CONTROL OF ELECTRICAL TRANSPORT MECHANISMS AT METAL-ZINC OXIDE INTERFACES BY SUBSURFACE DEFECT ENGINEERING WITH REMOTE PLASMA TREATMENT

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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ABSTRACT

ZnO has received renewed attention in recent years due its exciting properties as a wide band gap semiconductor. ZnO has several advantages over GaN including the availability of substrates, a room temperature excitonic emission, and an environmentally benign chemistry. ZnO applications include efficient blue light emitters, surface acoustic wave devices, transparent conductors, high power transistors, and solid state white lighting. Despite this versatility, several hurdles remain before device realization. Firstly, ZnO is almost always p-type. Although high quality n-type ZnO is abundant, there is no stable and reliable p-type doping scheme. Secondly, research into high quality Ohmic and Schottky contacts has been limited. Although there is an abundance of literature, there has yet to be an attempt to understand the physical and chemical mechanisms at metal-ZnO interfaces. In this work, plasma processing techniques are adopted to ZnO. These cold plasmas allow for room temperature modification of the subsurface. Implanting hydrogen has identified it as a primary n-type dopant responsible for a large fraction of the n-type conductivity. Oxygen plasma treatment has yielded an Ohmic to Schottky conversion by reducing oxygen defects at the near surface. Deposition of metals on clean
and ordered surfaces reveal the importance that defects play at the metal-semiconductor interface. Higher concentrations of defects promote reactions. This increased reaction eutectic forming and oxide forming. Understanding the nature of the metal allows for engineering of high quality blocking contacts. These contacts can provide added thermal stability to devices. Subsurface introduction of hydrogen and nitrogen provide a potential roadmap to p-type doping and high quality Schottky contacts. Overall, control of transport properties and contact integrity is achieved by remote plasma processing.
Dedicated to my wife Kristina, and my two sons Alex and Austin
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LIST OF ABBREVIATIONS AND SYMBOLS

AES – Auger Electron Spectroscopy
BEx – Bound Exciton
CASINO – monte CArlo Simulation of electroN trajectory In sOlids
DRCLS – Depth Resolved Cathodoluminescence Spectroscopy
E_g – Energy (Band) Gap
EHP – Electron Hole Pair
EMNLab – Electronic Materials and Nanostructures Laboratory
LEED – Low Energy Electron Diffraction
OSU – Ohio State University
PL – PhotoLuminescence
PMT – PhotoMultiplier Tube
RMS – Root Mean Square
RICP – Remote Inductively Coupled Plasma
ROP – Remote Oxygen Plasma
SED – Secondary Electron Detector
UHV – Ultra High Vacuum
Φ - Work Function

χ - Electron Affinity
INTRODUCTION AND BACKGROUND

1.1 Motivation

ZnO is one of the remarkable materials of our time, and applications utilizing its properties seem endless. For many years, ZnO has been used industrial applications for galvanizing rubber, skin ointment, lubrication, paints and phosphors. Since the ZnO rediscovery in 1954, it has been studied for its semiconductor properties. Due to its large direct band gap (3.3eV at 300K), a 60 meV exciton that persists at room temperature, and lattice matching to GaN, blue and ultraviolet optoelectronics have been an active area of research. The excitonic line would yield highly efficient blue and ultraviolet lasers and light emitting diodes, while its optical transmission makes it a good candidate for transparent thin film transistors (TTFTs). White light emitters of varying temperature colors have been developed. These emitters would play a major role in the integration of solid-state lighting, which could reduce global lighting power consumption by 50%. ZnO nanostructures have been widely reported and uses for electromechanical conversion at the nanoscale are documented. These devices make use of the materials’ piezoelectric attribute. ZnO is also calculated to be one of the few room temperature dilute magnetic semiconductors when doped with Mn, Fe, Co, or V.

Despite these promising applications, several hurdles remain before realization of ZnO devices. First, understanding the chemistry and physics at the metal/ZnO interface is essential for making high quality Ohmic or rectifying contacts. Secondly, there has been minimal process engineering based on the physical mechanisms responsible for electronic transport. Most studies have focused on using successful methods for III-V’s or Si based devices. This methodology has serious drawbacks and has yielded only phenomenological results. Another primary drawback is the difficulty in producing stable p-type material. While ZnO is easily doped n-type, which makes it an ideal choice for transparent conducting oxides, p-type doping has been challenging.

This work will focus on understanding the impact each of the below items, and their effect on electronic transport at metal-ZnO interfaces:

- Control of dopants
- Subsurface defects
- Role of adsorbates
- Surface morphology

1.2 Crystal Structure

II-VI compounds such as ZnO often manifest themselves in either zinc-blend or wurtzite structure. Each anion is surrounded by 4 cations forming a tetrahedral bond with its four neighbors. The stacking structure determines the difference between zinc blend (ABabA…) and wurtzite (ABCabc…). ZnO can be found in several allotropes that include rock salt (NaCl structure) as well as zinc blend and wurtzite, the latter being the
most stable and dominant configuration\textsuperscript{7}. Figure 1.1 illustrates the crystal directions in the wurtzite allotrope.

Figure 1.1: The crystal structures of ZnO. The most stable configuration is wurtzite.
(From ref. 7)

In the (0001) crystal direction there are alternating layers of Zn and O atoms that terminate in polar-Zn or polar-O surfaces at the interface. The chemistry of these faces is quite different because of sp\textsuperscript{3} hybridized orbitals. Although this is a covalent structure the bonds have significant iconicity. This leads to a polarization in the (0001) direction and the piezoelectric attribute of the crystal as well as no inversion symmetry.\textsuperscript{8} The Zn polar face is much less reactive as the orbitals are hybridized into the plane, while the unbounded electrons surrounding the O polar face extend out of the interface. The O polar surface can be identified by increased etching rates in solutions of hydroxide or other base solutions. These aspects are important when considering the chemical reactions that can occur at the metal-ZnO interface. Zn-metal alloys can form for metals that form eutectics with Zn, while other metals may form oxides. Both of these effects
can degrade the performance of electrical contacts at the interface. Internal polarity may also be responsible for space charge modification of rectifying contacts.

![Figure 1.2: Energy gap vs. bond length. ZnO can easily be latticed matched to GaN. Tailoring the band gap with MgO allows ternary compounds from 3.3eV to 8.0eV.](image)

Band gap engineering is an important requirement for optical electronics. In fig 1-2 energy band gap is plotted as a function of lattice constant. This clearly shows that not only can ZnO be latticed matched to GaN, but also ternary compounds Mg$_x$Zn$_{1-x}$O can be tailored with band gaps ranging from 3.3eV to 8.0eV. Quantum well structures for blue
and ultraviolet lasing can also be produced with superlattices of alternating layers of band gaps. This has been demonstrated in literature of lasing for both the superluminescence case as well as lasing (far field).

Although ZnO shares with GaN many attributes, ZnO has several advantages over GaN. The availability of high quality substrates makes ZnO a candidate for homoepitaxy. This is in contrast to epitaxial GaN. A 60meV room temperature exciton allows narrow line width optical transitions that surpass GaN. This is especially important for efficient blue and ultraviolet lasers. ZnO can also be grown into a myriad of nanostructures enabling a new generation of nanoelectronics and MEMS. The ZnO nanozoology includes nano rods, whiskers, sheets, tubes and rings. Some of these retain important properties like piezoelectricity. Lastly, ZnO is environmentally benign and doping with nitrogen and hydrogen could produce p and n type conductivity. This is appealing for solid-state lighting, and environmentally friendly applications.

Figure 1.3: Hexagonal nanorods grown of ZnO (left) and single crystal nanoring (right)
1.3 Growth Methods

Although ZnO can be grown epitaxial on sapphire and silicon with MOCVD, MBE, PLD and CVD, there are three primary methods for the growth of single crystal substrates:

- Hydrothermal (HYD)
- Vapor Phase (VP)
- Melt Grown (MLT)

Each of these processes has its advantages and drawbacks. Surface preparation is also a crucial step for device quality material. Therefore, each vendor maintains trade secrets for chemomechanical polishing. In recent years, single crystal substrates have been extensively studied from major vendors ZN Technology, Inc.\(^9\) and Cermet, Inc.\(^10\). Recent emergence of Tokyo Denpa hydrothermal ZnO has been an area of excitement due to the high crystalline quality as well as advantages for p-type and semi-insulating material\(^11\). Collaborations at Wright-Patterson Air Force Base (WPAFB) have revealed growth specific characteristics both in electrical and optical properties.
Figure 1.4: 2 inch single crystal substrates by hydrothermal growth. <0.2nm rms surface roughness and defect concentrations below $10^{13}$ cm$^{-3}$. Conductivity available from n-type to semi-insulating,

Hydrothermal ZnO

The figure below shows the autoclave used for growth of HYD ZnO. In this configuration a mineralizer (solvent) consisting of LiOH and KOH. This autoclave is Pt lined to prohibit chemical reactions with the steel autoclave that would lead to impurities in the ZnO. This Pt inner container is separated into two zones. These zones are known as the growth zone and dissolution zone. The seed crystals are located in the growth zone. The whole autoclave contains supercritical water between 300C and 400C. Convention transports the high temperature constituents from the dissolution zone to the lower temperature growth zone. The main parameters of the HYD growth system are pressure and concentrations of the mineralizer, the growth zone temperature and the temperature difference between the two zones. At the date of this paper, 3 inch diameter single crystal wafers have been produced.
Figure 1.5: A schematic for hydrothermal ZnO growth. Important parameters are the growth zone and dissolution zone temperatures, oxygen overpressure, and solvent concentration. (right) Hexagonal bulk crystal grown by Tokyo Denpa LTD.

Vapor Phase ZnO

This growth method as the name suggests is performed in a furnace where both constituents are in the vapor phase. This furnace contains several zones held at different temperatures. An inlet allows a carrier gas to transport Zn and O atoms to a seed crystal. The growth zone is a lower temperature to promote crystal precipitation and growth. ZnO is grown with a high background pressure of H$_2$O. This leads to hydrogen impurities that can create shallow donors. Consequently, VP material is often highly n-type. High quality VP substrates up to 3 in diameter, have been provided for years from ZN Technology (Formerly Eagle-Picher).
Melt Grown ZnO

Cermet Inc has produced high quality single crystal substrates up to 2in in diameter. In a setup as shown in the figure below, ZnO is melted in a crucible above 1450°C. The particular advantage in Cermet’s technique is the use of an inductive heating technique. Induced fields supplied by inductive coils surrounding the material cause eddy currents that provide joule heating, thus providing a molten state. The ZnO melt is held in a water-cooled crucible. The ZnO in the vicinity of the crucible forms a thin diffusion barrier to minimize contamination from the crucible. The entire growth process is maintained between 1atm and 100atm. This discourages the formation and evolution of some volatile components as well as chemical decomposition. An overpressure of oxygen is maintained to maintain stoichiometry. The appeals of a melt-grown crystal growth are increased scalability and cost-effective substrates. MLT grown ZnO often has high concentrations of hydrogen impurities and is predominately n-type. Introducing Li impurities into the process can create semi-insulating material.\textsuperscript{12}
1.4 Defects in ZnO

Understanding the role of defects in any semiconductor system is key for engineering the material for applications. These defects can affect electrical and optical properties of the semiconductor, in addition to the interface chemical reactions. The stability of native point defects in ZnO has been investigated by Van de Walle and Kohan et. al. Van de Walle has also reported on universal hydrogen levels in compound semiconductors including ZnO. Typical defect states are $V_{\text{Zn}}$, $V_{\text{O}}$, $O_{\text{Zn}}$, $Z_{\text{nI}}$, $O_{\text{nI}}$, and related complexes. Although there has been considerable debate, a consensus has emerged that the energies of the Zn-poor defects correspond to 3.0eV and 2.1eV, while the Zn-rich conditions lead to increased concentrations of 2.5eV states. This is illustrated in work by Ong et. al. and shown below in fig. 1-7. In the case of a) ZnO is grown
under Zn-poor conditions, the cathodoluminescence (CL) spectra shows the presence of two peaks at 2.1eV and 3.0eV. In the Zn-rich condition, CL spectra show the presence of a 2.5eV state.

Figure 1.7: Defects grown in high and low Zn conditions. Cathodoluminescence data shows peaks at 2.1eV, 2.5eV, and 3.0eV. Under Zn-rich conditions 2.5eV peak dominates, under Zn-poor conditions 2.1 and 3.0 peak dominates. [From ref. 15]

Figure 1.8: Calculated point defect levels in ZnO.
This trend in data taken by several authors indicates that the green luminescence band (2.5eV) corresponds to oxygen vacancies. Others\textsuperscript{16, 17} correlate the green band to Cu impurities, and this may be partially true. However, the trend in the past decade\textsuperscript{18, 19, 20, 21} has leaned in favor of the oxygen vacancy model.

1.5 Doping

The asymmetry of intrinsic carrier concentration type in most semiconductors is common. Usually the emergence of a material system is followed by extensive efforts to create both n-type and p-type material. This is especially true for ZnO, which because of the hybrid covalent and ionic bonding structure, the prevalence of intrinsic point defects, mobile shallow donors in the growth process, and group III impurities in Zn ore, leads to a predominance of n-type conductivity. Although it has been shown that point defects are deep centers, they nonetheless contribute through complex forming states. Up until the scope of work presented here it was questionable to the amount and nature of some of the contributing donors. Group III impurities such as Al, Ga, In have resulted in high quality conducting thin films. These transparent conducting films have many applications in displays and conducting semiconductor devices. Consequently, the developed processes form high-quality n-type conductivity.

