DEVELOPMENT OF HIGH VACUUM PLASMA-ASSISTED CHEMICAL VAPOR DEPOSITION AND ITS APPLICATION TO ZINC OXIDE

by

Teresa M. Barnes
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering).

Golden, Colorado
Date: __________

Signed: ________________
Teresa M. Barnes

Approved: _______________
Dr. Colin A. Wolden
Thesis Advisor

Golden, Colorado
Date: __________

_____________________
Dr. Anthony Dean
Professor and Acting Department Head
Department of Chemical Engineering
ABSTRACT

In this thesis, we describe the development of high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) for metal oxide thin film synthesis. The HVP-CVD chamber consists of a high density inductively coupled plasma (ICP) source and a high vacuum deposition chamber. The ICP source is used to dissociate reactants such as N\textsubscript{2} or O\textsubscript{2}, and these reactive products effuse through a small orifice into a collisionless high vacuum environment. Organometallic precursors are introduced directly into the high vacuum chamber, and they react with the plasma products on a heated substrate to form a thin film. \textit{In-situ} diagnostics of the ICP source and high vacuum environment enable the use of HVP-CVD for the study of deposition chemistry. Optical emission spectroscopy is used to monitor the plasma composition, and quadrupole mass spectrometry is used to observe the deposition environment.

We have demonstrated the utility of HVP-CVD for high quality film deposition and the analysis of deposition chemistry. First, we describe the deposition of ZnO, a wide bandgap semiconductor of enormous current interest. Significant achievements of HVP-CVD include room temperature deposition of highly oriented ZnO and systematic control of nitrogen doping. Using a combination of \textit{in-situ} diagnostics and \textit{ex-situ} film characterization, the surface reaction mechanism for ZnO growth from dimethylzinc (DMZn) and O was determined, and the precursor for nitrogen doping was identified.

High quality (002) oriented ZnO was deposited at temperatures between 25 and 230°C. Electrical and optical measurements revealed these films to be insulating and highly transparent. The deposition reaction is a surface mediated process consisting of an O atom attack on dissociatively adsorbed dimethylzinc. The growth rate of these films was first order in DMZn. Both the growth rate and carbon incorporation exhibited a similar Arrhenius dependence on the substrate temperature, suggesting that methyl desorption limited film growth.

Nitrogen incorporation in ZnO:N was systematically controlled by the addition of either N\textsubscript{2}O or N\textsubscript{2} to the plasma source. The amount of nitrogen in the films increased linearly with the fraction of total nitrogen introduced to the plasma, and was unaffected by the choice of nitrogen precursor. Comparison of ICP composition with \textit{ex-situ} measurements of nitrogen content
showed that atomic N is the primary source for N in the deposited films. These data also indicate that both nitrogen incorporation and detrimental carbon contamination were enhanced under low oxygen conditions.

It was found that the ZnO:N lattice constant decreases linearly with nitrogen incorporation. This decrease is attributed to lattice strain resulting from shorter Zn-N bond lengths and compressive stress. Seebeck and Hall measurements confirmed that the films exhibited p-type conductivity for films with a nitrogen concentration greater than 1.5 atomic percent. However, it was observed that p-type doping was unstable, and the conductivity reverted to n-type or semi-insulating behavior after a maximum of 5-7 days. The conversion to n-type conductivity was found to coincide with a slight increase in the lattice constant. This suggests the formation of compensating defects induced by a lattice relaxation, which lead to unstable p-type conductivity in these ZnO:N films. An alternate explanation is that hydrogen-generated free electrons are formed from atmospheric impurities.

We attempted to use diethylzinc (DEZn) to further reduce carbon incorporation, but DEZn was found to decompose on the reactor surfaces at room temperature. A comparison of DMZn and DEZn reactivity was used to establish criteria for precursor selection in HVP-CVD for ZnO and new material systems. Unlike traditional CVD processes, volatility is not a serious limitation but surface reactivity is more critical for HVP-CVD precursors. The ideal HVP-CVD precursor should be unreactive at room temperature, decompose on the substrate surface at moderate temperatures, and have organic ligands that desorb readily and form only volatile reaction products.

The combined film growth and deposition analysis capabilities of HVP-CVD make it ideal for complex material synthesis. Its ability to use low volatility precursors may enable the synthesis of compounds previously unattainable by CVD. The diagnostic capabilities could be of use for developing and understanding process-property relationships in a wide variety of materials systems.
ABSTRACT ...........................................................................................................................................iii
LIST OF FIGURES .................................................................................................................................ix
LIST OF TABLES ....................................................................................................................................xii
ACKNOWLEDGEMENTS ..........................................................................................................................xiii
CHAPTER ONE INTRODUCTION .............................................................................................................1
  1.1 HVP-CVD and its Application to ZnO .................................................................1
  1.2 Literature Review .................................................................................................................3
    1.2.1 Plasmas and Their Application in Materials Processing .................3
    1.2.2 Thin Film Semiconductor Deposition Techniques .......................8
    1.2.3 ZnO Background .........................................................................................12
      1.2.3.1 Basic Properties of Semiconductors .......................12
      1.2.3.2 ZnO Current and Potential Applications .................14
      1.2.3.3 Theoretical predictions for p-type conductivity in ZnO ..15
      1.2.3.4 Experimental Production of ZnO:N .........................17
    1.3 Motivation and Goals .........................................................................................18
CHAPTER TWO EXPERIMENTAL TECHNIQUES ....................................................................................21
  2.1 Reactor Description and Operating Procedures ..............................................21
  2.2 In-situ Film Deposition Analysis .................................................................25
    2.2.1 Optical Emission Spectroscopy .................................................26
    2.2.2 Quadrupole Mass Spectrometry ..............................................28
  2.3 Plasma Chemistry Modeling ...........................................................................29
    2.3.1 AURORA Software Description .........................................30
    2.3.2 Gas Phase Mechanism Development ..................................31
    2.3.3 Surface Chemistry Mechanism ............................................33
    2.3.4 AURORA Model Input .........................................................33
2.4 Film Characterization ..........................................................34
   2.4.1 Variable Angle Spectroscopic Ellipsometry (VASE) .................34
   2.4.2 Thermopower and the Seebeck Coefficient .............................34
   2.4.3 Hall Effect ......................................................................36
   2.4.4 Spectrophotometry ..........................................................37
   2.4.5 X-Ray Diffraction (XRD) ....................................................37
   2.4.6 Atomic Force Microscopy (AFM) ........................................38
   2.4.7 X-Ray Photoelectron Spectroscopy (XPS) .............................38
   2.4.8 Secondary Ion Mass Spectrometry (SIMS) .............................39

CHAPTER THREE  DEPOSITION OF INTRISIC ZnO .........................41
   3.0 Abstract ............................................................................41
   3.1 Introduction .......................................................................42
   3.2 Experimental Techniques ...................................................43
      3.2.1 Deposition Chamber and Diagnostics ..............................43
      3.2.2 Characterization of ICP Source ......................................46
   3.3 Results - Deposition Kinetics ..............................................51
   3.4 Results - Deposition Chemistry ..........................................53
   3.5 Conclusions ......................................................................57
   3.6 Acknowledgments .............................................................58

CHAPTER FOUR  LOW TEMPERATURE DEPOSITION OF HIGHLY ORIENTED
ZnO ..........................................................................................59
   4.0 Abstract .............................................................................59
   4.1 Introduction .......................................................................60
   4.2 Experimental Methods .....................................................61
   4.3 Results and Discussion ......................................................62
   4.4 Conclusions ......................................................................68
   4.5 Acknowledgements ..........................................................69

