 2.4 eV and with the 2.4 eV peak increasing into the bulk. AFM topography scans show an overall rms roughness of ~ 5.434 nm, with large hexagonal pits that are roughly microns in diameter and up to 30 nm in depth. KPFM potential maps appear to differ from the topography with large potential changes found again near the edges of the hexagonal pits.
Figure 6.4: (a) DRCLS spectra, (b) AFM topography, and (c) KPFM potential map for hydrothermally grown single crystal ZnO substrate Denpa A. Spectra shows a jump in defect emission from the surface (20 – 75 nm) into the bulk (220 – 370 nm) with deep levels at 2.1 and 2.4 eV. The dashed curves represent the Gaussian deconvolution.
Figure 6.5 shows the DRCLS spectra (a), topography (b), and potential maps (c) for the hydrothermally grown single crystal ZnO substrate H2. H2 has approximately 100x lower bulk and surface NBE emission intensities compared with the rest of the samples in our collection. H2 has some of the highest bulk and surface defect densities with deep levels at 2.1 and 2.4 eV. Fig. 5 shows that H2 is one of the least uniform from surface to bulk with a large jump in defect emission from near-surface (~20 nm) into the bulk (370 nm). Topography shows an overall rms roughness of ~ 0.393 nm. Its KPFM potential map does not follow the topography. There are noticeable electronic signatures that do not match anything seen in the topography.
Figure 6.5: (a) DRCLS spectra, (b) AFM topography, and (c) KPFM potential map for hydrothermally grown single crystal ZnO substrate H2. The spectra show deep levels at 2.1 and 2.4 eV. The dashed curves represent the Gaussian deconvolution. The KPFM map shows noticeable electronic changes of hundreds of mV that do not match the topography.
Figure 6.6 shows the DRCLS spectra (a), topography (b), and KPFM potential maps (c) for hydrothermally grown sample H1. Most notably, DRCLS shows a large and reproducible jump in defect emission from 2 keV (20 nm) to 5-20 keV (75-370 nm), making H1 one of the least uniform samples in depth. Its spectra also show high NBE emission intensities and very low surface defect emission. Deep level defect emissions are seen at 2.1 and 2.5 eV. AFM shows a small number of circular pits, roughly 2-6 nm in depth, and an overall rms roughness of ~ 0.633 nm. The topography and potential maps for H1 do not correlate. Similar to what is seen in H2, H1 has electronic signatures in its potential map that do not correlate with anything found in its topography.
Figure 6.6: (a) DRCLS spectra, (b) AFM topography, and (c) KPFM potential map for hydrothermally grown single crystal ZnO substrate H1. Spectra shows a large and reproducible jump in defect emission from 2 keV (20 nm) to 5 – 20 keV (75 – 370 nm) and deep levels at 2.1 and 2.5 eV. The dashed curves represent the Gaussian deconvolution.
In addition to the variations in surface morphology and the degree of correlation between morphology and surface potential, there is a striking correlation between the surface morphology and near-surface (2 keV incident beam energy) CL emission intensities. Figure 6.7 illustrates the ratio of NBE to deep level defect intensities \( \frac{I(\text{NBE})}{I(\text{defect})} \) as a function of AFM rms roughness or average roughness. The NBE energy shown in Figs. 2-6 is 3.36 eV. The defect emission extends over an energy range from ~2 to 2.5 eV. The maximum value of emission intensity is used. The noise level in the defect region is the leading cause of error in determining this ration, introducing a ~10% error in \( I(\text{defect}) \). Notwithstanding this source of error, Fig.7 demonstrates that the relative NBE intensities compared with the mid-gap defect intensities increases rapidly for rms roughness less than 0.5 nm or for average roughness less than 0.3 nm.

6.4 Analysis:

The results presented in this paper show wide variations in the DRCLS spectra, the AFM maps of surface morphology, and the KPFM maps of surface potential. Surface morphology varies throughout the set both spatially and in magnitude. We see large variations in surface morphology even for the same growth method and source. The surface potential also varies spatially and in magnitude, with large variations seen again even for the same growth method and source. DRCLS shows that ZnO defects vary with growth and vendor. We see the largest variations in defects with depth for the roughest surfaces. Higher surface versus near-surface defects seem to indicate that surface asperities are contributing electrically-active deep level defects. Previous work has shown
that defects within ZnO crystals may be due to nonstoichiometric growth conditions, thermal processing, impurities, or mechanical damage e.g. surface polishing. When the surface defects are much lower than the bulk, this correlates with additional surface polishing. Thus in Figure 6.6, the order-of-magnitude increase in defects between surface and bulk excitation depths is attributed to such additional surface polishing. Good polishing techniques are vitally important in order to avoid introducing more defects. The hydrothermally grown sample H1 is a great example of such a technique. Specifically, H1 was processed by ZN Technologies via chemomechanical polishing. The largest variations in defects with depth are evident when the surface morphology and potential maps do not match. This indicates that sub-surface electronic states are contributing to the surface potential, irrespective of the surface morphology. This is consistent with the orders-of-magnitude variation of DRCLS with depth over a range of tens to hundreds of nm shown in Figure 6.5.

6.5 Conclusions:

Nanoscale depth-resolved and scanning probes reveal surface and subsurface native point defects that may affect Schottky barrier formation. Variations in sub-surface defects correlate with AFM surface roughness and KPFM potential variations. These results reveal large variations in surface morphology, surface potential variations, and DRCLS defect density even for the same growth method and source.
CHAPTER 7  THE ROLE OF NEAR SURFACE DEFECTS AND nm SCALE SURFACE ROUGHNESS ON ZnO OPTICAL EFFICIENCY

7.1 Background and Previous Work:

Advances in ZnO growth and processing are enabling optoelectronic applications, in particular, light emitters with nanoscale dimensions,\textsuperscript{109,110,111,112} yet the impact of surface morphology and near-surface defects on ZnO’s optical emission properties are relatively unexplored. Previously, we showed that defect levels in the ZnO band gap, along with surface adsorbates and hydrogen affect interface charge transport and Schottky barrier formation.\textsuperscript{23,52,54} We also showed that at room temperature, remote O-He plasma treatment (ROP) produces clean ordered surfaces, removes hydrogen, and reduces deep level defects.\textsuperscript{52,50} Until now, there has been no quantitative information on how surface topography contributes to this defect emission. We have now used nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS), atomic force microscopy (AFM), and Kelvin probe force microscopy (KPFM) to measure the spatial distribution of native point defects within the outer 10-100 nanometers of the surface for ZnO grown by melt, hydrothermal, and vapor-phase transport methods and identified how surface morphology impacts the efficiency of near band edge (NBE) optical emission by introducing native point defects and competing recombination pathways. These crystals display independent, orders-of-magnitude variation in 2.1, 2.5, and 3.0 eV native point
defect optical transitions at their free surfaces and as a function of nanometer depth from <5 to ~1000 nm below the surface. AFM reveals large variations in surface roughness, asperities, and extended features related to the growth method, subsequent polishing and etching. KPFM maps of surface and subsurface electric potential acquired simultaneously exhibit systematic correlations with DRCLS-measured native point defect distributions. When DRCLS emissions vary with depth, potential maps can vary by hundreds of meV over uniform morphologies, emphasizing the impact of sub-surface defects on surface electronic properties. Detailed depth correlations show that chemomechanical polishing can reduce outer layer roughness and native defects while sub-surface defect and potential features remain. The relative strength of near band edge to deep level defect emissions exhibits a dramatic threshold dependence on surface roughness: surface optical emission efficiency increases over ten-fold as roughness decreases to unit cell dimensions, highlighting the coupled role of surface morphology and near-surface defects for high efficiency ZnO emitters.