N-type Donors

- Hydrogen
- Group III Impurities
- Intrinsic Defects ($V_O$)
The excitement of the ZnO room-temperature excitonic recombination has fueled the efforts for p-type material. The difficulty in wide band gap semiconductors for p-type applications is common (with the exception of diamond where the opposite is true). This arises for a few reasons. Dopants can be compensated by native point defects, mobile shallow impurities present in the growth process, and low solubility of the dopant.\textsuperscript{22} P-type dopants in ZnO include: Li, Na, Cu, K, Ag, N, P, As, and Se. Many of these acceptors do not contribute significantly to the conduction because of they are deep levels. Group V elements show the most promise, however complex formation with intrinsic defects may hinder their effectiveness. Nitrogen is the most sought after acceptor in ZnO, however p-type using N has yet to be realized.

1.6 Role of Adsorbates

Control and removal of surface adsorbates is important in any semiconductor system. Previous work over the past 30 years has shown that adsorbates can promote the formation of extended defects in semiconductor systems. It is therefore imperative to create abrupt clean ordered surfaces for device interfaces. Adsorbates can create degenerate layers between the contact and semiconductor that can degrade device performance. In ZnO, ultraviolet photoelectron spectroscopy has shown that adventitious carbon and hydroxide can create accumulation regions at the near-surface thus degrading rectifying contacts\textsuperscript{23}. Hydrogen can absorb onto the surface of ZnO giving up electrons to the polar Zn and O surfaces. This electron exchange creates states and increased carrier concentrations in the space charge region through the following:

$$H + O^2 => OH + e^-$$
This accumulation layer, a high layer of degenerate electron concentration would serve to increase the tunneling component of rectifying contacts. Ultraviolet photoelectron spectroscopy (discussed in chapter 2) spectra shown in the figure below illustrate this point. In case a) the as-received surface band bending occurs where the Fermi level is inside the conduction band. Subsequent processing removes this layer in case b) and further processing depletes the surface of donors causing upward band bending at the surface.
Figure 1.9: Ultraviolet photoelectron spectroscopy indicating adsorbate induced band bending creating accumulation region (a). After moderate surface cleaning (b) and extensive processing for 1 Hr (c) shows the removal of adsorbates decreasing band bending. [From ref. 23]

1.7 Role of Hydrogen

Hydrogen incorporation in ZnO is an important factor when fabricating electronic devices. Although hydrogen is amphoteric in most semiconductors, it behaves as a shallow donor in ZnO. This donor-like behavior of hydrogen in ZnO is one of the major hurdles in overcoming the persistent n-type conduction. Hydrogen is present during most types of crystal growth and fabrication processes. To achieve quality p-type material and
control conduction in ZnO electronic devices, it is important to understand how hydrogen can incorporate ZnO.

1.8 Role of Nitrogen

Along with oxygen and hydrogen the influence of nitrogen is of particular importance because its potential as a p-type dopant\textsuperscript{25,26} with relatively small atomic size compared to other dopants like P and As. Concerns around N arise because of the relatively deep acceptor level and possible compensation effects\textsuperscript{27,28}. However, codoping schemes\textsuperscript{29} using N and other elements such as Li, Ga and H have been suggested\textsuperscript{30,31,32}. Of these Li and H are important because of the ability to remove these species after incorporation to activate the acceptors remaining. In our investigations of these plasmas with nitrogen, hydrogen and oxygen we illustrate the effects of incorporation of these species and the differences their subsurface modification has on Fermi level position, band bending and Schottky barrier (SB) formation.
2.1 Ultrahigh Vacuum Technology

It is important when investigating the interfacial electronic and chemical properties to maintain environments that prohibit the formation of contamination layers. Much of the development of surface science techniques is a direct result of ultra high vacuum technology (UHV). On the timescales of experimental techniques in science, it is important to maintain pressures that are or below $10^{-10}$ Torr. Most vacuums consist of a stainless steel vacuum chamber, quartz viewports, a series or pumps, and electronics to measure the conditions inside the vessel. Many of these pumps work in parallel and series to maintain the low pressure. These pumps include roughing pumps (max $10^{-3}$ Torr), turbo molecular pumps (max $10^{-9}$ Torr), cryogenic pumps ($10^{-10}$ Torr), and ion pumps ($10^{-10}$ Torr). The starting range of each type of pump differs. Therefore it is important to use the pumps together. The roughing pump is the first to reach the $10^{-3}$ Torr range. After this turbo molecular pumps can be used to get pressures to $10^+ \text{ Torr}$. This is the point that the cryogenic pumps and ion pumps can be started to achieve UHV conditions. Water vapor can freeze to chamber walls and the vapor pressure at low pressures from water
vapor can create a background pressure that cannot be reduced below $10^{-7}$ Torr. To expedite the pumping of vapor the chamber walls can be heated up to 150°C or more increasing the pressure until the pumps can remove the gas. This process is known as bake-out. Several systems can be merged together using flanges and valves. Most surface science UHV systems consist of an introduction area, a process chamber, and analysis area. The introduction area is used to place samples from air for preparation into UHV chambers. The process area may involve surface processing, metal evaporation, or cleaving. Analysis techniques are described below. The system used in the Electronic Materials and Nanostructure Lab (EMNLAB) allowed for in situ analysis, processing, and device fabrication without breaking vacuum. Therefore, the adsorbate contribution could be neglected when interpreting results.

2.2 Auger electron spectroscopy

Auger electron spectroscopy (AES) is a powerful tool for determining the surface composition of solids. It is one of many photoelectron techniques available to surface scientists. The AES system consists of an electron gun, sample positioning stage, and photoelectron spectrometer the electron gun can range in energies from 0.5keV to 5keV. The electrons are focused and accelerated toward the sample surface. These energetic electrons knock core electrons out of their atomic energy levels. The empty hole is short-lived and electrons from higher energies in the atom will give up their energy to electrons according to selection rules. This results in the emission of an electron with a defined kinetic energy. These kinetic energies are such that the scattering length of the electron at this energy is on the order of nanometers. This means that electrons with defined kinetic
energies once they leave the material are from the first few atomic layers. Due to the complicated relaxation of the atom, Auger spectra are often more broad than other photoelectron processes. AES can detect contaminants on the surface of semiconductors and metals with concentrations as low as 1.0%. AES has a main advantage over other photoelectron spectroscopy techniques by being able to focus electron beams to achieve high lateral resolution. When coupled with a secondary electron microscope it is possible to acquire lateral AES maps with resolutions of 5nm.

Figure 2.1: Band diagrams for different photoelectrons spectroscopies. These spectroscopies can determine chemical information and band bending within the first few monolayers of the probed surface.
Figure 2.2: Cylindrical mirror analyzer (CMA) used to detect electrons with a given kinetic energy. This is a specific depiction of AES however the electron gun can be replaced with an ultraviolet source (UPS) or x-ray source (XPS).
2.3. X-ray photoemission spectroscopy

X-Ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) is a method similar to AES where x-rays are used to photoionize electrons from the first few monolayers of material. The quantitative information extracted from XPS can be elemental composition (C, Si, Zn), elemental state (CO, CO₂, CH₄), and band bending at the near surface. XPS can detect chemical state and elemental composition as small as 1%. Band bending can be detected as small as 0.1 eV. Employing angle resolved XPS enables surface coverage and thickness measurements. Utilizing a CMA, the binding energy of electrons can be calculated from the following relation:

\[ E_{BE} = E_{\text{photon}} - E_{KE} - \Phi_{\text{spec}} \]

The binding energy of the electron is just the photon energy from the x-ray source minus the kinetic energy of the electron minus the work function of the CMA.
2.4. Atomic Force Microscopy

Atomic force microscopy (AFM) is an experimental method to retrieve high-resolution images of the surface of a material. The resolution of the technique has been demonstrated below 1nm and has been successful in resolving collections of atoms in a periodic structure. Recent modifications to AFM systems have enabled manipulation on the nanometer scale. Techniques such as dip-pen lithography promise the top-down design of electronics and structures approaching sizes of a few nanometers. Variations of AFM include Kelvin probe force microscopy (KPFM) and scanning capacitance microscopy (SCM). KPFM used the AFM mode to take a morphology scan of the surface. Using this morphology information a computer scans maintaining a constant height of the scanning probe above the surface while recording the surface potentials.
These maps can contain information about the electrical nature of morphology features and interfaces between materials. SCM is similar in that the AFM measurement is used to maintain a constant height. The SCM measures capacitance rather than surface potential. SCM mapping is useful for mapping out regions of n-type and p-type conductivity.

Figure 2.4: Atomic force microscope schematic. The cantilever progresses along a line scan. The cantilever and surface attract each other creating a deflection that is measured with a laser beam reflecting to a photodiode. Successive scans are added to form a surface tomography.

An example AFM system is shown in the figure above. A microscopic cantilever is brought close to the sample. As the cantilever progresses along a line scan the sample and cantilever are attracted by Hooke’s Law. Correspondingly, the cantilever is deflected and measured using a laser beam that is deflected from the surface of the cantilever to a
photodiode. This deflection is measured and a detailed morphology of the surface can be reconstructed by compiling successive line scans.

2.5. Low energy electron diffraction

Low energy electron diffraction (LEED) is the process where electrons with energies less than 1000 eV are coherently scattered from periodically arranged atoms in a material. The electrons scatter from layers of atoms that provide a diffraction grating. The diffracted electrons are then collected on a fluorescent screen coated with ZnO or other phosphors. A typical LEED setup is shown in the figure below. The sample is placed in a UHV chamber and probed with electrons from an electron gun. Varying the accelerating voltages determines the electron energies. The diffracted electrons are collected with the use of grids held at a tunable potential. Monitoring the intensity difference between diffraction patterns allows for determination of crystal structure layer by layer. Representative diffraction patterns are shown below in the figures for SiC and graphite.

Molecular adsorption can change both the intensity and LEED pattern. Surface reconstruction can also be characterized before and after processing. LEED patterns are sensitive to contamination of 0.5 monolayer adsorption. Leveraging this sensitivity LEED can qualitatively determine a clean ordered surface.
Figure 2.5: Standard low energy electron diffraction experiment. Electrons are accelerated to the sample and collected on a phosphorus screen. These diffraction patterns are sensitive to adsorbates and crystal ordering.

Figure 2.6: Representative LEED patterns taken from SiC and graphite surfaces.
2.6 Secondary Electron Microscopy

Secondary electron microscopes (SEM) have proved to be a valuable tool to aid in characterization of semiconductors. These tools operate by emission of electrons in a high vacuum environment, either by field or thermionic means. These electrons are then guided by electron optics, focused and accelerated toward the sample. The focusing mechanisms include electrostatic condensers, accelerator grids and apertures. All of the electron optics are user-controlled to produce a confined electron beam that impinges the surface with energies between 0.5keV and 25 keV. The electrons are then rastered across the surface of the sample, which produces the image. When high-energy electrons are energetically injected into the surface of a material several interactions can occur as show below in the figure:
Figure 2.7: Electron beam interactions from 1keV to 30keV kinetic energies. Auger, backscattered, and x-rays can be used for identification of material composition. Secondary electrons can be used for microscopy with resolutions near 5nm. Luminescence spectra can give detailed information about depth resolved defect concentrations.

Secondary electrons are electrons with energy less than 30eV, and because of their low energy are confined to 5-50 nm from the surface. These electrons are then detected by a secondary electron detector comprising a scintillator-photomultiplier sensor. Thus, as the beam rasters across the surface, the secondary electron detector measures the intensity of secondary electrons as a function of position. Due to the relation of secondary electrons to surface morphology an image is produced. This type of system’s resolution is limited by the electron beam size. This size can be refined to 5nm depending on the accelerating
voltage. A table of beam size/resolution is given below for the JEOL JAMP-7800F UHV. This is the SEM for characterization in this scope of work.

Figure 2.8: EMNLAB Secondary electron microscope. The analysis chamber contains a low temperature stage and mirror for cathodoluminescence spectroscopy. The hemispherical electron analyzer has increased energy resolution over cylindrical mirror analyzers.

The high-energy electrons used in the SEM also interact with the sample by creating auger electrons, characteristic x-rays, and luminescence. Auger electrons can be collected in a hemispherical electron energy analyzer. The Auger process creates electron energies from the near surface region that are characteristic of the material. This chemical information can then be used with the SEM raster beam to create a 2D elemental map of
the surface. The complexity of the Auger process results in broad peaks that do not allow for the identification of bonding states, but can be useful for elemental concentrations above 1%. This coupled with the ability to sputter in UHV conditions allows for elemental depth profiling. Luminescence can also be collected with a mirror and directed to a monochromator and photomultiplier to perform cathodoluminescence (shown above). Attached to the SEM is a processing chamber that can prepare samples via deposition, cleaving or annealing. This allows the user to retain the ultrahigh vacuum condition, thus characterizing at the nanoscale, before and after processing, without surface contamination.
Below is a table of beam parameters for EMNLAB’s SEM:

<table>
<thead>
<tr>
<th>Beam Voltage</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>
</thead>
<tbody>
<tr>
<td>25 kV</td>
<td>4 nm</td>
<td>6 nm</td>
<td>10 nm</td>
<td>30 nm</td>
<td>80 nm</td>
<td></td>
</tr>
<tr>
<td>10 kV</td>
<td>8 nm</td>
<td>10 nm</td>
<td>20 nm</td>
<td>60 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 kV</td>
<td>14 nm</td>
<td>15 nm</td>
<td>43 nm</td>
<td>140 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 kV</td>
<td>18 nm</td>
<td>20 nm</td>
<td>52 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Beam spot size vs. beam voltage for JEOL SEM.

2.7 Cathodoluminescence Spectroscopy

Cathodoluminescence spectroscopy is a method to characterize radiative defect states in semiconductors. In addition to the above-mentioned excitations created by an energetic electron beam, a specific instance is the creation of electron-hole pairs (EHPs) in the semiconductor. These free carriers drift until recombination occurs through one or more channels. This may be through a conduction band to valence band transition, band to gap state, gap state to gap state, or gap state to valence band. Non-radiative transitions may also participate.