CHAPTER FIVE  NITROGEN DOPING OF HVP-CVD GROWN ZnO ........71
5.0 Abstract .................................................................71
5.1 Introduction .........................................................72
5.2 Experimental Methods ...........................................73
5.3 Results – ICP Source Characterization .........................75
5.4 Results - ZnO Film Properties ....................................83
5.5 Discussion ..........................................................89
5.6 Conclusions .........................................................93
5.7 Acknowledgements ................................................93

CHAPTER SIX  STABILITY OF P-TYPE CONDUCTIVITY IN ZnO:N ..........95
6.0 Abstract .............................................................95
6.1 Introduction ........................................................96
6.2 Results and Discussion ..........................................99
6.3 Conclusions .........................................................106
6.4 Acknowledgements ..............................................106

CHAPTER SEVEN  ORGANOMETALLIC PRECURSOR SELECTION FOR
HVP-CVD ...............................................................107
7.1 Introduction To Organometallics ...............................107
7.2 Organometallic Zinc Precursors .................................108
  7.2.1 Dimethylzinc .................................................110
  7.2.2 Diethylzinc ..................................................112
7.3 Precursors for New Metal-Oxides .............................114
7.4 Ideal Precursor Attributes for HVP-CVD ....................116
7.5 Conclusions .........................................................118

CHAPTER EIGHT  CONCLUSIONS AND FUTURE WORK ..................121
8.1 Major Results and Conclusions ....................................................... 121
8.2 Recommendations for Future Work ........................................... 123

GLOSSARY ............................................................................................. 129
REFERENCES CITED ............................................................................. 131
APPENDIX A1 HVP-CVD Operating Procedures ................................. 143
APPENDIX A2 CHEMKIN Equations and Background ....................... 145
LIST OF FIGURES

Figure 1.1 Illustration of a thermal CVD process .................................................10
Figure 1.2 Illustration of the bandgap and defect levels within ZnO .........................13
Figure 2.1 Top view schematic of the HVP-CVD System .....................................22
Figure 2.2 Gas flow diagram for the HVP-CVD chamber ....................................24
Figure 2.3 Schematic of the Seebeck effect for an n-type semiconductor ..................35
Figure 2.4 Schematic of the Hall effect on an n-type semiconductor .......................36
Figure 3.1 Top view schematic of HVP-CVD reactor ..........................................44
Figure 3.2 Representative OES spectra obtained from the ICP source for (a) O\textsubscript{2}/Ar and (b) N\textsubscript{2}O/Ar mixtures .........................................................47
Figure 3.3 (a) Comparison of the predicted (line, left axis) and measured O atom density (points, right axis) in the ICP source as a function of rf power for O\textsubscript{2}/Ar, and (b) the measured O atom density as a function of the N\textsubscript{2}O percentage in N\textsubscript{2}O/O\textsubscript{2}/Ar plasmas at 100W .................................................................48
Figure 3.4 QMS spectra obtained with and without plasma operation for (a) O\textsubscript{2}/Ar and (b) N\textsubscript{2}O/Ar mixtures. The spectra were normalized to the Ar 40 signal and offset for clarity ..........................................................................................49
Figure 3.5 The O/O\textsubscript{2} ratio in the deposition chamber as measured by QMS as a function of power for the O\textsubscript{2}/Ar mixture .........................................................50
Figure 3.6 Growth rate as a function of DMZn partial pressure. The lines indicate the ZnO growth rate that would result assuming DMZn sticking probabilities of $\gamma = 1$ (solid) and $\gamma = 0.2$ (dashed), respectively ........................................52
Figure 3.7 Growth rate as a function of O atom density ........................................52
Figure 3.8 XRD patterns for films deposited on glass (bottom) and silicon (top) .......54
Figure 3.9 Transmission spectra obtained from ZnO films on glass as a function of the N\textsubscript{2}O percentage .................................................................54
Figure 3.10 The QMS spectra obtained with and without plasma operation for (a) O\textsubscript{2}/Ar/DMZn and (b) N\textsubscript{2}O/Ar/DMZn mixtures. All spectra were normalized to the Ar 40 signal and offset for clarity ................................................56
Figure 3.11  Schematic diagram comparing (a) the thermal decomposition of DMZn on Si as described by Rueter and Vohs$^3$ and (b) the decomposition behavior observed at 500 K in the presence of atomic O in the HVP-CVD system ........................58

Figure 4.1  Arrhenius plot of growth rate on silicon (squares) and glass (circles) substrates .......................................................63

Figure 4.2  XRD patterns as a function of deposition temperature obtained from (a) silicon and (b) glass substrates .................................64

Figure 4.3  AFM images obtained in tapping mode of ZnO grown on silicon at (a) 230 °C, (b) 60 °C, and (c) 25 °C .........................................................65

Figure 4.4 Optical transmission spectra of selected films deposited on glass at different substrate temperatures .................................66

Figure 4.5  Arrhenius plot of the relative carbon density as measured by SIMS for films deposited on silicon ........................................68

Figure 5.1   QMS spectra obtained during plasma activation of a 100% N$_2$O/Ar mixture (top) and a 67% N$_2$/33% O$_2$/Ar mixture (bottom) ......................76

Figure 5.2:  OES spectra obtained during plasma activation of a 100% N$_2$O/Ar mixture (top) and a 67% N$_2$/33% O$_2$/Ar mixture (bottom) ......................77

Figure 5.3   Plots of the changes in relative density of (a) [O], (b) [N], (c) [N$_2^*$], and (d) [NO] as a function of % N$_2$ (solid symbols) or % N$_2$O (open symbols) in the ICP source ........................................80

Figure 5.4   High resolution XPS scans of nitrogen in the ZnO lattice for films grown at (a) 0% N$_2$O, (b) 60% N$_2$O, and (c) 100% N$_2$O ........................................84

Figure 5.5 Atomic percentage of N in ZnO:N as a function of the percentage N$_2$O in the feed gas as determined by XPS ................................................85

Figure 5.6 Relative nitrogen concentration as determined by SIMS as a function of the elemental nitrogen in the ICP source. Data are shown for both N$_2$O (triangles) and N$_2$ (squares) ......................................................86

Figure 5.7 XRD patterns of ZnO films as a function of (a) N$_2$O and (b) N$_2$ addition .....87
Figure 5.8  Optical transparency of films deposited on glass as a function of (a) N\textsubscript{2}O and (b) N\textsubscript{2} addition .................................................................89

Figure 6.1  Lattice constant measured by XRD vs. the percentage of nitrogen in the ZnO:N film measured by XPS .................................................................99

Figure 6.2  Seebeck coefficient measurements as a function of time for five ZnO:N films .................................................................102

Figure 6.3  Lattice constant as a function of time after deposition for films D, E, and F. The open symbols represent p-type films, and the filled symbols indicate n-type films as determined from the sign of the Seebeck Coefficient .........................103

Figure 7.1  Generic structures for organometallic precursors .........................108

Figure 7.2  A comparison of DMZn and DEZn mass spectra, illustrating the surface decomposition of DEZn before reaching the QMS .........................113
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Typical gas phase reactions</td>
<td>5</td>
</tr>
<tr>
<td>1.1</td>
<td>Comparison of CCP and ICP operating parameters</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>Bond dissociation energies of molecular precursors</td>
<td>16</td>
</tr>
<tr>
<td>2.1</td>
<td>Operating parameters for HVP-CVD deposition of ZnO</td>
<td>25</td>
</tr>
<tr>
<td>7.1</td>
<td>Physical properties of DMZn and DEZn</td>
<td>109</td>
</tr>
<tr>
<td>A.1</td>
<td>Gas Phase Chemistry Mechanism for AURORA</td>
<td>147</td>
</tr>
<tr>
<td>A.2</td>
<td>Surface Reaction Mechanism</td>
<td>148</td>
</tr>
<tr>
<td>A.3</td>
<td>Aurora Input File</td>
<td>149</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the National Science Foundation through CAREER Award No. CTS-0093611. We also thank Dr. Tom Mates for assistance with XPS and SIMS, which were performed at UCSB using the MRL Central Facilities supported by the MRSEC Program of the National Science Foundation under award number DMR00-80034. I also thank the CdTe team at the National Renewable Energy Laboratory for support during my first year at CSM.