7.2 Experimental Details:

All ZnO crystals underwent chemical cleaning consisting of 5 min. ultrasonic baths in acetone, toluene, dimethylsulfoxide, methanol, and deionized water, followed by N₂ drying. A JEOL 7800F ultrahigh vacuum (UHV) scanning electron microscope (SEM) with 5 nm focal diameter provided spatially localized, constant power excitation of the bare surfaces at 10 K and spectra via a parabolic mirror and Oxford MonoCL monochromator (0.15 nm maximum wavelength resolution). For incident electron beam
energy $E_B = 2, 5, 10,$ and $20$ keV, Monte Carlo simulations of the electron cascade yield depths $U_0$ of peak electron-hole pair production of ~ $25, 105, 330,$ and $990$ nm, respectively, below the free ZnO surface. While the injected carrier distributions peak over ranges defined by the Everhart-Hoff energy loss relation, the distributions themselves are strongly peaked at low $E_B$. Excitation with our beam currents ($<10^{-9}$ A) and probe areas ($\geq 50$ nm) fall below injection levels that saturate our deep level centers. Deep level features were fit using Gaussian lineshapes.
7.3 Results and Discussion:

Figure 7.1: DRCLS spectra of (a) high and (b) lower near-surface defect ZnO and order-of-magnitude changes with depth in deep level defect emission.
Figure 7.1 shows DRCLS spectra for two hydrothermally-grown ZnO(0001) crystal surfaces from different sources with relatively high (a) and lower (b) deep level defect emissions at ~ 2.1, 2.5, and 3 eV near their free surfaces. Figure 7.1(a) (Hydrothermal-16) shows broad defect emission that can be deconvolved into Gaussian peaks at ~ 2.1 and 2.5 eV for $E_B = 2$ keV with maximum $I(2.1-2.5 \text{ eV})$ vs. near band edge $I(3.36 \text{ eV})$ intensities such that $R(2 \text{ keV}) = I(3.3 \text{ eV})/I(2.1-2.5 \text{ eV}) = 203$. Note that $I(2.1-2.5 \text{ eV})$ refers to the aggregate intensity of both Gaussian peaks, proportional to their maximum defect emission intensity. The 2.1 and 2.5 eV intensities change with increasing excitation depth, first decreasing at 5 keV, then increasing such that $R(10 \text{ keV}) = 84$. Their intensities also vary independently, indicating different physical origins. Other hydrothermal ZnO crystals display DRCLS defect emissions that can vary by orders of magnitude. Figure 7.1(b) (Hydrothermal-1) exhibits sub-surface emissions with ratio $R(2 \text{ keV}) = 933$. In contrast, all higher $E_B$ spectra (5-20 keV, 105-370 nm) show a relative increase in 2.5 eV emission with dramatically and uniformly higher maximum defect emission such that $R(20 \text{ keV}) = 155$, i.e., ~ 6x lower band edge emission efficiency. The improved $R(2 \text{ keV})$ within the outer 25 nm is due to additional chemomechanical etching and polishing. Besides highlighting the distinction between bulk vs. surface emission, Figure 7.1(b) demonstrates that a ZnO crystal high in bulk defects can be dramatically improved in the near-surface region by chemomechanical polishing.
Figure 7.2: AFM morphology maps (a) and (b) corresponding to Hydrothermal 16 (6.5 μm x 6.5 μm) and Hydrothermal 1 (10 μm x 10 μm), respectively, in Figs. 1(a) and (b). KPFM potential maps (c) and (d) acquired simultaneously with AFM maps (a) and (b), respectively.

Figures 7.2(a) and (b) present corresponding surface morphology maps of Hydrothermal 16 and 1, respectively, measured ex situ at room temperature by AFM. Figure 7.2(a) shows sub-micron diameter circular pits covering the surface with depth ranging from ~ 2-20 nm with 2.0 nm rms and 1.5 nm average roughness. Figure 7.2(c)
displays the KPFM map acquired simultaneously with Figure 7.2(a), showing potential changes due to defects below the surface that appear consistent with the surface morphology (circles), decreasing by > 120 meV away from pit boundaries and elsewhere. Figure 7.2(d) acquired simultaneously with Figure 7.2(b) shows significantly different KPFM vs. AFM features for Sample Hydrothermal-1, indicating laterally nonuniform densities of electrically-active defects below the free surface. Rms roughness is 0.6 (0.4 ignoring pits) nm, > 3 times smoother than Sample Hydrothermal-16, with 0.3 (0.3) nm roughness average. Hydrothermal-1 potential variations are only ~ < 50 meV, consistent with the smoother overall surface.
Figure 7.3: The ratio of NBE to deep level defect intensities $I(3.3 \text{ eV})/I(2.1-2.5 \text{ eV})$ for $E_B = 2 \text{ keV}$, for hydrothermal, melt-grown, and vapor phase transport-grown ZnO as a function of AFM (a) average roughness and (b) rms roughness displays a well defined threshold dependence that increases rapidly for average roughness < 0.3 nm and rms roughness < 0.5 nm.
Figure 7.3 illustrates $R(2 \text{ keV})$ versus roughness average (a) and rms roughness (b) for a wide selection of hydrothermal, melt-, and vapor-phase-transport-grown ZnO(000$\bar{1}$) surfaces. Relatively rough surfaces exhibit $R$ values of $\sim 200$, while $R(2 \text{ keV})$ for much smoother surfaces is $> 13,000$. Furthermore, $R(2 \text{ keV})$ exhibits a well-defined threshold dependence, increasing rapidly for average roughness $< 0.3 \text{ nm}$ and rms roughness $< 0.5 \text{ nm}$. Here, melt- and vapor-phase-transport-grown ZnO exhibited the smoothest surfaces. $R(2 \text{ keV})$ is an indicator of near-surface optical efficiency, increasing dramatically when surface roughness decreases below a unit cell dimension, i.e., $c = 0.52 \text{ nm}$ for ZnO. This suggests that lattice imperfections at the unit cell dimension rather than extended morphological defects dominate the defect recombination signal and consequently the NBE emission intensity.

In general, the increase in $R = I(3.36 \text{ eV})/I(2.1-2.5 \text{ eV})$ and the corresponding relative emission efficiency of near band edge radiation is due to a lower concentration $N_D$ of radiative deep level defects at higher quality ZnO surfaces. The sharp increase in $R$ for rms roughness $\leq 0.5 \text{ nm}$ then corresponds to a strong $N_D$ decrease when roughness is due only to monolayer step edges. For all our samples, micron-size pits such as shown in Figure 7.2(a) are the major contributor to increased roughness. Asperities in Figure 7.2(a) account for the decrease in defect emissions for $E_B$ increasing from 2 to 5 keV in Figure 7.1(a) as excitation depth extends past these asperities into the bulk. Potential decreases of $\sim 100 \text{ meV}$ away from these pit edges over screening lengths of $\sim 0.12 \text{ um}$ are consistent with negatively charged sites near edge sites, for which Poisson’s equation
yields surface sheet charge densities $N_D > 10^{11}$ cm$^{-2}$ for bulk doping $\sim 10^{16}$ cm.$^{-3}$. This calculation underestimates $N_D$ because of potential screening by the depletion region normal to the free surface. We modified a formalism derived for spherical pores to find that, to within a precision of 10%, a hemispherical surface pore charge density of $4.2 \pm 0.8 \times 10^{11}$ and a carrier concentration of $8.4 \pm 0.5 \times 10^{15}$ yields a 100 meV potential decrease away from the pore perimeter over the 125 nm distance observed.\textsuperscript{117} Hence these lateral potential variations provide an approximate measure of fixed surface charge density within the pore and a bulk free carrier density at the surface.