Cathodoluminescence has both advantages and disadvantages than other techniques. One advantage is the ability of electrons to create EHPs according to the relation:
\[ E_i = 2.8E_g + M \]

Where \( E_i \) is the minimum energy of the electron required to excite an EHP and \( 0 < M < 1 \) eV is a material dependent quantity.\(^{33}\) This is important for wide band gap materials because it does not require a high energy laser to create EHPs which is the case for photoluminescence. In some materials, it is possible to detect CL signals from deep-level concentrations less than \( 10^{14}/\text{cm}^3 \), which is well below most characterization techniques. Notably the most important attribute of CL is the ability to extract depth resolved spectra. A simple model for this is given by Everhart and Hoff which studied the relationship between electron mean-free-path and energy.\(^{34}\) Using the Bohr-Bethe energy loss formula, \( N_d \) is Avogadro’s number, \( I \) is the \( Z \)-dependent mean excitation loss energy, \( \rho \) is the material density, \( A \) is atomic weight, \( Z \) is atomic number, and \( a = 1.1658 \):

\[
- \frac{dE}{ds} = (2\pi N_d e^4) \left( \frac{Z \rho}{A} \right) \left( \frac{1}{E} \ln \left( \frac{aE}{I} \right) \right)
\]

From this, one can calculate the Bohr-Bethe range and approximate this to:

\[
R^{E-H}_b = \frac{0.0398}{\rho} E_b^{1.75} (\mu m)
\]

Kanaya and Okayama (1972) have also proposed models that are accurate for elements with many atomic numbers\(^{35}\):

\[
R^{K-O}_e = \frac{0.276 A}{\rho Z^{0.889}} E_b^{1.67} (\mu m)
\]
Universally, Everhart and Hoff have proposed the following depth-dose equation:

\[ g(z) = 0.60 + 6.21z - 12.40z^2 + 5.69z^3 \]

CASINO\textsuperscript{36}, a Monte-Carlo simulation can give improved results over the previous models. This and its ease of use make it a powerful tool for determining CL depth profiles for materials and heterojunctions. CASINO simulates electron trajectories in these materials for electron energies equivalent to the CL method. It can also simulate x-ray emission, backscattered electrons, and lateral beam widening. This is important because electrons may penetrate through structures with large differences in atomic number. Reduction in the electron power density as a result could lead to inaccuracies in data comparisons. Below is a collection of CASINO models alongside predictions from theoretical models. It can be seen that there is strong agreement.

Figure 2.9: Theoretical electron energy loss as a function of incident electron energy (left). CASINO Monte-Carlo simulations of maximum depth of electron-hole pair generation with difference electron kinetic energies.

The generation rate for electron-hole pairs is:\textsuperscript{37}
\[ G = \frac{V_b I_b (1 - \gamma)}{eE_i} \]

\( V_b \) is the electron-beam voltage, \( I_b \) is beam current, and gamma is the fractional electron beam energy loss due to backscattering. To keep generation rates constant it is important to keep the product \( V_b I_b \) constant. This constant power condition must be met for accurate comparison of data at different depths.

Several limitations exist for CL for characterization of semiconductors. It is very important that the material have appreciable CL signal. In some cases the material may have an indirect gap or potentially contain large concentrations of non-radiative traps. It is also important that the electron beam cause insignificant time dependence of decay channels. It is possible in some systems to damage the semiconductor with prolonged bombardment of electrons. If this is the case, detailed experimental routines are necessary. Overall, CL is not a quantitative method and offers little information by itself the absolute concentration of defect states. When coupled with other techniques such as positron annihilation spectroscopy, deep level transient spectroscopy, and electron paramagnetic spectroscopy, it is possible to estimate the concentration of defects as extrapolated from the bulk to the near surface. ZnO is a material system that behaves well for CL characterization. It has been shown that ZnO exhibits moderate time effects and has strong CL signal due to its direct band gap.

It is important to carry out experiments at low temperatures (10K - 50K) as this offers many advantages including an increased signal-to-noise and reduction of thermal broadening of spectral features.\(^{38}\) Recombination through excitonic states is another
advantage of working at low temperatures. These states can bind to donors or acceptors and give information about the relative concentrations of impurities in the material.

In the EMNLab a JEOL JAMP-7800F UHV SEM electron beam is used as the excitation probe. This allows focusing up to resolutions of 5nm depending on the beam parameters. This joined together with SEM images allow for CL mapping. The electron beam passes through a hole in a parabolic mirror that sits atop the sample. This captures the luminescence and sends it through a quartz window to an Oxford MonoCL system for spectral filtering (diffraction grating) for a photomultiplier tube for intensity measurements. Liquid helium cooling is delivered to the stage, which can reach temperatures as low as 10K. For energies less that 1.4eV a high-purity germanium detector is employed. The ZnO region of interest lies between 1.5eV and 3.5eV.
CHAPTER 3
SCHOTTKY AND OHMIC CONTACTS

Schottky contacts play an important role in modern electronic devices. The Schottky diode is a simple rectifying device that exploits the potential barrier formed at some metal-semiconductor contacts. This device has several advantages over p-n junction diodes since majority carriers (electrons for n-type) control the operation of the device. This “majority carrier device” allows for fast switching times because the device response time is not limited by random recombination of minority carriers. These devices are used commonly in power converters, RF detectors and mixers. Optoelectronic uses of Schottky contacts include both metal-insulator-semiconductor and metal-semiconductor structures. These structures are employed in materials that necessitate low-temperature barrier formation (for low thermal budget devices), lack ion implantation of diffusion steps, grain boundary formation (for polycrystalline materials), semiconductors that exist in only one conduction type, and bare surface passivation of absorber material for increased short wavelength spectral response of photodiodes. Finally, the Schottky interface can replace dielectric gates to form metal-semiconductor field effect transistors (MESFETS), and Schottky barrier gate controlled charge coupled devices (Schottky Gate CCD). 40

35
3.1 Schottky Theory

A rectifying metal-semiconductor junction is known as a Schottky contact. The theory to its formation was proposed in 1931, although metal rectifying contacts were first reported in 1874. The basic model for barrier formation between a metal and a semiconductor is illustrated by figure 3-2. The potential barrier arises because of the difference between the metal work function (amount of energy required to remove an electron from Fermi level to vacuum) and the work function of the semiconductor. Before contact is made, the metal and the semiconductor energy bands show the difference in the Fermi levels. This difference, once contact is made, causes electrons to move from one material to the other until the Fermi level is constant throughout (a condition of thermal equilibrium). An example case is shown for an n-type semiconductor like ZnO and a metal with a work function $\phi_M > \phi_s$. According to this simple model, the barrier height is exactly the difference between the metal work function and the electron affinity as shown in the equation below. In the case depicted here, higher energy electrons flow from the semiconductor into the metal leaving behind ionized donors. This region devoid of charge carriers is called the depletion region and has a width $W_d$. This model suggests that there is a linear relationship between the work function of the metal and the barrier height for a given semiconductor. Not surprisingly however, this simple relationship does not hold for many semiconductor materials.\[41\]

$$\phi_B = \phi_M - \chi_s$$
3.2 Effect of Surface States

One modification to the Schottky model was made by Bardeen. This model suggests that the break in symmetry at the interface of the metal-semiconductor system could give rise to localized surface states. This is particularly important in covalent crystals, and may explain why there is some observance of the Schottky-Mott model in ionic crystals. The presence of surface states in a semiconductor can modify a barrier height by controlling the charge in the depletion region. If we assume that the states are distributed uniformly throughout the energy gap, we see that the level at which the states are filled when no band-bending is present is the neutral level $\phi_0$. Levels above $\phi_0$...
behave acceptor-like while levels below $\phi_o$ behave donor-like.\textsuperscript{42,43} Adsorbed layers of contaminant atoms can have a strong effect on the density of such states. The flat band condition for a semiconductor with the presence of surface states is a non-equilibrium state. Electrons must flow and occupy the states up to the Fermi level position. This causes a modification of the barrier height and results in band bending at the surface. If density of surface states is high, most of the charge transfer occurs within the surface states. This results in a barrier height independent of work function and the barrier is said to be “pinned”. Such observations are commonly made in metal-semiconductor contacts.

It has been suggested that semiconductor-metal interfaces can be divided into two categories, 1) covalently bonded semiconductors with a high density of surface states in the gap, and 2) ironically bonded semiconductors with few surface states.

Adsorbates can have a profound impact on Schottky barrier formation. Adsorbed species can donate electrons at the surface, create new states, or serve as an insulating interfacial layer. In ZnO, OH and C contamination can lead to a high surface charge density. This
can lead to band bending that can cause the Fermi level to increase to 0.3 eV above the conduction band. When a metal is deposited on this surface, the contact can form a quasiohmic barrier as shown below in fig. 3-3. This contact, due to the high concentration of carriers allows electrons to tunnel freely from the metal to semiconductor, neglecting any rectifying behavior.

Figure 3.2: Increased tunnelling produced by accumulation layer near the metal-semiconductor interface. This can result in quasiohmic contacts.

3.3 Tunneling through the Barrier

There are 3 basic mechanisms through which current can flow through a metal-semiconductor interface 1) thermionic emission, 2) recombination or generation and 3) tunneling. Thermionic emission over the barrier is what is dominant in an ideal Schottky diode. Much like a p-n junction, the electron current is created from diffusion, drift and emission over the barrier. The following relationship between current and voltage is given by the equation below. $I_o$ is the saturation current and is given by:

$$I_o = A A^* T^2 \exp\left(-\frac{q \phi_B}{k_B T}\right)$$
where A is the Richardson’s constant.

In the non-ideal case, modification to the current transport equation is shown by equation 2, where the quantity n is known as the ideality.

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

When doping concentrations are high, the Fermi level of the semiconductor can become close or even larger than the conduction band edge. This degenerate doping can lead to carrier emission through Schottky barriers by 3 methods: thermionic emission, field emission and a combination of both. Field emission occurs by transmission of the electrons through the barrier by tunneling. Thermionic-field emission occurs by transmission of thermally excited electrons tunneling through the barrier. A simple parameter, given in figure 10 can determine which method should dominate. If \( E_{oo} \ll kT \), then the contact should be characterized by thermionic emission, if the \( E_{oo} \gg kT \) then the contact should be characterized by field emission. When \( E_{oo} \sim kT \), we have the mixed case of thermionic-field emission. Whenever the transport mechanism is not thermionic emission, rectifying behavior deviates from the ideal case. Ideality factors of these contacts are large (n>>1) and exhibit large currents when operated in reverse bias. Most commercially available substrates contain donor concentrations of \( 10^{18} \), which predicts most Schottky interfaces on ZnO will conduct with thermionic field emission.
Figure 3.3: Three conditions for analysis of Schottky barrier contacts. Thermionic emission is the ideal case, thermionic field permits tunneling through thermal excitation, and field emission allows for tunneling at the Fermi level. This affects barrier height by increasing ideality above 2 and increasing reverse currents.
4.1 Plasma Processing

Plasma processing can functionalize surfaces of semiconductors in many ways to increase device performance and stability. One of the primary objectives of plasma processing is to remove contamination at the semiconductor surface. Plasmas can contain reactive species that impinge the surface and react with complex organic molecules. This breakdown of organics and solids into gases such as CO, H$_2$O, CO$_2$, O$_2$ and H$_2$ creates significant vapor pressures and then can easily be removed from the vacuum chamber. Incident species to substrates contain reactive neutral atoms and molecules, electrons, reactive ions, and photons in the IR, UV and visible spectrum. Depending on the desired process outcome, one or more of these can be selectively removed. Plasmas can be created by AC and DC sources either with capacitive or inductive methods in varying geometries. Traditional inductive geometries include a solenoidal coil and planar coil.
4.2 Basic Plasma Terminology

A plasma is a collection of free charged species consisting of electrons, ions, neutral atoms and radicals moving in random directions.\textsuperscript{44} The system itself is electrically neutral (quasi-neutral). Plasmas used for semiconductor processing are a subset of plasmas in general that have the following requirements: 1) The plasmas are produced electrically, 2) The particle collisions characterize the plasma dynamics, 3) surface dissipation is important, 4) the steady state is maintained by ionization of neutral species and 5) the electrons are not in thermal equilibrium with other plasma constituents. As shown in figure 4 below, plasma densities and temperatures can vary over orders of magnitude. Semiconductor processing is generally concerned with low pressure glow discharges although some high pressure arcs are used for refractory metal deposition. Figure 5 shows the energies of the various species vs. density. As one can see, the etching and cleaning constituents are much lower in temperature than electrons and bombarding ions. This is important to note when designing a plasma processing system. If the thermal
budget (e.g. amount of processing heat to disrupt device performance) of the device is low, it may be necessary to eliminate the high energy electrons and ions to reduce surface damage that would usually be removed by subsequent annealing steps.  

Figure 4.2: Electron densities and electron temperature for various plasma types. Most semiconductor plasmas operate in the region of glow discharges.

Figure 4.3: Energies of the components of plasmas. Electrons are the high energy component, with ions and neutrals causing the most damage to surfaces.
Plasmas etch, clean, and functionalize surfaces by creating radicals formed though bombardment of electrons that are typically at a much higher temperature than the ions. Therefore, it is the electrons rather than the ions that create the plasma conditions for functionalization, deposition or etching. Statistically, most electrons do not have enough energy to dissociate or ionize feedstock gases. However, there is a small distribution of electrons that do have the energies to ionize and dissociate. Ions, because of their high mass compared to electrons are useful in surface bombardment. This highly energetic treatment often changes morphology and is useful when sputtering from a surface and deposition occurs outside the plasma on a low-temperature substrate.