I would like to thank my advisor, Dr. Colin Wolden, for providing such a great project and mentoring me to get through it. My husband, Colin Davis, has been incredibly supportive. He is always there to help out, cheer me up, or convince me to take off for a weekend, and I am very grateful for his patience and tolerance. I would also like to thank both of our families for their faith and encouragement.
CHAPTER ONE

INTRODUCTION

1.1 HVP-CVD and its Application to ZnO

This thesis describes the development of high vacuum plasma assisted chemical vapor deposition (HVP-CVD) as a novel deposition technique developed for the synthesis of metal oxide thin films. Common applications for these films include semiconductors, transparent electrodes, gas sensors, dielectrics, and heat resistant window coatings. This technique combines a high density plasma source for the dissociation of precursors with a high vacuum film deposition chamber. An inductively coupled (ICP) plasma source operates around 50 mtorr and generates radicals and atomic species from molecular precursors. These active species then effuse through a small orifice towards the substrate mounted in the high vacuum deposition zone. The large pressure gradient, \((P_1/P_2 > 10^3)\) between the plasma and deposition zone effectively decouples the plasma and film growth environments. Metal precursors are introduced directly into the high vacuum chamber. The deposition chamber is maintained at \(10^{-5}\) torr during film growth, ensuring collisionless transport from the plasma to the film. Atomic oxygen and organometallic precursors react through surface mediated pathways to form high performance metal oxides.

The unique configuration of HVP-CVD enables \textit{in-situ} monitoring of both the plasma and the growth environment. Optical emission spectroscopy (OES) directly monitors the relative density of the active species in the plasma. In combination with plasma chemistry modeling, OES can be used to quantitatively determine the atomic species density in the plasma. Quadrupole mass spectrometry (QMS) is used to monitor
the subsequent chemistry in the deposition zone. These two complementary techniques enable the thorough study of both the plasma and film deposition kinetics.

HVP-CVD is potentially useful for the synthesis of many different metal oxides and metal nitrides. The ICP source is sufficiently energetic to dissociate nearly all molecular precursors, and the collisionless growth environment provides a convenient means to study the surface chemistry involved in deposition. In this work, the beneficial attributes of HVP-CVD are demonstrated through the deposition of intrinsic (undoped) and nitrogen doped ZnO. Through these examples, we illustrate the unique reaction pathways that occur in this system.

Zinc oxide (ZnO) is a wide band gap semiconductor that is routinely used as a transparent electrical contact, with many potential applications such as optical waveguides, UV lasers, and short wavelength light emitting diodes (LEDs). ZnO is especially attractive for UV laser applications due to its bandgap of 3.37 eV and high exciton binding energy of 60 meV. The exciton binding energy of ZnO is more than double that of GaN, enabling room temperature lasing and improved photonic device reliability.\textsuperscript{1,2} ZnO blue emitting LEDs\textsuperscript{3}, UV nanolasers\textsuperscript{4}, and quantum pyramids\textsuperscript{5} have already been demonstrated. In addition, doped ZnO is widely used as a transparent contact for amorphous silicon devices, and it is being pursued as a replacement candidate for indium-tin oxide (ITO) in organic LEDs and other applications.\textsuperscript{6-8}

ZnO is unique among the commonly used transparent conducting materials in that it can be doped p-type, most often with nitrogen. The ZnO devices mentioned above have tremendous potential for industrial and commercial applications, but require both n- and p-type ZnO to create active devices. Additionally, most solar cell absorber materials are p-type, and a high quality p-type transparent contact could aid in the development of high performance photovoltaics.\textsuperscript{9}

P-type ZnO:N was first proposed by Kobayashi in 1983\textsuperscript{10}, but experimental work has proven that it is difficult to produce. Challenges arise from an asymmetric doping limitation that strongly favors n-type conductivity.\textsuperscript{11,12} Theoretical calculations suggest
limited nitrogen solubility in the lattice and serious issues with its stability.\textsuperscript{13,14} The
difficulty of incorporating N in ZnO is compounded by the challenges of producing
reactive N species under reasonable deposition conditions. Several different nitrogen
precursors and deposition techniques have been used with sporadic success. Few
experimental efforts have studied the mechanism of nitrogen doping, and very little is
understood about the process.

HVP-CVD was used to produce both intrinsic and nitrogen doped ZnO, and to
analyze the deposition kinetics of both materials. Intrinsic ZnO deposition was studied as
a function of substrate temperature, precursor concentration, and ICP power to determine
the kinetics of film growth. Nitrogen doping was accomplished by substituting N\textsubscript{2}O or
N\textsubscript{2}/O\textsubscript{2} mixtures for oxygen to produce O and N precursors. These mixtures were used to
systematically incorporate nitrogen into the lattice and gain understanding of the
deposition chemistry. The electrical, structural, and optical properties of all films were
studied to develop process-property relationships.

1.2 Literature Review

This research relies on basic knowledge from several different fields. The
following sections present background material on plasma processing, semiconductor
deposition, and the characteristics of zinc oxide.

1.2.1 Plasmas and Their Application in Materials Processing

Plasmas are used in many different deposition techniques, either to drive a
chemical reaction or as an ion beam source. They can be thought of as a fourth state of
matter consisting of highly energized electrons, ions, and neutrals. The plasmas found in
nature, like the sun, are in thermal equilibrium, meaning that the electron, ion, and neutral
temperatures in the tens of thousands of degrees Kelvin.

Plasmas used in materials processing generally operate at low pressures and are non-equilibrium and weakly ionized. There are three distinct temperatures in these plasmas: electron \( (T_e) \), ion \( (T_i) \), and neutral gas \( (T_g) \). Although the electron temperatures in these plasmas are around 10,000 K, the ion temperatures are significantly lower, and the total gas temperature remains well below 1000 K. Despite the fact that electron and ion densities in non-equilibrium plasmas are three to five orders of magnitude lower than the neutral gas density, these species drive the chemistry. Due to their exceptionally high temperatures, electrons are primarily responsible for precursor dissociation in deposition processes.\(^{15}\) Although atmospheric pressure discharges are used for materials processing, only low pressure plasmas (1 mTorr-1 Torr) will be discussed here.