7.4 Conclusions:

In summary, these results stress the importance of achieving monolayer-scale surface roughness to minimize surface recombination of free carriers by defects. AFM surface roughness values can be a predictive tool for assessing surface optoelectronic quality, e.g., NBE emission intensity, especially for nanoscale optical devices.
CHAPTER 8  NANOSTRUCTURE GROWTH-INDUCED DEFECT FORMATION AND BAND BENDING AT ZnO SURFACES

8.1 Background and Previous Work:

ZnO has attracted much attention as an optoelectronic material as well as for the extraordinary array of nanostructures it can produce. The incorporation of ZnO’s bulk properties – high exciton binding energy, high sensitivity to adsorbate charge transfer, high carrier mobility and the potential for $p$-type doping, into nanostructures provides the basis for many electronic applications. Considerable literature is now devoted to growth and propagation of these ZnO nanoscale structures and their use in light emitters, transistors, and sensors.\textsuperscript{55,118} However, there is little work exploring electrical properties of these features on a nanoscale, how these electronic properties relate to the growth processes that form ZnO nanostructures, and how they impact electronic contacts.

8.2 Experimental Details:

We used atomic force microscopy (AFM), Kelvin force probe microscopy (KPFM), surface photovoltage spectroscopy (SPS)\textsuperscript{119,120} and depth-resolved cathodoluminescence spectroscopy (DRCLS)\textsuperscript{121} to observe electrically-active deep levels due to zinc vacancies ($V_{Zn}$) that form with the growth of nanoscale features on ZnO polar surfaces. These defects change the surface potential by hundreds of meV on a scale of
tens to hundreds of nanometers. We found that representative vapor phase transport, hydrothermal, and melt-grown crystal surfaces form nano-“mounds”—structures tens of nanometer high but hundreds of nanometers wide. In contrast to nanostructure growth using externally supplied feedstock, nanomounds form spontaneously on clean ZnO surfaces in air over periods of weeks or months at room temperature, distributing across the surfaces either as clusters or in patterns that align with symmetry axes of the hexagonal crystal. They are clearly evident on clean surfaces with initial unit cell root mean square (RMS) roughness. The variation in \( V_{Zn} \) density with proximity to these nanostructures and their growth under oxygen annealing indicate that such vacancies form due to diffusion of Zn atoms toward the growing nano-mound. The deep levels and potential changes introduced by this spontaneous growth change the surface free carrier density, band bending, and carrier trapping at subsequent interfaces.

While SPS is widely used to measure surface state properties at macroscopic surfaces, we have adapted an AFM to measure surface states with nanometer scale lateral resolution. By introducing monochromatic light at the KPFM tip, one can obtain nano-SPS spectra from surface areas localized to less than a few tens of nanometers. Figure 8.1 illustrates the experimental geometry. An optical fiber directs monochromatized light between the KPFM (Park Systems XE-70 AFM/SPM/KPFM enhanced EFM KPFM) tip (Ti-Pt or Cr-Au) and the surface. The fiber optic core determines a \(~5\) mm spot size under the tip. The tip blocks any AFM laser light from this monochromatic probe region. Measurements of the contact potential difference (CPD) between the surface and the vibrating tip as a function of incident photon energy \( h\nu \)
produce the surface photovoltage spectra. Nano-CLS spectra were acquired with a JEOL 7800F field emitter scanning electron microscope (SEM) with minimum 5 nm spot size.

Figure 8.1: Schematic of the nanoscale SPS monochromatized light source positioned at a commercial KPFM cantilever. The tip of the fiber optic cable is 2 cm from the metalized tip and illuminates a 5 mm diameter spot.

Figure 8.2 (a) and (b) show coincident AFM and KPFM maps, respectively of a ZnO(0001), i.e., Zn-polar, surface grown by vapor phase transport, chemo-mechanically polished, cleaned by a remote oxygen plasma anneal and stored in Columbus, OH air (66% average humidity) for eight months. Similar features are observed for ZnO surfaces from various ZnO suppliers stored for several months or less. This surface displays a relatively flat (1.27 nm RMS, area 2μm x 10μm) ZnO(0001) region bounded by two regions with clusters of nano-mounds. The corresponding KPFM map shows that the clustered regions have lower CPD voltages (i.e., higher work function Φ) than the flat
region between. Corresponding SPS spectra in Figure 8.2 (c) all show a CPD increase at 
hν=3.3 eV, corresponding to n-type band flattening and a Fermi level E_F movement to 
energies higher in the band gap for hν>E_G. However, Figure 8.3 (c) and (e) of the 
clustered regions display an additional CPD increase with an energy threshold at hν = 
1.7-1.8 eV. This feature corresponds to optical transitions that promote electrons from a 
state 1.7-1.8 eV below E_C to the conduction band, reducing the negative charge at the 
surface and reducing the band bending as well.

Figure 8.2: (a) AFM map of ZnO(000 1) surface with two adjoining surface 
morphologies: a 1.27 nm rms smooth surface region (2) bounded by surfaces with 
clustered nano-mounds (1 and 3). (b) KPFM map from the same area. Regions (1) and (3) 
show lower CPD (larger Φ) than (2). SPS spectra (c) and (e), respectively show clear 
onsets at 1.7 – 1.8 eV that are absent in spectrum (2).
Laterally-resolved and surface-sensitive DRCLS also detects these electronic transitions via luminescence for similar nanoscale structures on both ZnO(0001) and (000 1) surfaces. As shown in Figure 8.3, spectra obtained at T=12K with peak excitation depths (incident beam energies $E_B$) ranging from 2 nm (0.3 keV) to 7.5 nm (1 keV) below the surface exhibit optical emissions in this energy range near these nanostructures, increasing in intensity at $E_B$=0.3 keV, corresponding to the outer few atomic layers.\textsuperscript{124} DRCLS correlations with positron annihilation spectroscopy (PAS) studies of $V_{\text{Zn}}$ in ZnO identify the 1.7 eV transition with isolated $V_{\text{Zn}}$ defects and a related 2.1 eV optical transition with $V_{\text{Zn}}$ clusters.\textsuperscript{125}

![Near-surface DRCLS spectra (T = 12 K) normalized to the NBE for $E_B = 2$ keV on a Zn-(0001) surface with nanomounds bordering a hexagonal pit. Zn vacancy emission at 2 – 2.1 eV increase dramatically at the outer edge of the nanomounds.](image)

Figure 8.3: Near-surface DRCLS spectra (T = 12 K) normalized to the NBE for $E_B = 2$ keV on a Zn-(0001) surface with nanomounds bordering a hexagonal pit. Zn vacancy emission at 2 – 2.1 eV increase dramatically at the outer edge of the nanomounds.
8.3 Results and Discussion:

SPS spectra near isolated nano-mounds reveal that $V_{Zn}$ densities increase with proximity to these nanostructures. Figure 8.4(a) indicates four AFM locations around a 20 nm-high nano-mound. Corresponding SPS spectra in Figure 8.4 (c) and (d) show positive CPD slope changes both at $h\nu = E_G$ and 2.1 eV. At a distance $R = 750$ nm from the nano-mound (Figure 8.4(b)), the spectrum exhibits no apparent change at sub-band gap energies. At $R = 350$ nm (Figure 8.4(c)), a positive slope change is clearly evident at 2.1 eV. At $R = 500$ nm (Figure 8.4(c)), this threshold becomes more pronounced. At $R = 0$, the nano-mound edge, (Figure 8.4 (d)), this feature is most pronounced. However, atop the mound (Figure 8.4(e)), the SPS spectrum appears free of defect-related features. Analogous behavior is common to nano-mounds found across the ZnO surface and for crystals grown by different methods. The magnitude of the CPD slope change is proportional to the density of gap states. This lateral dependence of $V_{Zn}$ spectral features is consistent with increasing Zn depletion with decreasing nano-mound distance and nanostructure harvesting of Zn atoms.
Figure 8.4: (a) Topographical map of a single nano-mound on a Zn-(0001) face. Spectra show: (b) no evidence of a 2.1 eV feature, (c) a positive CPD change at 2.1 eV, (d) a larger CPD slope change at 2.1 eV at the nanomound edge, and (e) no evidence of gap states atop the nanomound.