In semiconductor processing one of the most notable characteristics in plasma, besides the glow regions of recombination, is the creation of the plasma sheath. Sheaths are present anytime the plasma comes into direct contact with a grounded vacuum component. The sheath is a positively charged area of the plasma where the electric field is large and the potential approaches ground. Since electron velocities are much larger than the ion’s velocity, electrons can drift 100 times faster near grounded components than the ions, thus creating a positive depletion region or “sheath”. Ion dynamics in the bulk are determined by the density of the plasma. At high densities, the bulk plasma properties are characterized by diffusing ions, while at low pressures ion free-fall. For remote plasma processes it is this ion free-fall in regions of low electric field that is used for gentle surface cleaning and functionalization.
Figure 4.4: Plasma sheath formation and potential distribution in a capacitively discharged plasma.

There are 2 types of configurations for developing plasmas for material processing. Capacitive discharges are created by typical parallel plate geometries. The plasma sheath itself acts as the capacitive unit in the circuit. These plasmas can be activated by ac and dc current sources. Their primary use is in thin film deposition, where high energy ion bombardment is needed for sputtering of materials. Inductively coupled plasmas are created utilizing an inductive coil through which feedstock gases are pumped.

4.4 Remote Plasma Processing

In semiconductor processing a primary concern is ion-induced damage that could reduce product yield. Another concern is the thermal budget of the fabrication process. As device size diminishes and heterostructure and doping profile integrity become
important it becomes infeasible to remove ion induced damage by means of annealing steps. High annealing temperatures are important for surface reconstruction, to passivate defects, as well as creating a suitable morphology for interfaces. Remote plasmas were developed to remove processing from regions of intense electric fields, and at room temperature. Plasmas have an anatomy that consists of a direct “glow” region and an indirect “afterglow” area. The indirect region of the plasma is a region where electron-ion recombination occurs, but where non-equilibrium of recombination outweighs generation. In this region, the ions velocity is reduced, and hence the resulting substrate damage is reduced. Remote plasma processing is often called a room-temperature plasma or cold-plasma process. Some applications of inductively-coupled plasmas include thin-film deposition, removal of oxides and contaminants without morphological changes.

Below is a schematic of an inductive coupled plasma generation system. Substrates are often placed outside of the coil producing regions.

Figure 4.5: Standard remote plasma configuration for inductively coupled systems. The substrate is downstream and removed from the high energy ions thus reducing substrate damage.
Previous to this work, ZnO plasma processing research could be divided into a few main categories. Etching of ZnO for device applications, cleaning of surfaces to remove contaminations layers, preparation of functional surfaces for ideal Ohmic or Schottky contacts, and dopant control. All of these areas are important for creating stable, high quality optoelectronic devices. In subsequent chapters, attention will be focused on parameters that affect Schottky barrier contacts and their derived electronic devices. A brief introduction to Schottky contacts will be presented as well as applications of Schottky interfaces. Finally, important remote plasma chemistries for ZnO will be discussed.
CHAPTER 5

SHALLOW DONOR GENERATION IN ZnO WITH REMOTE PLASMA EXPOSURE

5.1 Background and Previous Work

Hydrogen incorporation in ZnO is an important factor when fabricating electronic devices. Although hydrogen is amphoteric in most semiconductors, it behaves as a shallow donor in ZnO.\textsuperscript{47} Shown below in fig. 5-1 are the band alignments of many compound semiconductors. It has been predicted that the hydrogen levels of all these materials can be aligned when band offsets are considered.

![Figure 5.1: Universally aligned hydrogen levels in selected semiconductors. From ref \textsuperscript{47}](image)

\textsuperscript{47}
This donor-like behavior of hydrogen in ZnO is one of the major hurdles in overcoming the persistent n-type conduction. Hydrogen is present during most types of crystal growth and fabrication processes. To achieve quality p-type material and control conduction in ZnO electronic devices, it is important to understand how hydrogen can incorporate ZnO. Figure 5-2 shows the formation energy of hydrogen in the ZnO lattice as a function of Fermi level position relative to the valence band edge. From this is obvious that hydrogen forms n-type material. When comparing the relative sizes of the Zn and O atoms, it is also apparent that hydrogen should be very mobile in the lattice.

Figure 5.2: Hydrogen formation energy as a function of Fermi level position (right).
Illustration of hydrogen in the ZnO lattice.

Remote plasma exposure of ZnO to hydrogen has revealed valuable information about the nature of hydrogen in ZnO. Not surprisingly, hydrogen ions are very mobile in ZnO. Secondary Ion Mass Spectrometry (SIMS) has revealed that hydrogen easily
incorporates into ZnO from remote plasmas. This mobility differs with crystal growth methods and the differences in diffusion coefficient derive from the interaction of hydrogen with trace impurities (most likely group III impurities) delivered in the growth process. Figure 5-3 shows the diffusion characteristics of hydrogen incorporated by plasmas:

![Figure 5.3: Diffusion profiles of hydrogen (left) and Arrhenius plot of hydrogen diffusion incorporated by remote plasma exposure.](image)

5.2 Experimental Details

The first type of ZnO sample included single crystals grown by a chemical vapor transport (CVT) at Eagle-Picher Technologies. These samples were cleaved from a nominally undoped wafer, then cut and polished normal to the c-axis. The second type of specimen were single crystal thin films (thickness 0.53 µm) of ZnO grown on sapphire by molecular beam epitaxy (MBE). Processing procedures for both types of samples will be described in the next section.
Photoluminescence spectroscopy (PL) experiments were conducted independently with two different setups. In the first case, the photoluminescence was excited with a HeCd laser and measurements were made at 2 K with the sample immersed in liquid helium. The spectra were analyzed with a high-resolution 4 m spectrometer equipped with an RCA C31034A photomultiplier tube for detection. In the second case, a HeCd laser was used. The sample was mounted inside an evacuated cryostat having a temperature range between 9 K and 300 K. A variable frequency chopper was employed to provide the reference signal. The PL signal was probed by an Oriel-257 grating monochromator having a spectral resolution of ~ 0.1 nm and detected by an S-20 photodetector. Hall-effect measurements were carried out in a Lake Shore Model 7507 Hall-effect System, operating over the temperature range \( T = 20\)–\(320\) K. Secondary Ion Mass Spectrometry (SIMS) experiments were performed on a PHI TRIFT III TOF-SIMS instrument.

Initially, Eagle-Picher CVT samples were annealed for 30 minutes in air at various temperatures.\(^{24}\) Subsequently, they were processed in a UHV chamber with a remote hydrogen plasma. In our experimental setup\(^{25}\), a high-grade hydrogen gas was supplied into a vacuum chamber from a Parker-Balston hydrogen generator through a needle leak-valve and a quartz tube inductively coupled with an Advanced Energy RFX-600 radio-frequency generator. The plasma flame inside the quartz tube was controlled by the flow rate and pressure of the gas and the power supplied by the RF generator. The hydrogen flow rate, the gate valve on the turbo pump, and the turbo pump speed determined the amount of plasma leaking into the chamber. We employed a remote H-plasma with the following parameters: 13 mTorr of pressure, flow rate 3 sccm, employing RF Power of
40 W and samples at room temperature. The samples were placed ~ 20 cm downstream from the plasma-generating coil, with the polar Zn surface facing the plasma. Low temperature (LT) PL and T-dependent Hall measurements were taken before and after each stage of processing.

5.3 Results and Discussion

Figure 5-4 shows LT PL spectra of the bound exciton (BEx) regions for the as-received, air-annealed at 500°C, 600°C and 700°C respectively, and subsequently hydrogenated CVT samples. Transformations of the emission line conventionally labeled as I$_4$ (photon energy ~3.363 eV at 4 K) yield the most important information. Several authors have argued in favor of attributing the I$_4$ to a neutral donor-BEx. $^{22,24,26-29}$ It seems very likely that the I$_4$-related donors are the shallow donors responsible for the predominantly $n$-type conductivity in otherwise undoped material. Moreover, there have been several recent attributions of this line directly to H-related donor. $^{3,4,30}$ As seen in Fig. 5-4a, after air anneal for 30 min. at 500°C, the relative intensity of I$_4$ line is reduced. This suggests that hydrogen starts diffusing out of the ZnO at this temperature, thus reducing the concentration of excitons bound to hydrogen impurities. One hour of remote H-plasma treatment partially restores the intensity of I$_4$, indicative of an increased number of H-centers for excitonic recombination.

Figure 5-4b demonstrates similar effects for the ZnO sample that was air annealed for 30 min. at 600°C. The I$_4$ line almost disappeared after annealing, consistent with more hydrogen outdiffusion from the host matrix). After two hours of hydrogenation, the pronounced I$_4$ peak reappears. A modest increase in I$_4$ as a shoulder is evident for the specimen annealed at 700°C (Fig.5-4c) following H-plasma treatment.
Figure 5.4: LT PL results for the air-annealed CVT samples in the near band edge region, $T = 4$ K. The BEx peaks shown are commonly observed for the as-received CVT material. (a) After anneal in air for 30 minutes at 500°C, the relative intensity of the $I_4$ line ($\sim 3.363$ eV) is reduced. One hour of remote H-plasma treatment partially restores the intensity of $I_4$. (b) After anneal in air for 30 minutes at 600°C, the $I_4$ line is very weak. Two hours of hydrogenation bring back the $I_4$. (c) After anneal in air for 30 minutes at 700°C, the $I_4$ line is not discernible. Three hours of hydrogenation restore a small shoulder at 3.364 eV.
Temperature-dependent Hall measurements were performed on the air-annealed samples before and after hydrogenation in order to extract carrier concentrations and activation energies. Figure 5-5 illustrates those measurements for the 500°C air-annealed sample. It is clear that there is no significant change following hydrogenation. Similar results were produced by the samples annealed at different temperatures. At the same time, fitting of the T-dependent data showed that the positions of the two shallow donor levels didn’t change after hydrogenation and were close to those reported by Look et al. 1. This absence of bulk effects in the Hall results is not surprising since the penetration depth of hydrogen into ZnO is small compared with the thickness involved in the Hall measurement. In the SIMS studies by Ohashi et. al 31 on direct H-plasma treated ZnO CVT samples, the hydrogen insertion depth was measured to be only ~ 30 nm, quite small compared to the thickness of the wafer (~ 0.5 mm). Thus, in order to detect any variations due to hydrogen, the volume of hydrogenated ZnO must be significant compared with the Hall channel. One approach to achieve this is to reduce the initial carrier concentration of the entire crystal by rendering the bulk single-crystal sample semi-insulating. An alternative approach is to reduce the layer thickness of the semiconductive ZnO so that it is comparable to the insertion depth of hydrogen.
Figure 5.5: Hall results for the air annealed at 500°C/hydrogenated CVT sample. Average bulk carrier concentration (a) and mobility (b) seem to be insensitive to the remote hydrogen plasma treatment.

We employed Li doping of the CVT material to produce semi-insulating ZnO samples. The Li diffusion was carried out by positioning the sample on top of a 2-cm-high open quartz tube, placing LiOH powder in the bottom of the tube, and then heating the whole assembly in a furnace at 800°C. After Li processing, no Hall parameters were observable due to the semi-insulating nature of the material. This sample was treated in a remote H-plasma for one hour. Hydrogenation restored measurable conductivity and the Hall coefficient. Figure 5-6, displays sheet carrier concentration $n_0$ (a) and mobility $\mu$ as a function of temperature (b). An ultra-shallow SIMS depth profile was taken on the Li-
doped/hydrogenated ZnO specimen. As shown in Fig. 5-7, the H insertion depth in the case of a remote plasma is ~10 nm, which is somewhat smaller than that for the samples treated with direct plasma. This can be easily explained by the fact that the direct plasma effectively heats up the surface, thus promoting hydrogen diffusion to a greater depth.

Figure 5.6: Sheet carrier concentration (a) and mobility (b) for the Li-doped CVT sample after hydrogenation. Hall parameters were unobservable before H-plasma treatment since Li treatment makes ZnO semi-insulating.
Bearing in mind the measured Hall sheet carrier concentration of \(10^{14}\) cm\(^{-2}\) for the Li-doped sample (Fig. 5-6a) and the measured H insertion depth (~10 nm) (Fig. 5-7), one finds that the suggested donor concentration at room temperature is at least an order of magnitude higher than the known volume density of \(10^{17}\) cm\(^{-3}\) before Li diffusion. The rather weak temperature dependence of \(n_d\) in Fig. 5-6a is consistent with this higher volume concentration compared with the bulk sample in Fig. 5-5a. The lack of significant change in the Hall curves of Fig. 5-5a is understandable since the remote plasma is capable of creating additional sheet concentration only slightly greater than \(10^{14}\) cm\(^{-2}\), while even in the annealed samples the sheet carrier concentration associated with the bulk donors is almost \(10^{16}\) cm\(^{-2}\).

We performed LT PL measurements on the Li-doped/hydrogenated ZnO sample before and after each processing stage. The results are shown in Fig. 5-8. After Li diffusion, the \(I_4\) line is absent. We argue that this may be the result of either H outdiffusion due to high processing temperature or the Li-passivation of the donors, or both. Subsequent H-plasma treatment restores a conspicuous shoulder at ~ 3.364 eV where the \(I_4\) was expected. This shoulder is similar to the one seen in Fig.1c, where the annealing temperature was close to the Li-indiffusion temperature. In Figs. 5-6 and 5-8, the weakness and broadening of the \(I_4\) emission may be explained by the fact that its PL signal is coming only from the topmost layers of the surface (~ 100 nm) where the quality of the material is inferior to that of the bulk.
Figure 5.7: H\textsuperscript{1} SIMS depth profile of the Li-doped CVT sample after H-plasma treatment. The insertion depth of hydrogen is \(\sim 10\) nm.