Plasma processes are especially attractive for semiconductor synthesis because they allow for lower deposition temperature and reduced thermal stresses on complicated devices. The hot electrons in the plasma replace thermal energy as the main driving force for chemical reactions. \( T_e \) in low pressure plasmas ranges between 1-10 eV depending on the pressure, method of power coupling, and geometry. The electron density, \( n_e\), is strongly dependent on the input power. The electron temperature in the plasma obeys an electron energy distribution function (EEDF), which is ideally assumed to be Maxwellian as given in equation 1. Most electrons in the plasma have less energy than is required for dissociation or ionization reactions, and it is the high energy tail of this distribution that contributes heavily to the plasma chemistry. Equation 1 can be integrated to determine the fraction of electrons with sufficient energy for reaction.\(^{15}\)

\[
G(\varepsilon) = 2\pi \left( \frac{1}{\pi T_e} \right)^{3/2} \sqrt{\frac{\varepsilon}{T_e}} e^{-\varepsilon/T_e}
\]

Materials processing plasmas are non-equilibrium, however they operate at steady state. The positive and negative charges in the plasma must balance, but they may move freely. There is also a balance between the generation and loss of ions and electrons.
Electrons and ions are both generated in the bulk of the plasma, and they are lost primarily through surface reactions. A small fraction of ions impacting the surface create secondary, “hot”, electrons. These “hot” electrons are accelerated across the sheath and are responsible for the volume production of electrons and ions. Table 1 lists examples of some important gas phase reactions.\textsuperscript{16}

Table 1.1: Typical gas phase reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^- + A \rightarrow A^+ + e^-$</td>
<td>Excitation</td>
</tr>
<tr>
<td>$e^- + AB \rightarrow AB^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$e^- + A \rightarrow A^+ + 2e^-$</td>
<td>Ionization</td>
</tr>
<tr>
<td>$e^- + AB \rightarrow A + B^- + e^-$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>$e^- + A^+ + B \rightarrow AB$</td>
<td>Recombination</td>
</tr>
<tr>
<td>$e^- + A^- \rightarrow A + e^- + h\nu$</td>
<td>Relaxation/Light Emission</td>
</tr>
<tr>
<td>$A + B^+ \rightarrow A^+ + B + e^-$</td>
<td>Penning Ionization</td>
</tr>
<tr>
<td>$A^+ + B \rightarrow A + B^+$</td>
<td>Charge Exchange</td>
</tr>
</tbody>
</table>

Surface reactions are the main loss mechanisms for both ions and electrons, making the geometry of the plasma and its structure highly relevant to the discharge properties. Lighter electrons are far more mobile than heavier, cooler ions, and a negative charge builds up quickly on the exposed surfaces. This creates an adjacent boundary layer, called the sheath, of positive space charge which houses nearly the entire potential drop across the plasma. The Debye length, $\lambda_{\text{De}}$, is the characteristic length scale over which large potential drops can occur. Regions larger than $\lambda_{\text{De}}$ are generally neutral. It can be derived from Poisson’s equation, given in equation 2, and calculated according to equation 3. In equation 2, $\rho$ is the space charge, $\phi$ is the potential, and $\varepsilon_0$ is the
permittivity. In equation 3, \( n_0 \) is the plasma density, which is equal to the electron and ion density in the bulk neutral plasma, \( k \) is Boltzman’s constant, and \( e \) is the electronic charge. Ions need a minimum energy to cross the sheath. The Bohm criterion, given in equation 4, is used to determine the minimum energy required for an ion to be removed from the bulk plasma.\(^{15-17}\)

\[
\frac{d^2 \phi}{dx^2} = -\frac{\rho}{\varepsilon_0} \tag{2}
\]

\[
\lambda_{De} = \frac{\sqrt{\varepsilon_0 k T_e}}{n_0 e^2} \tag{3}
\]

\[
u_b = \frac{\sqrt{e T_e}}{M} \tag{4}
\]

Plasmas are generated by an electronic energy source coupled to a neutral gas in a controlled environment. A variety of energy source and coupling methods are employed in plasma deposition systems to optimize the reactions conditions for a particular process. These power sources can be a continuous direct current (DC) source, or an oscillating source operating at either radio-frequency (RF) or microwave (MW). DC discharges can be operated continuously or in pulsed mode. They are formed by applying a voltage between two parallel plates and are controlled by applied voltage and discharge current. The efficiency of DC plasma processes can be improved by adding a magnetic field perpendicular to the electric field to increase the electron mean free path and boost ionization rates. Pulsed operation allows for higher operating power and improved deposition control.\(^{18}\)

RF plasmas are slightly more complicated than DC plasmas because they require a match network between the plasma and the power source to match their impedances and maximize the discharge efficiency. The power can be coupled to the discharge either capacitively (CCP) or inductively (ICP). Both are widely used for materials processing.\(^{18}\)
A comparison of the operating parameters of CCP and ICP discharges is shown in Table 1.2, which is excerpted from Lieberman and Lichtenberg.\textsuperscript{15} This comparison shows that the coupling mechanism is very important to the properties of the rf discharge. CCP discharges are well understood and widely used in industrial applications for etching, deposition, and surface modifications. They can be constructed from two parallel plates either internal or external to the plasma. Table 1.2 shows their densities and electron temperatures are comparatively low, and the low ionization fraction and high ion bombardment are detrimental to deposition processes. The key limitation of CCP processes is the lack of independent control of the ion bombarding flux and energy, which induces wafer damage and hampers reproducibility in semiconductor processing. The low ionization fraction implies an inefficient use of precursors, which is a serious problem when using expensive or toxic feedstocks. Particle contamination is also a persistent problem in CCP plasmas. Most of the limitations can be improved with independent substrate biasing, appropriately sized asymmetrical electrodes, and magnetic enhancement.\textsuperscript{15,18}

ICP discharges rely on power coupling from a coil across a dielectric window, and either microwave or RF power sources can be used. Magnetic fields are usually used in combination with microwave power sources to produce an electron cyclotron resonance (ECR) discharge. These types of discharges are often operated “remotely”, meaning that the deposition process occurs downstream of the plasma. Low sheath voltages, and consequently low ion bombardment, are enabled by the inductive power transfer. Independent control of the ion energy and flux is possible with an independently biased substrate, alleviating the main difficulty with CCP processing. ICP processes operate at lower pressure, and therefore higher electron energy and higher precursor utilization. The low pressure enhances reaction rates, but it requires larger and more expensive vacuum pumps. ICP devices have been successfully scaled up for large scale coating operations with very good uniformity.\textsuperscript{15,18,19}
Table 1.2: Comparison of CCP and ICP operating parameters\textsuperscript{15}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CCP</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mTorr)</td>
<td>10-1000</td>
<td>0.5-50</td>
</tr>
<tr>
<td>Power (W)</td>
<td>50-2000</td>
<td>100-5000</td>
</tr>
<tr>
<td>Frequency (MHz)</td>
<td>0.05-13.56</td>
<td>0-2450</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>1-10</td>
<td>2-50</td>
</tr>
<tr>
<td>Cross-sectional Area (cm(^2))</td>
<td>300-2000</td>
<td>300-500</td>
</tr>
<tr>
<td>Magnetic Field (kG)</td>
<td>0</td>
<td>0-1</td>
</tr>
<tr>
<td>Plasma Density (cm(^{-3}))</td>
<td>(10^9-10^{11})</td>
<td>(10^{10}-10^{12})</td>
</tr>
<tr>
<td>Electron Temperature (eV)</td>
<td>1-5</td>
<td>2-7</td>
</tr>
<tr>
<td>Ion Acceleration Energy (V)</td>
<td>200-1000</td>
<td>20-500</td>
</tr>
<tr>
<td>Fractional Ionization</td>
<td>(10^{-6}-10^{-3})</td>
<td>(10^{-4}-10^{-1})</td>
</tr>
</tbody>
</table>

1.2.2 Thin Film Semiconductor Deposition Techniques

Thin film vacuum deposition techniques can be divided into two broad categories. The first consists of physical vapor deposition (PVD) techniques in which a preformed target of desired material is sputtered or ablated with highly energetic particles to form a thin film. Examples include many different sputtering configurations, thermal evaporation, and pulsed-laser deposition. The second category includes the systems that rely on chemical reactions to convert precursors into a thin film. Chemical vapor deposition (CVD), either thermal or with a plasma, and molecular-beam epitaxy are chemical methods to create thin films.