The spatial distributions of nano-mounds across clean ZnO surfaces provides insight into the mechanism of spontaneous growth. Larger area AFM and KPFM maps of these air-exposed surfaces indicate a preferential distribution of nanofeatures along crystallographic directions. The Figure 8.5 (a) AFM map shows nano-mounds propagating along straight lines with ~ 60° intersection angles. X-ray diffraction (XRD) analysis of this surface shows that these lines lie along (1100) and (11-20) wurtzite crystal directions, suggesting that nano-mounds form at step edges, where activation energies
for chemical activity are lower\textsuperscript{126,127} and/or that the activation energy $E_A$ for Zn diffusion is lower along crystallographic directions.

Figure 8.5: ZnO(0001) (a) AFM and (b) KPFM maps showing lines of nano-mounds extending along crystallographic directions. The large central nano-mound creates a low CPD (high $\Phi$) region extending microns away. Paralleling the lines of nano-mounds are trenches with lower CPD.
Bordering these lines of mounds are “trenches” visible under higher contrast that are only a few nm deep, suggesting depletion of Zn and transport to the nano-mounds. The AFM and KPFM maps in Figure 8.5 (a) and (b) show an isolated nanomound (circled) whose surrounding area is several hundred meV lower in CPD, again indicating higher Φ and Zn depletion. This potential decreases monotonically with decreasing radial distance from the nanomound. Similar radial CPD decreases are evident for each of the smaller nano-mounds as well. Closer inspection of Figure 8.5 (a) also reveals circular trenches surrounding the nano-mounds with 250 to 450 nm radii scaling with nano-mound heights and radii, further evidence that nano-mounds extract Zn from surrounding areas. The central nano-mound’s lower CPD surround is non-radial due to superposition of the potential changes induced by the lines of smaller nanomounds.

The increased work function induced by forming \( V_{Zn} \) corresponds to filling of acceptor levels located 1.7 – 2.1 eV below the conduction band and increased band bending. The bulk carrier density \( N_D \) in these crystals is \( 10^{16} \text{ cm}^{-3} \) and the conduction band density of states \( N_C = 4 \times 10^{18} \text{ cm}^{-3} \), corresponding to \( E_C - E_F = kT \ln(N_C/N_D) = 0.15 \text{ eV} \). Valence band photoemission of the initial surface after remote plasma oxidation determines \( E_C - E_F = 0.64 \text{ eV} \) and band bending \( qV_B = 0.49 \text{ eV} \) for the surface before nano-mound growth,\(^{42} \) corresponding to a depletion width given by,

\[
W = \left( \frac{2\varepsilon_S V_B}{N_d} \right)^{1/2} = 210 \text{ nm}
\]
where dielectric permittivity $\varepsilon_s = \varepsilon_{\text{average}} / \varepsilon_0 = 8.2$. For the $\sim 300$ meV decrease in CPD (increase in $\Phi = E_{\text{VAC}} - E_F$) shown in Fig. 4, W increases to 267 nm, corresponding to an additional surface charge density $\sigma = 57 \text{ nm} \times 10^{16} \text{ cm}^{-3} = 5.7 \times 10^{10} \text{ cm}^2$, assuming the depletion approximation holds. Using Figure 8.4 with Zn depletion from an area of $(300 \text{ nm})^2$ and an average nanomound volume of ca.20x160$^2$, the average number of Zn atoms in a nanomound over a typical surround yields $\sim 5 \times 10^{10} \text{ cm}^2$, remarkably close to the electrostatic value. For a metal-semiconductor contact, this trapped charge forms a nanoscale interface dipole, effectively reducing the bulk band bending.

We also performed temperature-dependent studies to define further the nature of spontaneous nano-mound growth on ZnO. To confirm the surface oxidation mechanism of nano-mound growth, we annealed this crystal in flowing oxygen using a tube furnace. An Arrhenius plot of thermally-activated nano-mound growth based on either maximum or average nano-mound heights vs. inverse temperature (not shown) yields logarithmic fits with slopes yielding an activation energy $E_A \sim 0.15 \pm 0.01 \text{ eV}$ in diffusion coefficient. For Zn interstitials, first-principles calculations indicate bulk $E_A = 0.57 \text{ eV}$, much lower than any other ZnO defect. Furthermore, our diffusion values should be lower since near-surface regions present lower energy barriers for atomic diffusion.

The depletion of Zn around nano-mounds and its exponential growth dependence on temperature under oxygen suggests that Zn extracted from the ZnO lattice reacts with oxygen from the air to grow the nanostructure. The preferential arrangement of nanomounds along crystallographic directions suggests that this process is initiated by step
edges. We have also observed nano-mounds decorating the edges of pits on ZnO surfaces.\textsuperscript{124} The dangling bonds and higher reactivity at these sites lowers the barrier for the energetically favorable reaction

\[ 2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO} \]

Given the dissociation energy of -498.4 kJ/mol for O\textsubscript{2} and the -350 kJ/mol heat of formation for ZnO,\textsuperscript{129} the corresponding heat of reaction is -2.09 eV/molecule. Our remote plasma oxidation promotes the intimate contact of these reactive Zn sites with O and the sizable energy gain by initially removing surface contaminants. The subsequent energy release then promotes further bond breaking and Zn\textsubscript{i} diffusion locally, albeit slowly at ambient temperature.

\textbf{8.4 Conclusions:}

Our nanoscale optical and electronic measurements show that ZnO nanostructures can grow spontaneously in air over long exposure periods according to a Zn harvesting mechanism driven by oxidation. The subsequent surface electronic changes can significantly impact local electron density and recombination due to the creation of additional deep level acceptors as well as Schottky barrier formation due to the trapped charge and dipole formation at the intimate metal-ZnO interface.
CHAPTER 9  
THE ROLE OF NATIVE POINT DEFECTS IN HEAVILY n-TYPE DEGENERATE Ga-DOPED ZnO:

9.1 Background and Previous Work:

Transparent conducting oxides (TCO) have many opto- and microelectronic applications including electrodes for photovoltaic cells and flat panel displays, LEDs, and laser diodes. Currently, indium tin oxide (ITO) is the TCO industry standard primarily because of its low resistivity. However, ITO suffers from high cost, moderate toxicity, and poor thermal stability. Ga-doped ZnO (GZO) with high carrier concentrations has emerged as a prime candidate to replace conventional TCO materials because it is cheap, nontoxic, thermally stable, and highly transparent. Practical TCOs, such as ITO and GZO, are nearly all donor-doped, and thus a major consideration is the presence of acceptors, which reduce both carrier concentration $n$ and mobility $\mu$. In GZO, the dominant acceptors have been shown to be Zn vacancies ($V_{\text{Zn}}$), arising from self-compensation, and thus it is important to understand these native defects so they can be eliminated if possible. Here we use depth-resolved cathodoluminescence spectroscopy (DRCLS), optical absorption, X-ray photoemission spectroscopy (XPS), and Hall-effect techniques to characterize their native defect effects in GZO.
9.2 Experimental Details:

GZO films were grown by pulsed laser deposition (PLD) using a 99.99%-pure ZnO target sintered with 3% wt. Ga₂O₃, or 2.6 atomic % Ga on quartz substrates. Films of thickness 58 – 230 nm were grown at substrate temperatures of 100, 200, 400, and 600 °C under either forming gas (FG: 5% H₂ in Ar) or pure Ar ambient. Film thicknesses were determined by ellipsometry to vary no more than 15% across the wafer. The rationale for growth in Ar, rather than in the usual O₂ ambient, stems from the earlier work of Scott et al., who showed that surprisingly high conductivities could be obtained by employing Ar ambient. Presumably, the presence of Ar inhibits the incorporation of O₂⁻ acceptors at surfaces and grain boundaries. The rationale for growth in FG was to see if a small amount of H would increase the donor concentration N_D by producing H₂O donors, and reduce the active acceptor concentration N_A by passivating isolated acceptors such as V_Zn and acceptor complexes such as Ga_Zn – V_Zn. It is already known that annealing in FG can increase conductivity; however, at least in some cases, the electrical properties are not uniform with depth. One goal was to see if growing in FG produced more uniform electrical properties than annealing in FG.

We used a Lakeshore 7507 Hall-effect System to determine carrier concentrations and mobilities from 15 – 320 K and over a range of growth parameters. Donor and acceptor concentrations were calculated from these data. DRCLS provided corresponding defect, band-gap, and below-band-gap transition spectra versus depth into the ZnO films at 80 K. For increasing incident electron beam energy E_B = 0.8 - 2 keV, Monte Carlo simulations show the rate of electron-hole pair creation peaking at depths U₀.
increasing from \( \leq 5 \) to \( \geq 18 \) nm and range \( R_B \) extending from \(<20\) to \(~50\) nm below the free ZnO surface\(^{34,136}\) over narrow nanometer-scale depth ranges.\(^{125}\) For incident beam current \( I_B \), we used constant power \( P = E_B * I_B = 2.5 \) mW in 0.5 mm diameter spots. CL spectra taken with \( E_B = 1\text{-}2 \) keV and \( I_B = 0.25 \text{–} 2.5 \mu\)A (i.e., 0.25 - 5 mW) exhibit no power dependence. For the highest depth resolution studies, we employed a differential DRCLS technique described elsewhere.\(^{137}\) CL spectral error bars based on emission signal-to-noise and repeatability were 1.6%. Defect peak areas were obtained by background subtraction and defect peak deconvolution (FWHM(1.8 eV) = 0.17 – 0.23 eV and FWHM(2.04 eV) = 0.23 – 0.37 eV) with 5\% error based on repeatability. Perkin Elmer Lambda 20 UV/VIS Spectrometer provided room temperature absorption spectra. A PHI Versaprobe provided XPS spectra versus \( \text{Ar}^+ \) sputter depth and elemental composition from surface through substrate interface.

**9.3 Results and Discussion:**

Figure 9.1 (inset) shows representative DRCLS spectra of the GZO for three \( E_B \), exhibiting defect-related emissions at 1.8 and \(~2.04\) eV and transitions from filled conduction band states to empty valence band states in an energy range \(~2.5 \text{–} 4.5\) eV. The lower energy can be taken as a rough value of the renormalized conduction band with respect to the valence band at wave vector \( k = 0 \). The upper energy reflects the fact that electron-hole pairs can be created throughout the Brillouin zone, so that luminescent recombinations can potentially occur at high \( k \) values and high energies. DRCLS correlations with positron annihilation spectroscopy (PAS) studies of \( V_{Zn} \) in ZnO identify
the 1.8 eV transition with isolated V\textsubscript{Zn} defects and transitions extending up to ~2.1 eV with V\textsubscript{Zn} clusters\textsuperscript{125} More recent PAS correlations with photoluminescence spectroscopy (PL) unambiguously associate the characteristic red PL band at ~1.75 eV with optical transitions involving V\textsubscript{Zn}-R acceptors.\textsuperscript{138} Similarly, electron irradiation studies produce electron-paramagnetic-resonance lines known to be due to zinc vacancies and also a strong photoluminescence band at 1.8 eV attributed to shallow-donor-zinc vacancy pair recombination.\textsuperscript{139} The integrated area (“A”) emission ratio of Zn vacancy-related (V\textsubscript{Zn}-R) emissions to conduction-band (CB) emissions, \textit{i.e.}, A(V\textsubscript{Zn}-R)/A(CB), provides a useful measure of the density of defects at a given excitation depth d(E\textsubscript{B}). The A(V\textsubscript{Zn}-R) was determined using Gaussian fitting of the 1.8 and 2.0 eV deep level features, while non-Gaussian A(CB) was determined from a simple Trapezoidal Rule integration with a zero baseline. It is expected that A(V\textsubscript{Zn}-R)/A(CB) ratios for these films will correlate with acceptor versus donor density ratios N\textsubscript{A}/N\textsubscript{D} measured by Hall-effect techniques.\textsuperscript{131} Since SIMS Ga profiles show that [Ga] is orders of magnitude higher than any other residual n-type dopant,\textsuperscript{131} the DRCLS integrated area of CB emissions should be a measure of N\textsubscript{D} \approx [Ga]. Likewise, the integrated area of V\textsubscript{Zn}-R emissions is proportional to V\textsubscript{Zn} densities as measured by PAS.\textsuperscript{125} For these films, acceptors can be explained only by V\textsubscript{Zn} and not any other impurity or point defect.\textsuperscript{131}

Figure 9.1 shows integrated area ratios A(CB)/A(V\textsubscript{Zn}-R) for characteristic bulk films probed with E\textsubscript{B} = 1.5 keV versus carrier concentration n for each GZO film, exciting the nominal center of each film and minimizing segregation effects to be discussed below. Isolated V\textsubscript{Zn} and V\textsubscript{Zn} clusters exhibit a ~1.3 - 2x ratio increase with
increasing $n$ for films with growth temperatures $T_G = 100 - 400 \, ^\circ C$ and a $> 3x$ increase at $T_G = 600 \, ^\circ C$, trends that are independent of $E_B$. The dramatic high temperature increase is due to thermally-activated Ga surface and interface segregation as shown below. As Ga atoms fill the $V_{Zn}$, the Fermi level rises, generating more $V_{Zn}$ which can in turn capture more Ga. The 1.8 and 2.04 eV emission intensities are linearly proportional across all our thin film spectra so that the variations in defect versus NBE intensity ratios are approximately the same for both. Previous work on similar samples show that $V_{Zn}$ clusters are expected to be neutral and not take part in compensation.\textsuperscript{131} If the $V_{Zn}$ can each accommodate two electrons, the carrier concentration $n = N_D - 2N_A \approx [Ga_{Zn}] - 2[V_{Zn}]$, and Figure 9.1 shows that the emission involving $Ga_{Zn}$ must increase faster than that involving $V_{Zn}$ as $n$ increases. Although the details of the transitions are not known, the simplest explanation is that $[V_{Zn}]/[Ga_{Zn}]$ decreases as $[Ga_{Zn}]$ increases. From a practical point of view, the 200 $^\circ C$ grown films are optimal, exhibiting the highest $n$ and lowest ($V_{Zn}$-R) densities, while the 600 $^\circ C$ grown films have the lowest $n$ and highest ($V_{Zn}$-R) densities (spectra shown in Figure 9.2).
Figure 9.1: $\frac{\text{A(CB)}}{\text{A(VZn-R)}}$ relationship to $n$ for GZO grown at the indicated temperatures for EB = 1.5 keV. In general, FG (open shapes) and Ar (closed shapes) growths exhibit the same trend: an order of magnitude ratio increase with an order of magnitude increase of $n$. Inset: typical DRCL spectra for GZO showing 1.8 and 2.04 eV $V_{Zn}$-R and CB emissions extending from < 2.5 to > 5 eV.