The results for the Li-doped/hydrogenated sample are consistent with a new donor being added by the hydrogenation, rather than an alternative explanation in which the Li would simply deplete near the surface and “re-expose” the existing donors. Indeed, our SIMS measurements of the average surface Li concentration show no such depletion. Furthermore, the mobility is lower than that before Li diffusion, which is consistent with a larger donor concentration as well as the additional acceptors introduced by the Li.

The second approach in altering the Hall experiment geometry was to use a thin ZnO film on an insulating substrate. This scheme was realized with a 530 nm thick, high quality ZnO single crystal MBE-grown on sapphire. Hall measurements were performed before and after hydrogenation (see Fig.6). One can see that hydrogen plasma increases
free electron concentration by at least an order of magnitude in the entire range of temperatures. This effect may be even more extensive if one accounts for the shallow, e.g., ~ 10 nm, hydrogen insertion depth. In the LT PL spectra, the original line width of the BEx features was too great to discern changes occurring with hydrogenation. In this case, the concentration of shallow donors introduced by H-plasma treatment is much higher than the bulk concentration of the as-received epitaxial film. For this sample, however, as opposed to the Li-doped sample discussed above, we are able to observe a direct electronic change due to the introduction of hydrogen donors.
Figure 5.8: LT PL results for the Li-doped CVT sample in the near band edge region, T = 10 K, incident power = 0.2 W/cm². After Li-diffusion treatment, the I₄ line is suppressed. Subsequent H-plasma treatment broadens the bound-exciton emission and restores a shoulder at ~ 3.364 eV.
Figure 5.9: Hall results for the epitaxial film on sapphire: (a) average bulk carrier concentration; (b) mobility. Remote hydrogen plasma treatment increases free electron concentration by at least an order of magnitude in the entire range of temperatures.

Figure 5.10: AFM images of hydrogen exposed single crystals. Before treatment the ridges due to the misalignment of the crystal plane and polishing plane (left). After treatment the appearance of micropits dot the surface. This indicates that remote hydrogen plasma can create surface damage. [From ref xxxiv].
CHAPTER 6

OHMIC TO SCHOTTKY CONVERSION OF Au CONTACTS TO ZnO USING REMOTE OXYGEN PLASMA

6.1 Motivation

Remote oxygen plasma treatments on ZnO substrates have been extensively studied. For stable plasma conditions it is necessary to have a 20%/80%He ratio, although the active feedstock is oxygen. This processing step was originally developed to dissociate contaminants such as organics, carbon and hydroxide on Silicon, however the process is extremely beneficial when used on ZnO. Carbon contamination and hydroxide creates degenerately doped n-type surfaces at the ZnO surface. Investigations by photoelectron spectroscopy indicate that the Fermi level at the surface can extend 0.3 eV into the conduction band that can lead to degrade the quality of Schottky contacts by increased tunneling. Contaminants can also create interfacial layers that can impede the creation of an abrupt metal-semiconductor interface. As studies continued and oxygen plasma treatment became a standard processing technique, further beneficial details emerged about the nature of the process that contamination removal was insufficient in describing Schottky contacts to ZnO.
Several studies have addressed various possible fundamental mechanisms affecting SB performance in ZnO, but none have considered the role of both the surface and subsurface. Thus, while several studies have proposed that surface morphology, hydroxide (OH) and carbon surface contamination play a dominant role, none have considered the role of sub-surface defects and impurities that could alter local carrier concentrations, depletion widths, and tunneling. Here, we address all these mechanisms using a combination of ultrahigh vacuum (UHV) surface and subsurface characterization and processing techniques.

6.2 Experimental Setup

Single crystal ZnO samples were grown by chemical vapor transport at Eagle-Picher Inc. (E-P) and polished on both the (0001) Zn and (000¯) O faces. We used samples of two grades: “high quality” material with relatively smooth surfaces (rms roughness ~0.1 nm) and low “green” defect (GD) luminescence versus “lower quality” ZnO with rougher surfaces (rms roughness ~5 nm), micropits, and approximately two times higher GD luminescence. We also used single crystal ZnO samples grown by a pressurized melt growth process at Cermet Inc. with rms roughness ~ 2.0 nm and relatively high GD luminescence. All samples were chemically cleaned with a 5-minute ultrasonic bath in acetone, toluene, dimethylsulfoxide, methanol and deionized water and then blown dry with nitrogen gas. Au circular contacts ~ 0.5 mm in diameter were deposited in a UHV-chamber by thermal evaporation from a tungsten filament through a shadow mask for both plasma-exposed and unexposed samples. ZnO crystals at room temperature were processed in situ with remote 20% oxygen-80% helium mix plasma
inductively produced by an rf generator operating at 30W, with a pressure of 10mTorr. The remote oxygen plasma permitted independent control of temperature and pressure. Both plasma-exposed and unexposed samples were characterized in situ with cathodoluminescence (CL), x-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). Ex situ atomic force microscopy (AFM), low temperature photoluminescence (LT PL), as well as I-V, and C-V measurements were also performed before and after plasma exposure. More detailed descriptions of the experimental setups appear elsewhere.\textsuperscript{14}

6.3 Results and Discussion

All Au-ZnO contacts formed without prior oxygen treatment exhibited ohmic transport characteristics. We found that ZnO exposure to the remote O/He plasma for 1 hour or more consistently changes Au contacts on ZnO from ohmic to rectifying regardless of surface polarity and material quality. Various oxidation treatments reported previously\textsuperscript{1,9,11,12} also report similar effects but attribute them to widely different mechanisms. Figure 6-1 illustrates this ohmic-Schottky conversion for different material grades and polarity. Corresponding C-V experiments (not shown) agreed with the I-V SB heights of 0.42-0.5 eV once image force lowering was taken into account. Figure 1b shows that gradual ohmic-to-Schottky-like I-V changes take place between 0, 30, and 60 min. room temperature plasma exposure. Cermet ZnO I-V changes (not shown) also vary within this exposure range, ranging from ohmic (0 min.) to \sim 0.4 eV SB and high ideality $n = 5$ (30 min.) to 0.5 eV SB with $n = 2$ (60 min.). The high ideality values calculated indicate that field emission and recombination contribute to the measured current
transport. Both direct and trap-assisted tunneling can occur and are affected by the carrier concentration and barrier shape as well as the concentration of tunneling-mediating defects.

Figure 6.1: I-V characteristics for remote plasma-exposed and unexposed E-P samples. (a) 1 hour exposure of the (000\text{I}) surface produces a SB of 0.5 eV with an ideality $\sim 2$ for the lower grade material. (b) The same transition occurs for a 1 hour exposed sample of higher quality with a calculated SB height of 0.42 eV and ideality $> 8$, however a 30 min. exposure indicates an ohmic behavior. (c) Higher quality (000\text{I}) surfaces change from ohmic to rectifying after 1 hour plasma treatment with 0.5 eV SB and $\sim 5$ ideality.
XPS results are given in fig. 6-2 for the unexposed and a 60 min. plasma-exposed sample. The OH/lattice oxygen ratio decreases from ~ 2.9 before exposure to ~ 0.3 (cylindrical mirror analyzer precision ±10-20%) after exposure, indicating almost complete removal of OH from the surface (fig.1a). Previous work\textsuperscript{9,11} suggested OH contamination on polar ZnO surfaces as the primary factor degrading rectifying contact performance: high surface OH can create a surface conductive accumulation layer that oxygen plasma removes, lowering the Fermi level $E_F$ into the band gap, resulting in a rectifying contact. Our post-treatment rigid O 1s and Zn 2p core level shifts (figs.6-2a, 6-2b) of 0.74±0.05 eV toward lower binding energy indicate n-type (upward) band bending, consistent with accumulation layer removal and similar to previous results.\textsuperscript{9,11} The O/He plasma also produces an apparent increase in oxygen near-surface composition, increasing the O/Zn ratio from 1.04 to 1.15 after plasma exposure. Since oxygen deficiency-related defects within the band gap could provide a mechanism for charge hopping, reduction of this deficiency would decrease possible tunneling through the SB. Figure 6-2c shows a removal of the C 1s peak, consistent with previous studies.\textsuperscript{9,11} A 30 min. plasma treatment of Cermet ZnO polar surfaces also results in C removal, negligible OH, and > 0.5 eV n-type band bending, indicating removal of any adsorbate-induced surface accumulation. However, the continued change in ohmic-to-Schottky behavior beyond this 30 min. exposure demonstrates that more than C and OH adsorbates are involved, implying that sub-surface electronic changes also play a role in the SB formation.
Figure 6.2: XPS results before and after 1 hr. 20% O\textsubscript{2}/80% He plasma treatment (low grade E-P sample). (a) Plasma treatment removes the (deconvolved) OH peak and shifts the O 1s peak rigidly by 0.74 eV, as well as the Zn 2p peak in (b), indicating n-type band bending. (c) The C 1s peak disappears after plasma treatment, leaving only a Zn Auger shoulder, indicating removal of adsorbed carbon.

\textit{In situ} LEED experiments shown in fig 6-3 revealed slight improvement of the hexagonal pattern subsequent to plasma treatment and adsorbate removal, consistent with clean atomically-ordered surfaces. AFM measurements indicated insignificant damage produced by the remote plasma. Evidently, this did not affect substantially the transport properties of the contacts.
Figure 6.3: Low energy electron diffraction (LEED) indicating clean ordered surface.

Depth-resolved CL spectra for both unexposed and exposed (000\̅1) ZnO in fig. 6-4 indicate electronic changes below the free surface. Typical spectra include a near band edge (NBE) 3.3 eV emission and a broad 2.5 eV GD emission often attributed to oxygen deficiency.\(^{15}\) Figure 3 shows that GD emission is dominant at the surface. This behavior is independent of the surface polarity and material quality. The ratio of the integrated green vs. NBE intensities increases by a factor of 2 at the surface and levels off to a constant value into the bulk at ~ 25 nm. After 1 hour of plasma exposure, the sample exhibits a 50% decrease in GD emission intensity, suggesting defect passivation or removal. Both high and low grade ZnO exhibit this effect. However, the higher quality ZnO required longer exposure time to achieve similar 50% GD intensity reduction (e.g., 30 min. plasma treatment produced only insignificant changes). If one assumes that the suppression of the GD emission is associated with the reduction in oxygen deficiency (independently confirmed by our XPS measurement) then we have an indication of removal of potential tunneling-promoting defects.
Figure 6.4: CL Spectra for treated and untreated E-P samples of a lower grade. (a) Relative CL intensity for the 2.5 eV (“green”) emission, often attributed to oxygen vacancies, decreases with increasing electron beam energy. All spectra are normalized to NBE. (b) The integrated peak intensity ratio (GD/NBE) vs. electron beam energy indicates a factor of 2 increase in GD defect concentration within 25 nm of the surface. After a 1 hr. exposure, the intensity decreases by 50%, indicating GD partial removal or passivation.
LT PL spectra were acquired before and after an hour of exposure to remote plasma (Fig. 6-5). The intensity of the peak with the photon energy of ~ 3.363 eV (commonly designated as $I_4$) is dramatically reduced after the plasma treatment. This reduction occurs for both polar faces, regardless of sample grade. There is strong evidence in favor of attributing the $I_4$ emission to a neutral hydrogen donor bound exciton,$^{16}$ recently demonstrated both optically and electronically.$^{17}$ The reduction of the $I_4$ peak by plasma treatment indicates removal of hydrogen attributed to this peak. Hydrogen may play an important role at the Au/ZnO interface as a shallow donor,$^{18}$ narrowing the depletion region or even forming an accumulation layer, both acting to lower the effective SB. Thus increased donor concentrations of ~ $2 \times 10^{18}$ cm$^{-3}$ correspond to depletion widths of only 100 Å or less.

Figure 6.5: PL spectra taken at 9 K in the bound exciton region for the (000$\bar{1}$) polar ZnO high grade E-P surface. The $I_4$ line attributed to hydrogen as a shallow donor in ZnO is significantly reduced after a 1 hr. plasma exposure.
Figure 6.6: XPS Shake-up lines reduced indicating a reduction in charged species. This is consistent with removal of oxygen vacancies.
Figure 6.7: Effect of oxygen plasma on as-received Au-ZnO contacts depicting the Ohmic to Schottky transition. In a subsequent step the sample is exposed with a hydrogen plasma, converting the contacts to Ohmic.
CHAPTER 7

NITROGEN PLASMA PROCESSING AND CODOPING IN ZnO

7.1 Motivation

Along with oxygen and hydrogen the influence of nitrogen is of particular importance because its potential as a p-type dopant, with relatively small atomic size compared to other dopants like P and As. Concerns around N arise because of the relatively deep acceptor level and possible compensation effects, . However, codoping schemes using N and other elements like Li, Ga and H have been suggested, , , . Of these Li and H are important because of the ability to remove these species after incorporation to activate the acceptors remaining. In our investigations of these plasmas with nitrogen, hydrogen and oxygen we illustrate the effects of incorporation of these species and the differences their subsurface modification has on Fermi level position, band bending and Schottky barrier (SB) formation.

7.2 Experimental Setup

We examined single crystal ZnO substrates grown by seeded chemical vapor transport chemomechanically polished on both Zn and O-polar surfaces. Atomic force microscopy of these samples indicated a smooth surface with rms roughness of 0.2nm.
These samples were from two batches produced by the same vendor with different donor concentrations. Sample A and Sample B had an initial donor concentration of $10^{17}$. The samples were processed by a remote inductively coupled plasma described elsewhere. Prior to plasma processing, the samples were chemically cleaned with a 5 min ultrasonic bath in acetone, toluene, dimethylsulfoxide, methanol, deionized water, then blown dry in flowing nitrogen.