ZnO and other oxides are commonly deposited by several different sputtering processes\textsuperscript{20-23}. Sputter deposition is accomplished by ablating a preformed target of the
desired film with some sort of energetic beam, generally in an inert atmosphere. The energetic beam can be electrons, positive ions, or a laser. Ion bombardment with Ar$^+$ ions is widely used for oxide deposition. The ions can be generated in either a DC or RF plasma. Sputtering chambers can be configured in several different ways. The substrate and target can act as the electrodes of the Ar glow discharge plasma, or they can be separate with a remote ion gun. Magnetron systems are frequently used in both DC and RF glow discharge processes to improve efficiency. The main advantage of sputter deposition processes is that nearly any film can be produced stoichiometrically. This is especially useful for ternary or quaternary oxide films with complicated stoichiometry. Sputtering processes require a high vacuum and a preformed target, both of which can be very expensive. They are also plagued by particulate contamination from the target. Sputtering processes are frequently used for large scale deposition oxide coatings for applications like touch screens, flat panel displays, and thin film solar cells. Target poisoning and degradation present serious problems, especially for costly materials.

Lasers replace the plasma ion energy source in pulsed laser deposition (PLD) processes. PLD is especially useful for materials requiring alternating layers, superlattices, or precise composition control because the switching time between targets is controlled by the laser rather than mechanical shutters. Oxidizing or reactive atmospheres are often used in PLD processes to improve film stoichiometry. PLD is especially amenable to research applications because of its flexibility and ability to easily produce complex multilayer structures.

Chemical vapor deposition of thin film metal oxide materials is routinely accomplished under a wide range of operating conditions. Pressure varies from atmospheric to the low millitorr range. Both atmospheric and low pressure MOCVD processes are extensively used for industrial and laboratory scale metal oxide deposition. Many different metallic precursors are used, including metal-halides and organometallic compounds. Film deposition is driven thermally in these systems, and the substrate
temperature is often high. CVD processes generally have higher deposition rates than sputtering and lower pumping requirements while still producing high quality films. Unlike PVD, CVD depositions do not require a direct line of sight between the precursor and substrate, and excellent conformal coatings are easily achieved. Precursor selection presents some challenges not encountered in PVD. The precursor must be sufficiently volatile to flow into the chamber, yet stable enough for safe handling. It must react neatly to the desired product with minimal undesirable side reactions and be available in sufficient purity. Multi-component oxides require compatibly reacting precursors. Many organometallic precursors are highly toxic and require special handling.\(^{27}\)

CVD processes rely on the basic steps illustrated in Figure 1.1 to deposit a film. The precursors are mixed, flow through the chamber and begin to react in the gas phase. Reactants then diffuse towards the substrate where they can be adsorbed or reflected with higher energy from the hot substrate. The adsorbed species diffuse along the substrate until they either react with another surface or gas phase entity or desorb to react further in the gas phase. The remaining adsorbed species can then become part of the bulk deposited film.\(^{24,27}\)

High processing temperatures and precursor incompatibility are the main limitations of thermal CVD processes. Plasma-enhanced CVD (PECVD) processes allow
for reduced operating temperatures and more uniform reaction of different precursors. They also operate at lower pressures than thermal CVD, which can ease complications cause by low precursor volatility. Lower temperatures reduce thermal stresses on devices and enable deposition on flexible substrates. The plasma power provides an additional adjustable control parameter for film property optimization. The plasma itself also presents some complications for deposition processes. New applications for PECVD are constantly being developed despite the fact that they are not nearly as well understood as thermal CVD and PVD processes. Materials deposited by PECVD include metal oxides, polymers, superconductors, nitrides, diamond, silicon, and silicates.\(^{27,28}\)

Like sputtering processes, PECVD can be performed with the substrate directly in contact with the plasma or the plasma can be operated remotely. Most processes rely on alternating current operating at either r.f. (13.56 MHz) or microwave frequencies (2.45 GHz) to alleviate sample charging and instabilities that can occur at lower frequencies.\(^{28}\) Both CCP\(^{29-32}\) and ICP/ECR\(^{33-36}\) reactors are widely used for thin film depositions.\(^{27,28}\) CCP processes usually have the substrate directly attached to one of the plasma electrodes. ICP and ECR plasmas are more often used remotely, with one or more of the precursors introduced downstream from the plasma in the film deposition zone. While CCP systems have higher growth rates, they can also have serious problems with ion bombardment and particle contamination. Ion bombardment leads to sputtering off of the deposited film. Remote ICP and ECR devices alleviate these at the expense of a reduced growth rate and increased pumping requirements.\(^{27}\) Additionally, the higher electron energy in these systems increases precursor dissociation, even of highly stable species.\(^{37}\)

Molecular beam epitaxy (MBE) is a high vacuum technique that is similar in many ways to CVD with a solid metallic source replacing the organometallic precursor. Plasma-assisted MBE (P-MBE) adds a remote ICP or ECR plasma for the dissociation of the reactant gasses. The high vacuum environment makes the growth process entirely dependent on surface chemistry. These systems are able to deposit very high quality epitaxial films, but at low growth rates. Epitaxial films are precisely lattice matched to
the underlying substrate and are perfectly oriented in one crystal direction. This level of quality is required for semiconductor devices, and MBE techniques are widely used to produce heterojunction devices.\textsuperscript{24}

HVP-CVD is a highly modified plasma assisted chemical vapor deposition technique. The high density ICP plasma is operated remotely, and is quite similar to the remote-PECVD technologies that are extensively used for SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} depositions.\textsuperscript{34} In R-PECVD, oxygen and nitrogen precursors are dissociated in an ICP device, while the silicon precursor is introduced directly into the downstream deposition zone. Remote plasma operation reduces substrate damage from ion bombardment. The key difference between HVP-CVD and conventional R-PECVD is the high vacuum deposition environment in HVP-CVD. Film growth in R-PECVD processes occurs at pressures in the millitorr range, allowing for gas phase reactions between the precursors. The low pressure in HVP-CVD effectively eliminates gas phase collisions and relies entirely on surface mediated processes. HVP-CVD is also quite similar to P-MBE, except that an organometallic precursor replaces the metal effusion source.

1.2.3 ZnO Background

ZnO is a wide bandgap semiconductor with a wide array of potential applications. A basic understanding of the properties of semiconductors in general and past research on is required to develop better processes for the production of ZnO

1.2.3.1 Basic Properties of Semiconductors

Semiconductors are the basic building blocks of opto-electronic devices like diodes, switches, transistors, photovoltaics, lasers, and sensors. They have conductivities somewhere between insulators and metals. Semiconductors can be either elemental, like silicon or germanium, or compound, like ZnO, GaAsP, SiC, or CdTe. One crucial
A characteristic of any semiconductor is its bandgap. An illustration of the bandgap is given in Figure 1.2. This shows a direct bandgap semiconductor, meaning that the top of the valence band and bottom of the conduction band are vertically aligned in k-space. The bandgap determines which wavelengths of light will be absorbed and which will be transmitted. It also determines the wavelength that an LED or laser will emit. Electrical properties are also strongly influenced by the bandgap. Charge can be primarily carried by either holes in the valence band (p-type) or electrons in the conduction band (n-type). A semiconductor would be perfectly insulating if either the valence band was full or the conduction band was empty. Their conductivity results from electrons being thermally excited into the conduction band, resulting in a hole in the valence band.  