The decreasing $n \approx [\text{GaZn}] - 2[V_{Zn}]$ with increasing growth temperatures above 200 °C can be explained in large part by typically lower $N_D \approx [\text{GaZn}]$ and higher $N_A \approx [V_{Zn}]$ at higher temperatures, as shown explicitly in Table 1. The higher $[V_{Zn}]$ seems
reasonable from thermodynamic considerations\textsuperscript{16}, and the lower $[\text{Ga}_{\text{Zn}}]$ suggests either that the sticking coefficient of Ga is diminished or that Ga diffuses away from Zn sites and/or forms neutral oxides (e.g., $\text{Ga}_2\text{O}_3$) during growth at a higher rate. FG and Ar-grown films follow the same trend, indicating that the same mechanisms are involved.
Table 9.1: The variation in donor ND and acceptor NA densities in GZO grown at various temperatures under FG or Ar ambient.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Anneal T °C</th>
<th>Thickness (nm)</th>
<th>n x10^20 cm^-3</th>
<th>N_D (Z_D=1) x 10^20 cm^-3</th>
<th>N_A (Z_A=2) x 10^20 cm^-3</th>
<th>N_D/N_A</th>
<th>E_CRN (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZO-159</td>
<td>600 FG</td>
<td>58</td>
<td>1.63</td>
<td>5.86</td>
<td>2.11</td>
<td>2.78</td>
<td>3.11</td>
</tr>
<tr>
<td>GZO-147</td>
<td>600 Ar</td>
<td>75</td>
<td>1.92</td>
<td>6.48</td>
<td>2.28</td>
<td>2.84</td>
<td>3.03</td>
</tr>
<tr>
<td>GZO-145</td>
<td>100 Ar</td>
<td>90</td>
<td>4.39</td>
<td>7.41</td>
<td>1.51</td>
<td>4.91</td>
<td>2.79</td>
</tr>
<tr>
<td>GZO-146</td>
<td>400 Ar</td>
<td>85</td>
<td>4.47</td>
<td>6.94</td>
<td>1.23</td>
<td>5.64</td>
<td>2.76</td>
</tr>
<tr>
<td>GZO-158</td>
<td>400 FG</td>
<td>92</td>
<td>4.92</td>
<td>7.82</td>
<td>1.45</td>
<td>5.39</td>
<td>2.74</td>
</tr>
<tr>
<td>GZO-155</td>
<td>100 FG</td>
<td>123</td>
<td>8.01</td>
<td>18.7</td>
<td>5.35</td>
<td>3.50</td>
<td>2.38</td>
</tr>
<tr>
<td>GZO-148</td>
<td>200 Ar</td>
<td>235</td>
<td>8.21</td>
<td>11.8</td>
<td>1.82</td>
<td>6.48</td>
<td>2.63</td>
</tr>
<tr>
<td>GZO-156</td>
<td>200 FG</td>
<td>133</td>
<td>9.6</td>
<td>15.8</td>
<td>3.1</td>
<td>5.10</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Figure 9.2 shows DRCLS spectra on a linear scale to better illustrate the peak as well as the high and low-energy cutoffs. Indeed, we argue that the peak energy $E_{\text{CL, max}}$ is closely related to the bandgap at $k = k_F$, where $k_F = (3\pi^2n)^{1/3}$, the Fermi wave vector, illustrated in the inset. Here, it is important to note that, this set of GZO samples contained several that showed two peaks and asymmetric features in the CB emission. Such features are easily seen in the CB emission shown in the inset of Figure 9.1. Since the conduction band density of states varies smoothly, we conclude that such multiple features correspond to different carrier densities within the same film. Since the Hall Effect densities should correspond to the lowest resistance channels within the film, we chose the higher of the two maxima, if present, to correspond with the transport measurements. We first note that, as is well known, the absorption threshold energy $E_{\text{abs}}$ (not shown) must occur at $k_F$, because there are no CB states empty below $k_F$. Then, $E_{\text{abs}} = E_C(k_F) - E_V(k_F) = E_{\text{CRN}} + E_{\text{BM,CB}} + E_{\text{BM,VB}} = E_{\text{CRN}} + (\hbar^2/2m_e^*)(3\pi^2n)^{2/3} + (\hbar^2/2m_h^*)(3\pi^2n)^{2/3}$, where $E_{\text{CRN}}$ is the renormalized CB at $k = 0$, “BM” denotes the Burstein-Moss shift$^{140,141}$ in a particular band, and $m_e^*$ and $m_h^*$ are the electron and hole effective masses, respectively. Similarly, $E_{\text{CRN}} = E_{\text{abs}} - E_{\text{BM,CB}} - E_{\text{BM,VB}} = E_{\text{abs}} - (\hbar^2/2m_e^*)(3\pi^2n)^{2/3} - (\hbar^2/2m_h^*)(3\pi^2n)^{2/3}$. The values of $E_{\text{abs}}$ for each sample are determined from linear extrapolation of absorption coefficient $\alpha^2$ vs. $h\nu$ thresholds (not shown) and are plotted as a function of $n$ in Figure 9.3 (lower dashed line). In contrast, whereas the absorption process depends on empty states (holes) in the CB, the emission process depends on holes in the VB, mainly holes with wave vectors $k = 0$ to $k_F$. These holes originate from collisions between VB electrons and the exciting high-energy electrons.
and will have a wide range of wave vectors. Thermodynamically, however, they will all tend to percolate toward \( k = 0 \), through phonon interactions, and once they reach a state \( k \leq k_F \), they can recombine with equilibrium CB electrons and emit photons. For holes that begin this process with \( k > k_F \), they will likely not recombine in large numbers until they reach the large reservoir of CB electrons at \( k = k_F \), and thus we expect the emission peak to be at \( k = k_F \). If this model is basically correct, then \( E_{abs} \) should be close to \( E_{CL,max} \).

Figure 9.2: DRCLS spectrum of FG-grown GZO grown at 600 °C versus EB and excitation depth. \( E_{CL,max} \) corresponds to transitions \( EC(k_F) - EV(k_F) \). Inset shows possible absorption and emission transitions, including those for \( k \neq 0 \).
Figure 9.3 compares plots of $E_{\text{abs}}$ and $E_{\text{CL,\text{max}}}$ as functions of carrier concentration $n$, and indeed, the curves are quite similar. Neglecting the weak ($\sim n^{1/3}$) expected concentration dependence of $E_{\text{CRN}}$, we can write $E_{\text{gap}}(n) = E_{\text{gap}}(0) + Cn^{2/3}$ and a least-squares fit of the combined abs and CL data gives $E_{\text{gap}}(n) = 3.36 + 0.504 n^{2/3}$, where $n$ is
in units of $10^{21}$ cm$^{-3}$ and $E_{\text{gap}}$ is in units of eV. For this fit, max-dev = 0.0967, std-error = 0.0541, and $r^2 = 0.853$. A more detailed analysis at this stage would not be fruitful because of the scatter in the data, but clearly our basic interpretation of $E_{\text{CL, max}}$ appears to be justified.