The plasma processing of the samples were dived into 3 steps. Step 1, a 20% O2-80%He plasma (ROP), at a pressure of 10mTorr and power of 30W was used to remove surface contamination and reduce the subsurface point defect concentrations for one hour. Step 2, a 50%N2-50%H2 plasma (RNP) was used for codoping the near surface region to a depth of ~150nm. This processing pressure was 10mTorr and a power or 40W for 2 hours. Finally, step 3 an identical ROP was used to remove any excess hydrogen that was incorporated in step 2. After each processing step, circular Au contacts of diameter ~0.5mm were deposited using thermal evaporation from a filament through a mechanical shadow mask. X-ray photoelectron spectroscopy measurements (XPS) were acquired after each step to determine surface composition and relative Fermi level changes when compared to the starting point before step 1. This repeatable series of processing, evaporation, and photoelectron measurements were done in a connected ultrahigh vacuum system without intervening air exposure. Current-voltage curves were obtained ex situ for Schottky barrier and ideality factor calculations using thermionic emission analysis. Thin films of ZnO grown by RF sputtering on glass were also exposed to the same 3 steps of plasma processing and characterized with room temperature hall measurements to determine their resistance.
7.3 Results and Discussion

As shown in fig 1(a), XPS measurements of the O 1s, Zn2p, and the N 1s core levels were obtained before and after each plasma processing step. These core levels were then fitted and aligned to Au core levels. The Fermi level movement was calculated using the rigid core-level shifts of the O1s and Zn 2p spectra, independent of chemical core-level shifts. The Fermi level change is plotted in fig 1(b), and is measured from the starting position of the AR (unprocessed) core levels. As shown before a one hour room temperature ROP can cause a Fermi level shift of ~1.1eV toward lower binding energy. This is consistent with the removal of OH surface contamination, reduction in subsurface defects, and removal of hydrogen. This was observed independent of sample, however there was a significant contribution to the polarity of the surface. Step 2 XPS measurements reveal that a RNP containing equal parts of hydrogen and nitrogen create no Fermi level change. It is important to note, that when the nitrogen or hydrogen components are added separately the core-level shifts return to their AR positions, but that when added together create no additional change from step 2 processing. Step 3 varies slightly with sample, and may depend on the relative differences in initial donor and acceptor concentrations. XPS data reveals that Fermi level shifts occur for the near surface region from -0.5eV to -1.0eV from the unprocessed position. Therefore the total Fermi level shift from unprocessed to the end of step 3 can be as substantial as 2.2eV. It is unclear with our XPS system where the Fermi level position starts relative to the conduction band, however a 2.2eV shift would have a profound impact on the electrical characteristics of the near surface. In order to better understand the nature of the Fermi level changes, an addition processing step was performed using a pure hydrogen plasma
for 2 hours and the same plasma parameters as the RNP, excluding the nitrogen. XPS measurements for sample B show that the Fermi level returns to within 0.3 eV of its unprocessed position. This is consistent with creation of hydrogen related donors. XPS spectra of the Zn-2p core level is shown in fig 2a; this spectra is aligned to Au peaks and is corrected for any chemical shifts. Figure 2b reveals the presence of nitrogen that is incorporated on the surface of ZnO during the RNP in step 2. Hall measurements of the sputtered thin films revealed that after an initial resistivity of 1.9x10^6 ohm-cm for the unprocessed sample, the resistivity increased after step 1 to 1.7x10^6 ohm-cm, which is consistent with the Fermi level change measured by XPS. After step 3, the samples were too resistive to measure to any certainty. Au contacts deposited on the (0001) surface of sample A as shown in fig 2, are ohmic for the unprocessed sample. After step 1 the Au contacts deposited are rectifying with a SB of 0.53eV and an ideality of 2.5, consistent with thermionic-field emission. After step 2, contacts deposited are weakly rectifying, however after step 3, contacts deposited show a intense improvement, with an SB of 0.7eV and ideality lowered to 1.24. Furthermore, the reduction in reverse current is striking, which decreases ~4 orders of magnitude from step 1. These results are consistent with the formation of an intermediate layer that may reduce the amount of tunneling across the Au-ZnO interface.
Figure 7.1: Remote inductively coupled plasma processing steps and a plot of their effects on the Fermi level position when compared to the unprocessed sample (AR). Step 1- remote oxygen plasma (ROP) removes surface contamination and reduces point defects in subsurface. Step 2 introduction of nitrogen and hydrogen to increase solubility of N dopant acceptors. Step 3 removal of hydrogen to activate N acceptors. This is a plot of rigid core level shifts not associated with chemical changes.
Figure 7.2: X-ray photoelectron spectroscopy of the Zn-2p core level is shown in a) after each plasma processing step and in b) the addition of nitrogen to the surface of ZnO.
Figure 7.3: Current voltage (IV) curves after each plasma processing step for circular Au contacts of 0.5mm diameter. The unprocessed sample yields an Ohmic contact. After an ROP, the a rectifying contact is deposited. Step 2 creates a weakly rectifying contact, while step 3 raises the SB to 0.7eV, lowers the ideality to 1.24 and reduces the reverse current ~4orders of magnitude. This is consistent with removing donors in the subsurface and reducing the tunneling contributions with an increased depletion region width.

In summary, we report the ability to control the Fermi level position and band bending at the near surface. We use a 3 step process in which we remove surface contamination and oxygen vacancies, introduce nitrogen and hydrogen together, and remove excess hydrogen donors. Our results are consistent with creating an insulating layer by codoping with hydrogen and nitrogen, and reducing the tunneling contributions in rectifying metal contacts on polar ZnO surfaces.
CHAPTER 8

METAL-ZnO INTERFACE CHEMISTRY

8.1 Experimental Setup

We examined both melt-grown and hydrothermally-grown single crystal substrates of ZnO. The surfaces were chemomechanically polished by their manufacturer. All substrates were subjected to a standard rinse for 5 minutes each in acetone, toluene, dimethyl-sulfoxide, methanol and deionized water, after which the samples were blown dry in nitrogen. One set of samples from each vendor were subjected to a 20% O₂/80% He remote inductively coupled plasma (RICP) with a background pressure of 10 mTorr. Gas concentrations were maintained with mass flow controllers, and were mixed before entering the process chamber. The RF plasma power was maintained at a constant 33 watts. The RICP-treated samples were processed for one hour, then 0.4 mm diameter circular contacts were electron-beam-deposited through a shadow mask to a thickness of 30 nm. These contacts are thin enough to permit detection of luminescence through the diodes. We produced both in-situ and ex-situ contacts for each vendor’s ZnO and each surface process. X-Ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were previously used to verify clean ordered surfaces for metal deposition. Atomic force microscopy (AFM) shows that the RICP process does not
damage the surface of the material, and depth-resolved cathodoluminescence spectroscopy (DRCLS) indicates that the process reduces defect related luminescence in the near surface region. AFM shows a mild increase of rms surface roughness from 0.1 nm to 0.2 nm while DRCLS reveals the reduction of point defect luminescence by a factor of 5.0.

We performed current-voltage (I-V) measurements following DRCLS studies using a HP 4100 Semiconductor Analyzer. Capacitance-voltage (C-V), deep level transient spectroscopy (DLTS) measurements, and deep level optical spectroscopy (DLOS) as described elsewhere were performed on Schottky diodes.

DRCLS spectra were taken using a JEOL 7800F ultra-high vacuum (UHV) scanning electron microscope (SEM) (fig.1(a)). A parabolic mirror connected to a photomultiplier collected the luminescence. The sample was cooled with 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. The SEM electron beam was varied with constant power from 2 keV to 20 keV with a maximum spot size of 50nm. DRCLS were acquired though the metal diode and on the free surface as shown in figure 1(b). Transmission measurements were carried out that indicated negligible light absorption in the 1.8-3.0 eV region of interest. Monte Carlo simulations of electron energy loss and electron-hole (e-h) pair creation were calculated to determine the electron beam penetration through the metal and into the bulk crystal. For electron beam energies $E_B = 1, 2, 5, 10,$ and $20$ keV, depths of peak e-h pair excitation rate $U_0$ were $10, 20, 75, 220$ and $370$ nm, respectively. In general, these results indicated that both a 2 keV beam
at the free surface and a 5 keV beam through the 30 nm metals both penetrate ~ 25 nm into the ZnO. All measurements were performed on arrays on eight diodes for each metal, all on the same ZnO-processed surface.
8.2 Results and Discussion

DRCLS measurements of ZnO revealed pronounced deep level emissions that varied strongly with growth method, surface preparation, and subsequent metallization. A DRCLS survey of ZnO single crystals grown by hydrothermal, melt-grown, chemical vapor transport and molecular beam epitaxy showed orders of magnitude difference in crystal quality in terms of the magnitude of near band edge (NBE) and deep level (DL) emissions as well as their uniformity with depth. Pronounced differences are observed even within growths from the same vendor. This paper will address effects of bulk and metal-induced defects for representative “high defect” and “low defect” ZnO material. Thus Figure 2 illustrates DRCLS spectra from a “high defect” (a) vs. a “low defect” ZnO(000\(\bar{1}\)) surface. The “high defect” ZnO exhibits broad DL emissions at approximately 2.1, 2.5, and 3.0 eV in addition to some excitonic features in the NBE region. These DL emissions are comparable to or higher than NBE intensities and vary by orders of magnitude with \(E_B\) and excitation depth. In contrast, the “low defect” ZnO
exhibits many orders of magnitude higher NBE/DL intensity ratio and much more uniformity vs. depth. The distinct series of LO phonon replicas in Fig. 2(b) are an additional indication of high crystal quality.

Figure 8.2: Comparison of DRCLS spectra vs. excitation depth for relatively high (a) and low (b) deep level defect ZnO(000\text{\textbar}) bare surfaces. “High defect” ZnO exhibits subsurface defect emissions at 2.1, 2.5 and 3 eV that exceed NBE emission and vary by orders of magnitude vs. depth over a 10-400 nm range. “Low defect” ZnO exhibits orders of magnitude lower deep level emission and greater uniformity over the same depth range.

Previously we showed that RICP treatment of ZnO surfaces removes surface adsorbates, removes hydrogen, and reduces deep level emissions at depths tens to hundreds of nm below the surface. Figure 3 illustrates the effects of RICP treatment on DL intensities vs. depth and I-V curves. In Fig. 3(a), the ratio of 2.5 eV “Green” DL vs. NBE intensities $I(2.5 \text{ eV})/I(NBE)$ decreases with increasing $E_B$ and
excitation depth. After a 30 min. RICP exposure, these ratios decrease by a factor of 3 and all surface carbon and hydroxide is removed. After a 60 min. RICP exposure, I(2.5 eV)/I(NBE) decreases even further. Figure 3(b) shows the corresponding I-V curves. The as-received (AR) surface exhibits straight-line, Ohmic behavior. With a 30 min. RICP exposure, a SB with $\Phi_B = 0.4$ eV and ideality factor $n > 5$ is obtained. With 60 min. RICP exposure, $\Phi_B$ increases to 0.5 eV and $n$ decreases to 2.0. Thus defect removal improves SB characteristics substantially even after surface contamination is removed.

![Figure 8.3](image_url)

**Figure 8.3:** (a) $I(2.5 \text{ eV})/I(\text{NBE})$ vs. $E_B$ for as-received, 30 min. and 60 min. RICP exposure showing increase near surface and overall decrease vs. RICP exposure time. (b) Corresponding I-V curves showing transition from Ohmic to Schottky behavior with increasing RICP treatment time.

The concentration and distribution of defects below the ZnO(0001) surface varies dramatically between vendors. Figure 4 (a) illustrates $I(2.5 \text{ eV})/I(\text{NBE})$ vs. depth for specimens grown from the melt (a) vs. vapor phase transport, (ZN Tech) and (b). Here
the I(2.5 eV)/I(NBE) ratios vary by orders of magnitude and are labeled “high,” “medium,” and “low defect” accordingly. Figure 4 (b) illustrates log I-V characteristics for Au diodes deposited on these specimens subsequent to RICP treatment. “High defect” diodes exhibited high reverse currents and a $\Phi_B = 0.43$ eV. “Medium defect” diodes showed similar reverse currents and a slightly higher $\Phi_B = 0.5$ eV. “Low defect” ZnO diodes displayed reverse currents two orders of magnitude lower and the highest SB, $\Phi_B = 0.60$ eV. In general, higher defect densities result in higher reverse leakage currents and lower barriers for the same metal diode.

Figure 8.4: (a) High, medium and low ZnO I(2.5 eV)/I(NBE) vs. $E_B$. (b) log I-V curves for the corresponding Au diodes. Reverse leakage current increases and SB decreases with increasing defect ratio.

The RICP treatment affects not only the ZnO(000\bar{1}) near surface chemistry and defect concentrations, but also the types and intensities of defects under metal contacts. Figure 5 illustrates DRCLS spectra for Au, Pt, Pd, Ir, Al, Mo, Ni and Ta on both as-received (AR)
(a), i.e., unprocessed, versus RICP-treated (b) surfaces. Without processing, all metals appear to yield qualitatively similar spectra with defect emission at 2.1 eV exceeding NBE intensities by more than an order of magnitude. Significant deep level emission is also evident at ~ 3 eV in all cases. In contrast, RICP-treated ZnO(000\bar{1}) spectra exhibit orders of magnitude NBE emission and substantial differences between metals. In particular, 2.1, 2.5 and 3 eV emissions appear to vary significantly depending on the metal.

Figure 8.5: DRCL spectra with $E_B = 5$ keV obtained through diodes of the metals indicated, all on the same AR (a) vs. RICP-treated (b) ZnO(000\bar{1}) surface. The AR spectra are relatively independent of metal, in contrast to the RICP-treated surface spectra.