Pure semiconductors are often poor electrical conductors. In order to produce functional devices, they must be “doped” with an impurity atom. The conductivity actually arises from introducing an impurity or defect into the lattice. Doping is often accomplished by adding an impurity with a valence charge that is either larger or smaller than the valence on the atom it is replacing. For example, silicon (group IV in the periodic table) is routinely doped p-type with boron (group III) or n-type with phosphorus (group V). The impurity atom needs to form four covalent bonds in the Si lattice, so the
group III atom will be short one electron and form a hole. The group V atom will have one extra electron to contribute to the conduction band.  

Some materials can easily be doped both p- and n-type, while others can be easily doped one way but not the other. N-type dopants are called donors. Donor atoms provide extra electrons to the lattice, thus potentially increasing the electron carrier concentration and improving the conductivity. However, certain conditions must be met for these extra electrons to be usable. Each type of dopant resides in a defect level somewhere in the bandgap. In order for a donor electron to contribute to the lattice, this level must be very close to the conduction band. These electrons must be close enough in energy to be excited thermally into the conduction band. Defects levels that are thermally accessible are described as shallow, and a deep level indicates that the defect is too far from the band to contribute. P-type dopants produce acceptor defects in the lattice. This acceptor defect should be very close to the valence band so electrons can be thermally excited up to it, yielding holes in the valence band. These acceptor and donor defect levels can vary widely depending on the host material and the dopant atom.  

In compound semiconductors like ZnO, dopants can be introduced on either the Zn or the O site. Either a group III atom (usually Ga or Al) can replace Zn, or a group VII atom (F) can replace O to generate extra electrons in the lattice. A p-type dopant in ZnO would need to come from group V and sit on the O site, meaning that N, P, and As are potential p-type dopants. Group I atoms occupying Zn sites could also be p-type dopants. A junction between p-type material and n-type material is required to form semiconductor devices, meaning that both p and n-type ZnO must be available to make ZnO devices.

1.2.3.2 ZnO Current and Potential Applications

ZnO belongs to a group of materials known as transparent conducting oxides (TCOs). TCOs are a unique class of materials that are both transparent to light and electrically
conductive. They are used in a wide range of applications including photovoltaics, flat panel displays, “low-e” and electrochromic windows, touch screens, transparent heaters, and heat reflectors. Each TCO application requires a different blend of optical and electrical properties. In architectural windows, it is critical that the TCO be transparent to visible light, but not ultraviolet or infrared radiation. Both electrical conductivity and transparency to visible light are critical for optoelectronic applications like photovoltaics and flat panel displays (FPDs). Other important properties of TCOs include their ease of production, mechanical characteristics, chemical stability, toxicity, and raw material costs. Industrial TCOs are all n-type, which is perfectly adequate for many of the above applications. However, a p-type transparent contact would be extremely useful for high performance photovoltaics and organic semiconductor devices.

The material properties of ZnO make it extremely attractive for the development of a range of wide bandgap electronic devices. High quality n-type ZnO is readily available. ZnO has an ideal room-temperature band gap of 3.3 eV for use in UV and blue light emitting diodes (LEDs), and a high exciton binding energy of 60 meV. The high exciton binding energy allows for efficient room temperature excitonic laser action. The wurtzite crystal structure of ZnO has ferroelectric and piezoelectric properties too. The raw materials for ZnO are relatively cheap and non-toxic, and the film is easily etched yet stable enough for most uses. ZnO is also radiation hard and resistant to H-plasmas.

1.2.3.3 Theoretical predictions for p-type conductivity in ZnO

Kobayashi made the first theoretical prediction of P-type ZnO:N in 1983, but experimental work has proven that it is difficult to produce. ZnO has asymmetric doping limitation that strongly favors n-type conductivity making acceptor defects difficult to form and creating an abundance of compensating donor defects. The challenges to p-type ZnO production arise from three rather thorny issues. The first set of problems comes from the thermodynamic hurdles to incorporating nitrogen into ZnO. The
locations of the various defect levels in the ZnO bandgap presents the second set of difficulties. Even in intrinsic (undoped) ZnO, n-type defects, mainly Zn interstitials and O vacancies, have low formation energies and shallow donor levels. This explains the intrinsic n-type conductivity of ZnO. Depositions conditions for p-type ZnO tend to also favor the formation of these native n-type defects. Additionally, hydrogen acts as a shallow donor in ZnO. It is difficult to exclude from the lattice and may compensate any acceptor defects.

Theoretical calculations suggest that the nitrogen solubility in ZnO is strongly affected by the nitrogen source. Unfortunately, nitrogen can act as a shallow double donor if it is incorporated as N$_2$. This requires breaking the N$_2$ bonds in the precursor gasses for the creating of acceptor defects. The bond dissociation energies for the most commonly used nitrogen precursors are given in table 1.3. These data show that breaking the N$_2$ bond is a formidable task in molecular N$_2$ and N$_2$O. The high formation enthalpy values in the literature for N doping from N$_2$ and N$_2$O incorporate this bond breaking energy, and the support for NO or NO$_2$ as superior precursors are based on this reasoning. Incorporating atomic N does not guarantee p-type conductivity. Simply incorporating N on an O site yields a rather deep acceptor level, making it difficult to produce holes. Compensation from intrinsic n-type “hole killing” defects must also be overcome.

<table>
<thead>
<tr>
<th>Precursor Gas</th>
<th>Bond Dissociation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>9.8</td>
</tr>
<tr>
<td>$N_2O \rightarrow N_2 + O$</td>
<td>1.66</td>
</tr>
<tr>
<td>$N_2O \rightarrow NO + N$</td>
<td>5</td>
</tr>
<tr>
<td>NO</td>
<td>6.6</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Two strategies have been proposed to improve the solubility and stability of N in ZnO and to lower the acceptor level in the bandgap. Codoping with both N and Ga or
other group III atoms was proposed first in 1999.\textsuperscript{45} Gallium is most often used as the codopant, and is thought to both reduce the acceptor level of the N and increase the donor level of the Ga when incorporated as N-Ga-N. Codoping is also believed to increase the solubility of N in ZnO.\textsuperscript{46} Subsequent work supported intrinsic donor defects or possibly hydrogen as codopants to enhance acceptor solubility and as hole killers.\textsuperscript{12-14} The actual role of the codopant is the subject of much debate, and more recent work has suggested cluster doping as another method of achieving the same goals. This theory suggests incorporating clusters of Ga-N\textsubscript{4} or GaN\textsubscript{3}O for stable p-type doping.

1.2.3.4 Experimental Production of ZnO:N

Nitrogen doped ZnO has been synthesized by a variety of techniques including plasma-assisted molecular beam epitaxy (P-MBE), pulsed laser deposition (PLD), and metallorganic chemical vapor deposition (MOCVD). P-MBE processes have produced ZnO:N from the reaction of elemental Zn with active O and N containing species generated from an N\textsubscript{2}/O\textsubscript{2} plasma source. A film fabricated in this manner was characterized as p-type by Look et al.\textsuperscript{2}, while those grown by Iwata and coworkers\textsuperscript{47} were not. PLD relies on irradiating a ZnO target in the presence of an N\textsubscript{2}O plasma, but only a small fraction of these films exhibit p-type conductivity.\textsuperscript{48,49} A MOCVD process combined diethyl zinc and NO in a thermally driven reaction to form ZnO:N, again identifying a narrow processing window for p-type conductivity.\textsuperscript{50} None of these reports provided information about the gas composition in the growth environment. There has been little discussion of the nitrogen-containing species responsible for ZnO:N formation, or an explanation for the wide disparity in nitrogen doping results. A recent study compared ZnO:N synthesis by PLD using three plasma-activated sources (N\textsubscript{2}, N\textsubscript{2}O, and NO).\textsuperscript{51} All three sources provided a high level of N incorporation as determined by SIMS, but all films remained n-type. Using a very qualitative assessment of optical
emission spectra from the plasma, these authors suggest that both vibrationally excited \( \text{N}_2^* \) and NO were potential origins of nitrogen incorporation.