Carrier densities $n_{\text{DRCLS}}$ obtained from $E_{\text{CL, max}}$ vary with depth of excitation on a nm scale and anti-correlate with the 1.7-2.1 eV ($V_{Zn}$-R) defects. Here, $n_{\text{DRCLS}}$ is obtained by inverting the relationship $E_{\text{CL, max}} = 3.36 + 0.504 n_{\text{DRCLS}}^{2/3}$. We define our error bars by letting $dE = (\text{std-error})$, giving $dn = \pm 0.05$ about each point. Figure 9.4 shows the $n_{\text{DRCLS}}$ and $I(V_{Zn}$-R)/$I$($CB$) vs. depth for the 600 °C spectra in Figure 9.2. Here $I(V_{Zn}$-R)/$I$(NBE) decreases (increases) as $n_{\text{DRCLS}}$ increases (decreases) with undulations spaced only a few nanometers apart, an effect more pronounced in FG- than in Ar-annealed GZO. Thus carrier densities display the same dependence of Zn vacancy density as that shown in Figure 9.1, even on a nanometer scale. This decrease in carrier density with increased $V_{Zn}$-R density further confirms
the acceptor nature of these defects. Figure 9.4 also suggests that pronounced variations in carrier density vs. depth using the curve fit in Figure 3 are possible (up to 20% here) on a nm scale.
Figure 9.5: (a) XPS depth profile of 58 nm-thick 600°C FG-grown GZO. (b) Interface concentration of Ga as a function of growth temperature.
XPS elemental depth profiles provide evidence for temperature-dependent dopant diffusion in these films. Figure 9.5(a) shows a representative XPS depth profile of 58 nm thick GZO on quartz, employing a ~ 1 nm/min sputter rate. At the GZO/SiO$_2$ interface, the Ga content increases substantially, indicating Ga accumulation that extends tens of nanometers back into the GZO. Less pronounced but significant Ga segregation occurs within 2 nm of the free GZO surface as well. For both FG and Ar-grown GZO films, the bulk Ga content increases from < 1.5% to ~ 4.2 atomic % with increasing growth temperature, indicating that thermal desorption of Ga during deposition is less likely than Zn desorption.$^{142}$ Figure 9.5(b) shows that the Ga segregation increases with growth temperature, indicating a thermally activated process. Based on the increasing Ga segregated to the GZO/substrate interface versus increasing growth temperature, we estimate a ~ 2.5 eV activation energy for Ga segregation from the bulk film. The Ga segregation occurs for both Ar and FG-grown ambients, but the higher segregation in FG suggests that hydrogen may play a role in both temperature-dependent Ga incorporation as well as Ga interface segregation during growth.

9.4 Conclusions:

The interplay between Ga donors and Zn sites, the spatial variations in doping coupled to $V_{Zn}$-R defects on a nanometer scale, and their impact on the electronic properties of degenerately doped ZnO demonstrate a direct relationship between $V_{Zn}$-related defects and n-type degenerate doping by Ga in PLD-grown ZnO. Increasing segregation of Ga to GZO interfaces with increasing temperature shows that Ga diffusion
takes place within the lattice during growth and partially accounts for the decreasing donor/acceptor density ratio as Ga diffuses away from Zn sites. Analogous to results for Li in ZnO, these results demonstrate that migration of Ga to V\textsubscript{Zn} sites plays a significant role in forming substitutional dopants so that native point defects are actively involved in ZnO doping. Given that V\textsubscript{Zn} acceptors become more thermodynamically stable as n-type doping increases, this coupling highlights a delicate temperature balance for engineering ZnO doping with V\textsubscript{Zn} sites, by diffusing Ga to V\textsubscript{Zn} sites at the surface and bulk while minimizing Ga segregation and V\textsubscript{Zn} formation. The strong interplay between dopants and vacancy sites and the ability to monitor their formation and migration with growth conditions could open up new pathways to obtaining high and controllable p-type conductivity in ZnO through doping and co-doping methods. Analogous coupling between defects and dopants may extend to other semiconductors as well.
10.1 Metal Sensitivity and Polarity Dependence on Native Defects, Traps, and Interface Chemistry:

The polarity-related asymmetry in Zn- (0001) and O- (000-1) polar surfaces and metal diodes has been studied by DRCLS and electrical measurements. These results show that the Zn-polar surface shows higher NBE emission, lower near surface defect emission, and more stability during electron beam exposure. The O-polar surface shows higher oxygen vacancy density and rapid CL quenching with electron beam exposure time. Even with ROP treatment, the Zn-polar surface shows stronger emission than the O-polar surface. Au and Pd diodes on as-received and O₂/He plasma-cleaned surfaces display not only a significant metal sensitivity but also a strong polarity dependence that correlates with defect emissions, traps, and interface chemistry. Pd diode is always more leaky than Au diode due to the diffusion of H. Furthermore, these results show that the Zn-polar surface is more stable, forming higher quality Au Schottky barriers compared to the O-polar surface. The qualities of the Zn- and O-polar surfaces of ZnO presented here could serve to making higher quality Schottky diodes for future device applications.
10.2 Polar Dependence of Native Defects in ZnO:

Remote Oxygen Plasma processing is a valuable tool for developing clean and ordered ZnO surfaces. This work reveals the evolution of surface and near surface states at polar ZnO surfaces with ROP treatment. DRCLS measurements reveal a decrease in oxygen vacancy related defects with ROP on the O-polar surface, while creating new zinc vacancy related defects on the Zn-polar surface that increase with ROP exposure time. Such capabilities could serve useful for defect engineering and Schottky barrier tenability on ZnO. These findings further demonstrate the importance of polar surface effects and ROP processing on surface and near-surface defect densities.

10.3 The Effects of Near Surface Electrically-Active Defects and Surface Quality on the Optical Efficiency of ZnO:

The understanding of how surface preparation and near-surface defects affect ZnO surface quality is of greatest importance for next generation micro- and optoelectronic devices. ZnO crystals grown by vapor phase, melt, and hydrothermal growth methods display orders-of-magnitude variation in native point defect densities at their free surface and as a function of depth on a nanometer scale. We used a complement of nanoscale DRCLS and scanning probe microscopy to show that these variations in sub-surface defects correlate with AFM surface roughness and KPFM potential variations. These results reveal large variations in surface roughness related to both the growth and processing methods as well as strong potential variations (> 100 meV) due to near-surface electrically active native point defects that may affect surface recombination
efficiency. AFM and KPFM maps reveal a threshold dependence of near surface defects and luminescence on surface roughness. This apparent threshold behavior shows that roughness values acquired via AFM could prove to be a predictive tool for (i) assessing optoelectronic quality in terms of band edge emission intensity and (ii) assessing the extent of defect-assisted recombination and effective Schottky barrier height from the gap state densities that promote tunneling and hopping. Likewise, the degree of correlation between AFM and KPFM may provide an indicator of the presence of sub-surface electronically-active defects and their variation with depth. Furthermore, These results stress the importance of monolayer-scale surface roughness to minimize surface recombination of free carriers by defects.

10.5 The Role of Native Point Defects in Spontaneous Nanostructured Growth on ZnO Surfaces:

The stability of ZnO surfaces in atmospheric conditions is vital for future device applications. Here we presented nanoscale optical and electronic measurements of ZnO polar surfaces after extended periods of air exposure. Our nanoscale optical and electronic measurements reveal that ZnO nanostructures can grow spontaneously on ZnO polar surfaces due to oxidation of mobile Zn from in the underlying lattice. Scanning probe measurements reveal that these nanostructures form along crystallographic directions that may act as preferred diffusion pathways. Annealing experiments in pure oxygen environment show an acceleration of ZnO nanostructured growth resulting in increases in zinc vacancy densities near these formations. These studies reveal a Zn atom
diffusion, extraction, and nanostructured growth with activation energy of \( Q = 150 \pm 10 \) meV, consistent with Zn-interstitial diffusion. The subsequent surface electronic changes can significantly impact local electron density and recombination due to the creation of additional acceptor-type defects as well as Schottky barrier formation due to the trapped charge, diode inhomogeneities, and dipole formation at the metal/ZnO interface.