The RICP treatment also has a dramatic effect on the Schottky barriers for these metals. Figure 6 shows log I-V characteristics for Au, Pd, Pt, and Ir for AR vs. RICP-treated surface diodes with the same “high defect” ZnO crystal. As already presented, the
Au diodes were Ohmic prior to plasma treatment but had $\Phi_B = 0.43$ eV and $n = 3.7$ for the plasma-treated surface. Similarly, Pt diodes were Ohmic for AR surfaces but showed $\Phi_B = 0.42$ eV and $n = 3.45$ for the RICP-treated surface. Pd diodes had $\Phi_B = 0.49$ eV and $n = 1.48$ before RICP treatment and $\Phi_B = 0.70$ eV and $n = 1.5$ after RICP processing. Finally, the AR diodes for Ir showed $\Phi_B = 0.65$ eV and $n = 2.42$ (AR) versus $\Phi_B = 0.69$ eV and $n = 1.58$ post RICP. In each case, $\Phi_B$ increases and $n$ decreases with RICP cleaning and defect reduction. The corresponding $\Phi_B$s and ideality factors for “low defect” material are summarized in Table 1. Similarly, $\Phi_B$s and ideality factors for “low” vs. “high defect” material are summarized in Table 2.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Process</th>
<th>Schottky Barrier</th>
<th>Ideality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>As-received</td>
<td>0.46</td>
<td>1.56</td>
</tr>
<tr>
<td>Au</td>
<td>1Hr He-O² RICP</td>
<td>0.48</td>
<td>1.30</td>
</tr>
<tr>
<td>Ir</td>
<td>As-received</td>
<td>0.54</td>
<td>1.66</td>
</tr>
<tr>
<td>Ir</td>
<td>1Hr He-O² RICP</td>
<td>0.64</td>
<td>1.36</td>
</tr>
<tr>
<td>Pt</td>
<td>As-received</td>
<td>Ohmic</td>
<td>NA</td>
</tr>
<tr>
<td>Pt</td>
<td>1Hr He-O² RICP</td>
<td>0.39</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 8.1 Low defect ZnO Schottky barrier heights and ideality factors for Au, Ir, and Pt before and after 1 hour O2 plasma treatment. In general, RICP treatment raises barriers and lowers ideality factor.
Low vs High Defect ZnO Substrates

<table>
<thead>
<tr>
<th>Metal</th>
<th>Process</th>
<th>Defect Level</th>
<th>Schottky Barrier</th>
<th>Ideality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1Hr He-O(^2) RICP</td>
<td>High</td>
<td>0.43</td>
<td>3.57</td>
</tr>
<tr>
<td>Au</td>
<td>1Hr He-O(^2) RICP</td>
<td>Low</td>
<td>0.48</td>
<td>1.30</td>
</tr>
<tr>
<td>Ir</td>
<td>1Hr He-O(^2) RICP</td>
<td>High</td>
<td>0.65</td>
<td>2.62</td>
</tr>
<tr>
<td>Ir</td>
<td>1Hr He-O(^2) RICP</td>
<td>Low</td>
<td>0.64</td>
<td>1.36</td>
</tr>
<tr>
<td>Pt</td>
<td>1Hr He-O(^2) RICP</td>
<td>High</td>
<td>0.42</td>
<td>3.45</td>
</tr>
<tr>
<td>Pt</td>
<td>1Hr He-O(^2) RICP</td>
<td>Low</td>
<td>0.39</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 8.2: ZnO Schottky barrier data for Au, Ir, and Pt diodes on the same high vs. low defect ZnO(000\(\bar{1}\)) surfaces, both treated with a 1 hour O\(_2\) plasma. The low defect ZnO typically exhibits higher Ψ\(_B\) and lower n values.

Deep level transient spectroscopy (DLTS), deep level optical spectroscopy (DLOS) as well as capacitance-voltage (CV) measurements were performed on the high defect material in order to obtain DL concentrations, their gap state energies and their depth distribution in the sub-surface regions. C-V measurements for Ir-ZnO(000\(\bar{1}\)) diodes with Ψ\(_B\) =0.69 eV show carrier density increasing from 3 x 10\(^{16}\) cm\(^{-3}\) at 200 nm depth to 10\(^{17}\) cm\(^{-3}\) at 90 nm below the metal interface. This increase is mirrored by a similar 3x increase in 2.5 eV DL emission observed with DRCLS over the range from 200 nm to ~50 nm. DLTS measurements of this interface show a deep level with activation energy corresponding to a level 0.53 eV below the conduction band E\(_C\) with a density 3.35x10\(^{14}\) cm\(^{-3}\). DLOS spectra reveal multiple deep levels across the ZnO band gap at E\(_C\)=1.88, 2.88, and 3.14 eV as well as E\(_V\)+2.7 eV.
Figure 8.6: Log I-V characteristics for Au, Pd, Pt, and Ir diodes on high defect AR vs. RICP-treated ZnO(000\bar{1}). For each metal, the RICP treatment increase $\Phi_B$ and lowers both reverse leakage current and $n$ values.

In addition to the deep level defects resident in the bulk ZnO, similar defects are observed to form at the metal-ZnO interface following metal deposition. Such metal-induced states depend on the particular metal. Figure 7 illustrates DRCLS spectra for Au and Al diodes deposited on the same low defect ZnO(000\bar{1}) surface. In the Au case relative to the bare surface nearby (a), Au induces relatively little change in the already
low mid-gap defect emission at 2.5 eV and slight increases at 3 eV and the NBE region. In contrast, Al induces an order of magnitude increase in the 2.5 eV emission as well as small NBE changes relative to the bare surface nearby. Thus Al produces metal-induced deep level defects at its ZnO interface. Furthermore, the contrast between (a) and (b) shows that this metal-induced defect creation depends on the specific metal.

Figure 8.7: DRCL spectra compared for Au (a) vs. Al (b) on low defect ZnO after 1 hour RICP treatment. The bare surface defect emission at 2.5 eV is nearly $10^3$x lower than NBE peak intensity. Au deposition induces only relatively small changes, particularly around 3 eV and the NBE region. Al deposition on the same surface induces a 10x increase in 2.5 eV deep level emission.

The results indicate that deep level defects are a common feature of ZnO single crystals and that they can have a major impact on Schottky barrier properties. The wide variation in deep level defect emission reflected in, e.g., fig. 2, and the strong correlation of such defects with SB properties in figs. 3 and 4 underscore the importance of
determining the quality of ZnO used for electrical or optical studies as well as for device structures.

RICP treatment dramatically improves SB characteristics. Fig. 3 shows that the conversion from Ohmic to Schottky-like I-V characteristics takes place for exposure times longer than needed to clean the surface, thereby establishing the importance of subsurface defects and impurities such as H. Figure 4 demonstrates the effect of different concentrations of such DL concentrations in the near surface region on electrical properties. The low defect ZnO has two orders of magnitude lower DL emission vs. the high defect ZnO shown in Fig. 4(a). The corresponding I-V curve in Fig. 4(b) shows a reverse current decrease of 100x and corresponds to an increase in barrier height from 0.43 eV to 0.6 eV.

C-V measurements confirm our DRCLS results showing an increase in defects and carrier density toward the free ZnO surface for specific interfaces. Such defects within ZnO crystals may arise due to nonstoichiometric growth conditions, thermal processing, impurities or mechanical damage, e.g., surface polishing. Such results provide evidence for either defect diffusion toward surface or defect creation at metal interface. Defect creation via chemical bonding between metals and Zn or O atoms is readily understood. However, defect diffusion can also occur – driven, for example, electrically in the case of charged defects. Calculations suggest that vacancy and interstitial diffusion in ZnO can occur at relatively low temperatures.\textsuperscript{53} For high deep levels concentrations, hopping transport can occur that enables tunneling through barriers, increased reverse currents and effective SB reductions. For shallower levels, such defects can alter the carrier
concentration within the near-surface depletion region. Thus new donors can increase n-type doping near the surface (as observed in our Ir-ZnO C-V measurements), thereby narrowing the depletion width and increasing tunneling currents. Temperature-dependent electrical measurements are underway to establish the relative contributions of these mechanisms.

Figure 5(a) reveals that the spectra for the unprocessed ZnO exhibit the same DL emission for each metal. RICP processed surfaces however indicate significantly larger DL variations. The spectra in Fig. 5(b) show the emergence of a shoulder at 2.5eV for some metals, while others resemble those of the unprocessed surface. This suggests that the contamination layer observed with XPS on the unprocessed surface retards any metal-ZnO interaction. Once the RICP treatment removes this layer, metals can react with the surface and generate changes in defect concentration. Since the chemical bonding between different metals with Zn and O varies considerably, substantial differences are not surprising if specific metal-ZnO bonding generates particular localized states. Note that metals such as Au and Pd that do not bond strongly with O can also interact with ZnO since they can induce eutectics such as Au with Zn.

Figure 6 illustrates the improvement in I-V characteristics and SB height with RICP treatment for Au, Pd, Pt, and Ir on high defect ZnO. For Pd, Pt, and Ir, large decreases in reverse current are evident after plasma processing. In terms of optimal ZnO SB metallizations, Table I shows that 1 hour RICP treatments on low defect ZnO produces higher SBs and lower ideality factors for Au, Ir and Pt. Likewise, Table II shows that plasma processing in general produces higher barriers, lower reverse currents, and lower idealities for low defect vs. high defect ZnO. In addition to the data presented in Tables
I and II, we found (1) All metals on AR high defect ZnO with the exception of Ir and Pd displayed Ohmic characteristics. (2) Ir contacts seemed to have the largest SBs of 0.65 eV for AR high defect ZnO and 0.69 for its RIC-treated counterpart. The RICP step changed n from 2.42 to 1.58 and decreased the reverse current by 2 orders of magnitude. Pt diode rectification was poor, with a large n indicating that the contact is dominated by non-thermionic transport. Pd seemed to have the lowest n before and after RICP. Its SB height increased from 0.49 to 0.7 eV with an n relatively unchanged from 1.48 to 1.50.

Palladium and Iridium typically are the best choice metals for high defect material with barrier heights of 0.69 and 0.7 with low idealities. However, SEM images of Ir contacts show that Ir does not adhere well to ZnO surfaces. The stability of the Ir contact degrades as the metal “peels” away from the semiconductor with time or temperature.\textsuperscript{52}

Figure 7 demonstrates that metals do in fact induce defects at ZnO interfaces. Here the low defect ZnO permits clear identification of defect changes due to metal interaction that would otherwise be masked by the much higher densities of other crystals. For this low defect, vapor phase transport-grown ZnO, Al induces nearly an order of magnitude increase in the 2.5 eV DL emission within the 25 nm depth below the metal junction, whereas Au induces little change. This data clearly shows that such metal-induced states depend on the specific metal-ZnO interaction. Indeed, this 2.5 eV emission can been attributed to oxygen vacancies and may arise from Al reaction that extracts O from the ZnO lattice near the interface. Interactions observed at higher temperatures for all these metals suggest chemical trends consistent with this picture.\textsuperscript{52}
8.4 Conclusions

The results presented here demonstrate that high defect ZnO creates poor rectifying contacts. Defects at both the surface and extending into the bulk affect electrical measurements substantially. Metals induce defects at ZnO surfaces. These metal-induced states depend on the specific metal interaction. Overall, clean, ordered surfaces of low defect ZnO produce the highest Schottky barriers and lowest ideality factors for rectifying contacts. Hence, one must consider the role of subsurface bulk defects and metals reactions when fabricating ZnO electronic devices.
9.1 Motivation

ZnO is a promising material for next-generation opto- and microelectronics. However, several technological hurdles remain before devices are realized, including the fabrication of thermally-stable rectifying and ohmic contacts. Previously the authors showed how oxygen plasma processing removes adsorbates, subsurface hydrogen and deep levels to improve Schottky barriers. In this Letter, we emphasize the importance of thermally-induced interface chemical interactions in forming blocking layers and defects. These interactions depend on the metal-ZnO bonding, the annealing temperature, and the initial bulk native defect concentration. Depth-resolved cathodoluminescence spectroscopy (DRCLS) measurements reveal two classes of metal-ZnO reactions that determine the contacts’ current-voltage (I-V) properties and thermal stability. DRCLS emissions at 2.1 eV vs. 2.5 eV appear characteristic of Zn- vs. O-deficient native point defects based on alloy vs. oxide formation, respectively. High work function metals such as Au, Pt, and Pd form high Schottky barriers that degrade with thermally-induced alloying. Oxide-forming metals such as Ta, Al, and Ir can form interfacial layers at intermediate temperatures that block transport with both forward and
reverse bias. Higher temperatures degrade these blocking layers. Higher initial bulk native defect densities promote additional reactions and defects that accelerate these effects.

9.2 Experimental Setup

The DRCLS, plasma processing, and metallization techniques have been described previously. We exposed several bulk ZnO single crystals from two vendors to a 20%O$_2$-80% He remote plasma for 1 hour, then patterned sets of 5-6 each, 30 nm thick, 0.4 mm diameter contacts of Ta, Al, Ir, Ni, Pt, Pd, and Au on each (000ī) O-polar surface using filament evaporation without intervening air exposure or electron beam evaporation following air exposure. The ZnO substrates varied in growth technique, deep level defect density, and near band edge (NBE) emission intensity. Depending on the intensity ratio R of deep level (DL) vs. NBE emissions, these crystals are termed “high” (e.g., R $\approx$ 1) or “low” (e.g., R $\sim 10^{-3}$) defect. A JEOL 7800F ultrahigh vacuum (UHV) scanning electron microscope (SEM) provided spatially-localized excitation through the metal diodes of the ZnO interfaces vs. the bare surface next to the diodes. For incident electron beam energies $E_B$ = 2, 5, 10, and 20 keV, Monte Carlo simulations of the electron cascade yield depths of peak electron-hole pair creation $U_0$ $\sim$ 55, 85, 330, and 990 nm, respectively, below the free ZnO surface. Peak excitation through 30 nm metal overlayers for $E_B$ = 2, 5, 10, and 20 keV corresponds to $U_0$ $\sim$ -20 (inside the metal), 40, 270, and 960 nm, respectively, varying slightly with metal density. For most metals, a 5 keV beam through the 30-nm-thick metal overlayer and a 2 keV beam into the bare ZnO surface have comparable $U_0$. Optical transmission through the various metals showed negligible
variation across the 1.4-6 eV spectral range. Schottky barriers and ideality factors were extracted from I-V curves using thermionic field emission analysis. We measured 10 K DRCL spectra and I-V characteristics of patterned surfaces following 1-hr anneals at temperatures up to 650ºC in a tube furnace with 1 atm flowing Ar.