### 1.3 Motivation and Goals

Despite the tremendous interest in p-type ZnO:N, very little experimental work has been done to identify the mechanism of nitrogen doping in ZnO. Systematic control of nitrogen incorporation has not been demonstrated, and the actual nitrogen species responsible for doping is not known. P-type ZnO has a wide range of potentially lucrative applications, but all require very high quality material and reproducible synthesis. Developing an understanding of the nitrogen doping mechanism will aid in meeting those goals.

HVP-CVD is extremely well suited to analyzing the deposition kinetics of intrinsic ZnO and the chemistry of nitrogen doping. The high density ICP source can easily dissociate \( \text{O}_2, \text{N}_2, \text{N}_2\text{O, NO} \) or nearly any other potential precursor. OES allows for continuous monitoring of the reactive species in the plasma. The high vacuum deposition chamber precludes gas phase reactions enables the transport of reactive atoms and radicals to the deposition surface. In addition, it allows deposition of high quality material and careful analysis of the deposition surface chemistry with the QMS. This data combined with careful ex-situ film characterization can yield valuable information on the deposition kinetics of ZnO and ZnO:N from several different precursor combinations. It can be used to identify the exact nitrogen entity incorporated in the lattice under plasma assisted conditions. Further work to improve the stability and electronic properties will be needed, but cannot be carried out until systematic control of nitrogen incorporation is achieved.

The primary goals of this thesis are:

- Develop and characterize the HVP-CVD technique for thin film deposition and kinetic analysis
- Deposit intrinsic ZnO with HVP-CVD
- Determine deposition kinetics for ZnO synthesis from dimethylzinc and O₂
- Identify the nitrogen dopant precursor and achieve control of nitrogen incorporation in ZnO
- Determine potential improvements in ZnO:N deposition process to yield high quality p-type material
- Identify other material systems where HVP-CVD may be of use for the study of reaction kinetics or precursor selection
CHAPTER TWO

EXPERIMENTAL METHODS

This chapter details the deposition system, characterization equipment, and the procedures used for the production and analysis of ZnO thin films. The operating procedures and principles of the HVP-CVD system are presented. The capabilities and applications of the \textit{in-situ} deposition analysis tools are given along with the details of the plasma chemistry model used to quantify their results. The various \textit{ex-situ} film characterization tools are described in the last section.

2.1 Reactor Description and Operating Procedures

Fig. 2.1 shows a schematic cross section of the HVP-CVD system used in this work. The reactor was a custom vacuum grade stainless steel chamber (HPS Instruments) exhausted by an Edwards diffusion pump to a base pressure of $10^{-7}$ torr. Five 2.75 inch conflat (CF) flanged feedthrough ports were located on top of the chamber for precursors, thermocouple, and power feedthroughs and the cold cathode (MKS Ins.; Boulder, CO) high vacuum pressure gauge (P2). One additional 2.75 inch CF feedthrough located opposite the substrate served as the ICP gas inlet. Two 4.75 inch CF ports were located on each side of the chamber. One was fitted with a quartz window for optical access, and the other was used to attach the quadrupole mass spectrometer (QMS). The diffusion pump was connected to the chamber through a 6 inch gate valve (MKS Instruments; Boulder, CO) An oil sealed rotary vane mechanical pump (Stokes or Varian) was used as a roughing pump and to back the diffusion pump.
The ICP source was a custom two inch long, one inch diameter Pyrex tube (Allen Scientific Glass; Boulder, CO). The source was fused to ¼ inch flexible stainless steel tubing with a Kovar glass-to-metal seal (Larson Electronic Glass). Stainless steel Swagelok fittings were then used to connect the ICP source to the gas feedthrough. The ICP source had a 0.125 inch outlet hole directed towards the substrate. Power was coupled to the ICP source by a six turn water-cooled copper coil. A convection gauge (Kurt Lesker, Pittsburgh, PA) located upstream of the gas inlet was used to monitor the pressure (P1) in the ICP tube.

The ICP tube was supplied by ultra-high purity O₂, N₂, and N₂O, and industrial grade Ar. All flowrates were controlled by Unit electronic mass flow controllers. The organometallic precursors, dimethylzinc (DMZn) and diethylzinc (DEZn) (both 95% purity, Strem) were introduced without carrier gas directly into the chamber through a port in the top of the reactor using a metering valve calibrated with the high-vacuum pressure gauge. A fixed temperature bath was used to control the vapor pressure of the organometallics. The gas flow diagram for the chamber is given in figure 2.2.
Under typical growth conditions the pressure upstream of the ICP tube pressure was $P_1 \sim 200$ mtorr and the deposition chamber was $P_2 \sim 10^{-5}$ torr. The actual pressure in the plasma is substantially lower ($\sim 50$ mtorr) due to losses from the expansion into the tube and friction along the lines and the tube. The substantial pressure difference ($P_1/P_2 > 10^3$) between the tube and deposition chamber ensures that the two regimes were effectively decoupled. This allows the plasma to operate at sufficiently high pressure to efficiently decompose all of the precursors, while maintaining collisionless transport from the plasma to the substrate surface. Ballistic transport conditions preclude gas phase reactions in the deposition zone, enabling direct observation of the surface chemistry.

The plasma was ignited with a 500 W RF Power Products power supply operating at 13.56 MHz. It was coupled to the deposition system through an Advanced Energy AM5 automatic match network. The match network was connected to the chamber through a two pole ¼ inch hollow copper tube power feedthrough. This feedthrough is water cooled, and connected to the 1/8 inch copper coil with brass Swagelok fittings. These connections are electrically insulated from the chamber with Teflon heat shrink tape. A Neslab 5B chiller was used to supply cooling water to the coil. The ICP tube and coil were surrounded by a grounded copper mesh Faraday cage to contain stray RF leakage. This allowed simultaneous operation of the plasma, pressure gauges, and the QMS without electrical interference.
ZnO films were deposited on Corning 1737 glass and p-type silicon (100) substrates. The substrates were mounted on a water cooled stainless steel susceptor that was connected to the chamber with a custom o-ring sealed 6 inch ASA flange. A resistive heater (Watlow; St. Louis, MO) and thermocouple were mounted on the backside of the susceptor, and the temperature was maintained by a PID controller (Omega). Temperature calibrations were performed between the control thermocouple and
thermocouples that were taped to the surfaces of the respective substrates. The maximum substrate temperature was 230°C.

The control parameters for the HVP-CVD system are power, substrate temperature, gas flowrate and composition of the ICP source, substrate-source distance, and the precursor partial pressures. The total gas flow rate was used to control the pressure because there was no pressure controller. For the experiments with nitrogen doping, the total gas flowrate was kept constant, but the ratio of O₂ to N₂O or N₂ was varied from zero to one. Table 2.1 lists the common operating range for each of these parameters.