10.6 The Role of Native Point Defects in Doping Ga-doped ZnO:

The interplay between Ga-substitutional (\( \text{Ga}_{\text{Zn}} \)) donors and Zn-sites demonstrate a direct relationship between zinc vacancy related (\( V_{\text{Zn}}^- R \)) defects and \( n \)-type degenerate doping. This interplay reveals itself in the spatial variations of the measured Fermi level position and subsequent carrier density coupled to \( V_{\text{Zn}}^- R \) defects on a nanometer scale. Increasing Ga segregation to GZO interfaces with increasing growth temperature shows that Ga diffusion takes place within the lattice. These results demonstrate that the migration of Ga to zinc vacancy sites plays a significant role in forming substitutional dopants. The strong interplay between dopants and vacancy sites and the ability to monitor their formation and migration with growth conditions could open up new pathways to obtaining high and controllable \( p \)-type conductivity in ZnO through defect engineering, doping, and co-doping techniques.
CHAPTER 11  FUTURE WORK

11.1 Tunable Schottky Barriers:

While some alternative formalisms have been suggested in literature over the past few decades, as of the writing of this work, there is no comprehensive model for Schottky barrier formation on ZnO. It is known that Schottky barrier formation is weakly dependent on metal the metal work function while surface adsorbates and near-surface to bulk defect can have significant affects. As shown in Figure 11.1, previous work by Brillson et al.\textsuperscript{23} shows that even bulk defects can have strong affects on barrier formation. They were able to show that high defect ZnO material produces nearly ohmic contacts while medium and low defect material producing rectifying contacts with ideality factors that decrease with decreasing defect densities. A natural extension of the work presented here centers around developing a quantitative model for Schottky barrier formation on ZnO surface that is strongly dependant on surface and bulk defect densities. It is already well known that when the defect density of states is high, the Fermi level will be “pinned” at that particular defect energy level within the band gap. Previous work by Allen et al.\textsuperscript{58} has shown the Fermi level pinning effects of near-surface $V_O$ densities generated by chemical reactions with highly oxidizing metal contacts. The effect of Fermi level pinning at the $V_O$ defect energy level ($E_C-0.7 \text{ eV}, \sim 2.5 \text{ eV})$ is rectifying
contacts with barrier heights no greater than ~0.7 eV. Similar pinning may be possible at the VZn defect (~2.1 eV – EV) level as well.

![Figure 11.1: (a) I(2.5 eV)/I(NBE) versus EB excitation depth and (b) corresponding I-V characteristics for high, medium, and low defect density ZnO.](image)

The ability to “tune” Schottky barrier formation by introducing defect densities in a controlled manner would be a significant contribution towards realizing high quality next generation devices. In the proposed work here, the goal is to introduce VO and VZn by controlled bombardment with inert ions. By bombarding ZnO surface with calculated fluencies, it should be possible to introduce defects and produce controlled Fermi level movement towards the chosen defect energy level. If only VO are produced then EF could be tuned from ~ EC (3.36 eV) all the way to EC - 0.7 eV (~2.5 eV). One could expect similar pinning behavior towards the VZn energy level, however different consideration may need to be made for acceptor type defects.
Figure 11.2: XPS valence band edge following Ar-ion bombardment at various energies and fluencies. XPS core level measurements reveal a slight preferential sputtering of oxygen for all Ar-ion energies.

Figure 11.2 shows preliminary XPS valence band and Zn/O atomic percentages for Ar-ion bombarded ZnO. XPS VB reveals that bombarding ZnO surface with various fluencies of Ar-ions can move the Fermi level from above the CBM down to ~ 3.0 eV. XPS Zn/O atomic percentages reveal a slight preferential sputtering of oxygen for all Ar-ion fluencies. SRIM/TRIM ion implantation and scattering simulations were used to further investigate the effects of Ar-ion bombardment on ZnO. These simulations reveal...
that the depth of defect generation is determined by the Ar-ion energy while the concentration of defects is determined by the Ar-ion current. Figure 11.3 shows SRIM/TRIM simulations at Ar-ion energy of 2 keV, bombardment and scattering effects peak at ~ 3 nm. These events produce vacancy generation that peaks at a depth of ~ 1nm. Calculations using an Ar-ion current of 10 nA result in a generation of ~10^{20} cm^{-3} (~10^{14} \text{ cm}^{-2}).

![Graph showing SRIM/TRIM simulation and vacancy generation calculation for 10 nA of 2 keV Ar-ions in ZnO.](image)

The generation of both $V_{Zn}$ and $V_{O}$ is something that will need to be addressed. A combination of pre/post bombardment treatments using ROP could allow for more
control over individual native defects. For example, previous work has shown that ROP can produce $V_{\text{Zn}}$ on Zn-polar ZnO with long ROP exposure time while reducing the overall $V_O$ content. Similarly, annealing ZnO at high temperatures has been shown to remove oxygen. One could imagine using a combination of treatments to isolate the contributions of individual defects to Fermi level movement and subsequent barrier heights.

UPS and XPS measurements prove extremely valuable for such an experiment. The ability to monitor the VB position, subsequent Fermi level position, as well as the work function with very high surface sensitivity is something that has never been done before. Preliminary UPS scans show that shifts in both the VB edge and secondary electron cutoff are detectable following staged Ar-ion bombardments using 500 eV, 10 nA, and a spot size of 6 x 6 mm$^2$. These results confirm previous preliminary results where the Fermi level has been successfully shifted down to ~3.0 eV. Given that both $V_O$ and $V_{\text{Zn}}$ are generated, the acceptor nature of $V_{\text{Zn}}$ may be forbidding the Fermi level from reaching the $V_O$ energy level. This may also reveal a lower bound for Ar-ion bombardment. The combination of ROP to functionalize surfaces, Ar-ion bombardment to generate defects, UPS to measure VB ($E_F$) movement and variations in ZnO work function, and DRCLS to monitor bulk defects and generated surface states through metal over-layers could allow for a fully comprehensible quantitative model on the effects of native point defects on Schottky barrier formation. These techniques coupled with the various surface treatments could result in new pathways towards tunable Schottky barriers on ZnO surface.
With device profiles trending towards nanoscale geometries the research of
nanostructures has increased rapidly. ZnO is an ideal candidate for next generation
electronic and biological nanoscale devices due to its piezoelectric properties, non-
toxicity, and expansive catalogue of potential geometric nano-formations. Within the last
decade, researchers have become quite proficient in growing ZnO nano-rods, whiskers,
rings, needles, helicopters, combs, helixes, and dots. These unique geometric structures
are ideal for nano-devices and sensors due to their dramatic increase in surface area.
Potential applications include biological sensors that can be inserted directly into the
blood stream to measure glucose levels as well as other gas and chemical sensors.4

However, the characterization of these surfaces and subsequent interfaces has yet to be
done. While the physics of reduced dimensional ZnO structures (i.e. 1D and 2D) is still
widely unknown, the facilities in the EMNLab at The Ohio State University are well
equipped to produce significant results. The ability to probe defect densities using SEM
with nm lateral and depth resolution could provide powerful insight into the role of native
point defects and surface states. Furthermore, nanoscale electronic scanning probe
techniques, such as SPS, KPFM, and I-V coupled to SPM, could prove valuable for
measuring both the contributions of surface states and defects as well as transport
properties through nanostructures.
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