9.3 Results and Discussion

Previously we showed that metals induce native point defects at ZnO interfaces with CL emissions at 2.1, 2.5, and ~ 3 eV, similar to energies reported previously for Zn-rich or poor crystal growth. Among possible native defects, Zn and O vacancies are predicted to be most energetically favorable; positron annihilation and electron paramagnetic resonance spectroscopies associate the 2.1 and 2.5 eV optical transitions with Zn and O vacancies. Elevated temperatures produce large changes in these emissions, depending on the metal and the bulk native defect concentration. Figure 1 presents DRCL spectra for (a) Au and (b) Ta on low defect ZnO(000̅1). Annealing up to T = 550ºC leaves the Au/ZnO I(2.5 eV)/I(NBE) ratio nearly unchanged and introduces no new spectra features. However, at 650ºC, new emission appears at ~2 eV that dominates the deep level spectra. Significantly, Au forms a eutectic with Zn at 625ºC, and a ~2.1 eV emission has been reported with Zn-deficient growth, suggesting Au-Zn alloying that extracts Zn from the substrate. In contrast, I(2.5eV)/I(NBE) increases by >3x with initial Ta deposition but adds no emission at ~2 eV or 2.5 eV up to 650 ºC.
Figure 9.1: 5 keV DRCLS of 30nm Au (a) and Ta (b) deposited on low defect (000ī) ZnO. For Au, annealing induces only slight changes for T<650 °C but a large ~2 eV peak at 650 °C. Initial Ta deposition triples 2.5 eV emission, but annealing induces no ~2 eV emission or further 2.5 growth.

I-V curves display electrical features that correlate with these DRCL spectra and reflect thermal stability up to 550°C for low defect ZnO. Figure 2 (a) shows that Au diodes remain strongly rectifying with increased Schottky barrier following a 450°C anneal. This is in contrast to thermal instability reported elsewhere\textsuperscript{62} for Au-ZnO contacts
and, significantly, to our high-defect ZnO studies. Figure 2 (b) illustrates the formation of stable, blocking Ta-ZnO contacts. Initially Ohmic, they become blocking following a 350°C anneal and remain blocking at higher temperatures. Since Ta oxidation is highly exothermic, this suggests formation of an insulating oxide layer by extracting O from the substrate. As with Au, the Ta contacts’ thermal stability is consistent with the low defect concentrations evident from DRCL spectra and the major effect of such defects on electrical properties.
Figure 9.2: Low defect $I$-$V$ characteristics show a) Au–ZnO Schottky contacts improving at $T=450^\circ C$ and remaining rectifying up to a $550^\circ C$ annealing and b) annealed Ta contacts blocking and stable up to $550^\circ C$. High defect $I$-$V$ characteristics show c) Au Schottky barrier steadily degrading starting at $350^\circ C$ and d) Ta contacts that become blocking at $450^\circ C$ with leakage increasing at $550^\circ C$. Both metals show lower thermal stability vs low defect ZnO.

Figure 3 shows a similar qualitative difference in spectral features between Au and Ta contacts on high-defect ZnO. For both metals, the bare ZnO $R = I(\text{deep level}) / I(\text{NBE})$ intensities are $\geq 1$. Au deposition increases 2.1 eV and 3 eV emissions, which increase proportionally with annealing. At $650^\circ C$, 2.1 eV defect emission again dominates. In contrast, both 2.1 and 2.5 eV emissions are evident for Ta diodes, with spectra dominated by 2.5 eV emission for intermediate temperatures, consistent with Fig.1 (b). However
unlike Fig.1 (b), the balance of 2.1 eV vs. 2.5 eV emissions reverses at 650°C. These
defect changes are reflected in corresponding I-V spectra shown in Fig. 4. Here, Fig.4 (a)
displays the initially rectifying characteristics, corresponding to a 0.43 eV barrier,
steadily degrading with elevated temperatures starting with 350°C. Likewise, Fig. 4 (b)
displays initially Ohmic features that become blocking only at 550 °C. The oxide layer
responsible for this blocking is evident from the 5 keV DRCL spectra inset in Fig. 3 (b)
displaying new emission at ~ 4.1 eV (Ta₂O₅ band gap ~ 4.2 eV⁶⁴) that appears only after
the 550°C anneal. Significantly, this blocking feature degrades with 650°C anneal and
this 4.1 eV emission disappears.

For both high and low defect ZnO, Au and Ta contacts produce qualitatively different
DRCLS and I-V features. Similar differences are evident for Pd and Pt, which like Au,
alloy with Zn at elevated temperatures vs. Al and Ir, which, like Al, form oxides.⁶⁵ Thus
the increased 2.1 (2.5) eV emissions for Au (Ta) can be associated with Zn (O)-deficient
ZnO near the metal interface. Furthermore, Figs. 3 and 4 demonstrate that high defect
ZnO has lower thermal stability for both Au and Ta contacts. Taken together, these
results demonstrate that metals on ZnO form thin interfacial alloy or oxide layers whose
nature depends on thermodynamic driving forces. These interfacial layers require either
Zn or O atoms from the ZnO, resulting in Zn- or O-deficient layers near the interface
only nanometers thick. For Au on low defect ZnO, the Schottky barrier remains stable
and alloying begins only at temperatures above the known eutectic, while for high defect
material, the Schottky barrier degrades steadily as resident defects redistribute. The Zn-
deficient emission dominates only above the eutectic temperature. For Ta on low defect
ZnO, a blocking layer associated with O-deficient defects forms at low temperatures and
remains stable with increasing temperature, while for high defect ZnO, the contact is Ohmic up to intermediate temperatures and its blocking layer becomes leaky above 550 °C. This contrast between low and high defect ZnO contacts and defect emission demonstrates that the presence of high defect concentrations promotes interface alloying and reactions that produce additional defects which degrade Schottky barriers and blocking layers. In order to achieve high Schottky barriers or blocking layers, defect production at the intimate metal-ZnO interface must be minimized. For alloying metals such as Au, sub-eutectic temperatures are required to preserve Schottky barriers. For oxidizing metals such as Ta, temperatures must be high enough to promote oxide thicknesses sufficient to block current without concomitant defect concentrations high enough to disrupt this layer.
Figure 9.2: 5 keV DRCLS of 30nm Au (a) and Ta (b) on high defect (000\bar{1}) ZnO. Intense 2.1, 2.5 and 3.0 eV emissions are dominated by ~ 2.1 eV emission for Au diodes at 650°C. For Ta contacts, the 2.5 eV intensity increases with Ta deposition and subsequent annealing up to 550 °C. A ~ 4.1 eV peak associated with Ta oxide appears only at 550 °C.
CHAPTER 10

CONCLUSIONS

10.1 Hydrogen in ZnO

One of the most powerful contributions made by this work is solidifying the nature and role of hydrogen in ZnO. Not only has it been shown that hydrogen plasmas can increase surface conduction and that by using room temperature processing we can eliminate other contributions. Low temperature photoluminescence has illustrated the direct correlation of I4 intensity to hydrogen concentrations. Furthermore, control of hydrogen in the lattice can be achieved by annealing or oxygen plasma treatment. This allows for control of conductivity and perhaps a route to codoping schemes in ZnO with nitrogen.

10.2 Nitrogen in ZnO

Nitrogen has been shown to increase the conductivity of ZnO when implanted or diffused. This is the result of its low solubility and the formation of point defect related complexes that create shallow donors rather than shallow acceptors. After identifying methods to control hydrogen concentrations, nitrogen and hydrogen can be incorporated in codoping schemes that increase the solubility of nitrogen while in parallel prohibiting the formation of shallow donor complexes. Reduction in the near surface vacancies also
aids in the reduction of these complexes. Photoluminescence has illustrated that donor-acceptors pairs attributed to nitrogen are introduced with hydrogen codoping. Removal of hydrogen can be achieved by oxygen plasma treatment. Further studies on annealing for surface reconstruction should be performed. X-ray photoelectron spectroscopy reveals that these techniques allow for control of the near surface conductivity. This data suggests that n-type ZnO can be converted to slightly p-type material. Although Hall measurements of conductivity suggest this effect may not be stable. Regardless, the diode performance is greatly increased for the O-face and may prove to be a valuable processing step for realization of devices.

10.3 Oxygen vacancies, defects, and subsurface modification

Processing ZnO with remote oxygen plasmas has shown that subsurface defects can affect Schottky barrier formation. Oxygen plasmas consistently change Ohmic as-received contacts to ZnO into rectifying contacts. XPS and DRCLS measurements reveal that adsorbate removal and reduction in shallow donor concentrations play an important but secondary role to defects at the metal-ZnO interface. Prolonged exposure to oxygen plasmas completely remove adsorbates and the effects of hydrogen in the subsurface. These plasmas create a clean and ordered surface on low grade and high grade ZnO materials for improved device characteristics. Finally, an important result is the ability to remove hydrogen and reduce tunneling through the barrier.
10.4 High defect and low defect ZnO

ZnO material of varying defect concentrations was examined. Qualitatively these samples were partitioned into categories of high medium, and low defects. Low defect ZnO had several advantages to others. Low defect ZnO was more thermally stable, had better device characteristics, and correspondingly had little change in DRCLS spectra. Both high and low defect metals did show changes in DRCLS spectra at room temperature. High defect ZnO exhibited large changes in DRCLS and electrical measurements. After annealing steps, high defect samples showed that the presence of defects could increase the rate of defect formation. High point defect formation can provide increased diffusion and reaction for metals and ZnO. These new states where then characterized by DRCLS and showed metal-ZnO chemical dependency.

10.5 Metal-ZnO chemistry impacts defect formation

DRCLS of various metals on ZnO show that metal-ZnO chemistry plays an important role when considering electrical transport at these interfaces. Metals that form oxides show increases near the interface of oxygen vacancy related defects. These defects are present at room temperature and increase with annealing. High defect materials enhance the formation of these defects. Metals that form eutectics with Zn also are present for room temperature evaporations. DRCLS shows increases in zinc vacancy related defects. Au contacts show that annealing beyond the known eutectic temperature for Au-Zn, there is a dramatic increase in zinc vacancy related defects. Secondary electron microscopy reveals that Au-ZnO nanowires form. This verifies the formation of this eutectic and is common practice for producing these structures.
10.6 Blocking contacts form through oxide formation with Ta

Creating thermally stable blocking contacts is important for device realization. Thin blocking layers could provide a diffusion barrier interfaces. The increased thermal stability added to ZnO devices could be used to better understand and characterize as well as creating reliable electronics. DRCLS measurements reveal the formation of a TaO layer between ZnO and Ta layers. These blocking layers seem to form easily on the O-face but it is at this point inconclusive the formation mechanisms for other crystal faces.

10.7 Depth resolved cathodoluminescence spectroscopy

Depth resolved cathodoluminescence is a powerful tool for characterizing the influence of defects at the surface and bulk for semiconductors. This technique provides detection for defect concentrations as low as $10^{13}$ cm$^{-3}$. Utilizing ultra high vacuum environments, surface science techniques and DRLC allows for nanometer scale resolution both laterally and across interfaces to understand the formation of defects and their effects on device performance.
CHAPTER 11

FUTURE WORK

Moving beyond the scope of this work is important for the future of ZnO devices and processing. One major goal would be to examine the differences in the polar surfaces. These surfaces are interesting because they provide templates for homoepitaxy and heterojunction devices. Some authors report that differences exist for the electrical properties of contacts on these polar surfaces. This may be due to differences in the active chemical bonds present at the O-face. It may be a result of preferential adsorbate accumulation. These differences could manifest themselves in the polishing steps from vendors. Therefore it is important to examine not only the defects, adsorbates, and electrical differences. Close examination to morphological features with AFM or KPFM could provide valuable insight. Vendor wide surveys, as well as different growth methods should be pursued. Overall, a combination of metals, substrates, and polar surfaces with a round-robin approach of processing and characterization could be carried out to determine the effects of these variables.

Another important contribution to ZnO device engineering would be the fabrication of diodes or transistors utilizing a thin blocking layer of Ta. This layer would provide useful if there is increased thermal stability or reduced leakage current across the
barrier or gate. Current research indicates that ZnO metal semiconductor field effect transistors for power applications could be realized for commercial applications above others. Micro Raman spectroscopy or DRCLS can be used between contacts to determine temperature at these interfaces. Increasing the thermal stability of Schottky contacts is vital for using other electrical characterization techniques like deep-level transient spectroscopy (DLTS) and deel-level optical spectroscopy (DLOS).

DLTS could be combined with DRCLS to give a quantitative measurement of defects from the bulk to the near surface. To achieve this, DLTS biasing must allow for probing of the interface traps from the bulk to ~500nm from the interface. Thermally stable contacts would allow for these measurements. Using DLTS activation energies for traps can be calculated and compared with DRCLS. This information could be used to predict Schottky barrier heights with metal chemistry and point defect information quantified. Transmission electron microscopy can be employed to image vacancies and determine diffusion parameters. This would give an improved understanding of thermal stability.
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