Table 2.1: Operating parameters for HVP-CVD deposition of ZnO

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rf input power</td>
<td>40-200 Watts</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>25 – 230 °C</td>
</tr>
<tr>
<td>Total flow to the ICP source</td>
<td>0.5-1.0 sccm</td>
</tr>
<tr>
<td>Substrate source distance</td>
<td>7 cm</td>
</tr>
<tr>
<td>DMZn/DEZn partial pressure</td>
<td>1<em>10⁻⁵ – 6</em>10⁻⁵ torr</td>
</tr>
<tr>
<td>O₂ to N₂/N₂O ratio</td>
<td>0-1</td>
</tr>
</tbody>
</table>

2.2 In-situ Film Deposition Analysis

Two in-situ monitoring techniques were used in HVP-CVD. Optical emission spectroscopy (OES) was used to observe the chemistry in the plasma source, and quadrupole mass spectrometry (QMS) was used to study the composition of the deposition zone. The use of these two techniques was made possible by the separate and decoupled operating pressures of the plasma and the film growth zone.
2.2.1 Optical Emission Spectroscopy

Optical Emission Spectroscopy (OES) is a widely used optical tool for monitoring plasma processes. OES works by detecting the light emitted as an excited state atom or molecule relaxes to a lower energy state. Unlike laser-induced fluorescence (LIF) and other more complex techniques, no outside stimulation is used. OES simply measures the light emission that occurs naturally due to relaxations of excited species in the plasma. It is commonly used to detect contamination, leaks, and etching endpoints because small changes in the plasma environment can produce large variations in emission. This is often exploited to monitor process reproducibility.\textsuperscript{15} OES can also be used to monitor changes in the electron and ion temperatures if the resolution is very high.\textsuperscript{52} OES monitors the plasma conditions directly, but with the probe located outside of the plasma. This is an important and attractive attribute since diagnostics in the plasma itself tend to disturb it, and are subject to extremely harsh conditions.\textsuperscript{53}

The OES tool on this system consists of an Ocean Optics SD2000 spectrometer, a fiber optic cable mounted on the chamber window connected to the spectrometer, and a Pentium 1 computer for data collection. This spectrometer has a range of 179 – 900 nm, but practical use was limited to about 300 nm on the low end due to absorption in the Pyrex tube and window. It can produce spectra and also provide time resolved measurements of up to five selected peaks and two peak ratios. In addition to monitoring plasma conditions, the OES was used to determine when the Pyrex ICP tube needs to be cleaned and when there is contamination in the chamber.

Changes in the plasma emission intensity and OES data result from a combination of changes in the electron energy distribution function (EEDF) and the plasma species involved. OES depends on two basic processes. First, an atom or molecule must be excited from the ground state by an electron impact. The excited state then decays spontaneously to the ground state through the emission of a photon. The measured intensity is dependent on the electron density, the excited species density, the excitation
energy and probability of excitation, and the ground state species density. This makes it very difficult to use OES alone except to determine the presence or absence of a species by observing the corresponding emission line in the spectra.

OES by itself cannot determine even the relative amounts of species present. Actinometry is a method developed initially by Coburn and Chen to quantitatively measure atomic fluorine density in the plasma. The method has been extended to many other plasma systems, including oxygen-argon plasmas. Actinometry requires the addition of small quantities of an unreactive noble gas such as argon or helium to the plasma. The emission intensities of both the species of interest, O in this case, and the tracer gas are then monitored. The density of O is then given by equation 2.1. In equation 2.1, $k_e$ is a rate coefficient for excitation, $I$ is the emission intensity, and $\gamma$ is a ratio of geometric information, photon energy, and the Einstein coefficients for the two transitions. It is very difficult to accurately determine $k$, which requires knowledge of the EEDF, and $\gamma$, so equation 2.1 is usually replaced with the proportionality given in equation 2.2. Comparison with two-photon LIF (TALIF) shows that actinometry captures the changes in O density very well, but it does not give the absolute density very accurately even when $k$ and $\gamma$ are known.

\begin{equation}
[O] = \frac{k_e^{(Ar)}}{k_e^{(O)}} [Ar] \frac{I_{(O)}}{I_{(Ar)}} \frac{1}{\gamma} 
\end{equation}  \tag{2.1}

\begin{equation}
[X] \propto [Ar] \frac{I_X}{I_{Ar}} 
\end{equation}  \tag{2.2}

The two transitions used for actinometry must be carefully chosen to produce even qualitative results. First, the excitation cross sections should have the same shape. The excited states producing the emissions should have only minimal contributions from
de-excidations of higher states or two step excitations. There should be no contributions from dissociation, and quenching without emission should be negligible.\textsuperscript{55}

There are two pairs of signals that are used often for O atom actinometry. The first is $\text{O}_{777}/\text{Ar}_{750}$, and the second is $\text{O}_{844}/\text{Ar}_{750}$. This Ar line is chosen because it is only weakly affected by excitations of metastables compared to other Ar lines. Neither pair of emissions ideally meets the criteria for similar excitation cross-sections or excitation thresholds. The emission lines are relatively unaffected by quenching, and only the $\text{O}_{777}$ state is significantly populated by dissociative channels. The $\text{O}_{844}/\text{Ar}_{750}$ actinometry results show better agreement with the TALIF results in both the Katsch and Walkup papers and gave the correct qualitative trends.\textsuperscript{54,55} Unfortunately, the $\text{Ar}_{750}$ peak was somewhat obscured by $\text{N}_{2}$ bands in the case of $\text{N}_{2}\text{O}$ and $\text{N}_{2}$– containing plasmas. The Ar emission line at 811 nm was used instead as the actinometer since it was a prominent signal that was not compromised by the $\text{N}_{2}$ bands. Good agreement was observed between the data evaluated with the $\text{Ar}_{750}$ and $\text{Ar}_{811}$ lines in $\text{O}_{2}/\text{Ar}$ plasmas.

2.2.2 Quadrupole Mass Spectrometry

The QMS used in these experiments was a Stanford Research Systems model RGA300 (SRS; Sunnyvale, CA). This QMS has a range of 0-300 amu, with a resolution of 0.5 amu. It was mounted directly to the chamber with a 2.75” CF flange without any differential pumping. The QMS head is located adjacent to the outlet of the ICP tube. The QMS was used to calibrate the organometallic flowrate, check precursor purity, and monitor the deposition chemistry.

A QMS can be divided into three parts: The ionizer, the quadrupole filter, and the ion detector. A ThO\textsubscript{2}/Ir filament supplies electrons which are accelerated away from the probe. These electrons create ions by electron impact in the surrounding gas, which are then drawn back into the probe towards a biased focus plate. This process can only function below $10^{-4}$ torr. Positive ions are then filtered by their mass-to-charge ratio in
the quadrupole. Four carefully aligned conductive cylindrical rods make up the quadrupole. One pair of rods is connected to a positive DC voltage with a superimposed sinusoidal RF voltage, and the other is connected to a negative DC voltage with a superimposed sinusoidal RF voltage that is 180° out of phase with the other rods. These voltages are adjusted to create a mass filter, though which only one mass-to-charge ratio ion may pass for each setting. The entire mass spectra can be scanned by varying the DC and RF voltages simultaneously. Ions that pass through the mass filter enter the detector. The detector operates with a Faraday cup detector for most applications. An electron multiplier is used for low pressures or situations requiring very high sensitivity. Ions enter the Faraday cup and are neutralized by impact with a metal wall. The resulting current from the wall is equal to the ion current from the filter, and is fed into the electrometer in the control unit. This data is then converted into mass spectra with the RGAWindows software.56

2.3 Plasma Chemistry Modeling

Several different options are available for modeling plasma chemistry. They range from the continuum models, either perfectly stirred or with transport, to the computationally intense non-continuum particle models. Due to their low operating pressures, non-continuum models often provide a more accurate description of the transport in a high density plasma reactor. Direct simulation Monte-Carlo models have been developed for this purpose, and they also provide information on the electron energy distribution and local reaction rates. But, these models are computationally quite expensive and are very inefficient for working with large reaction mechanisms. Additionally, regular continuum models require transport data, which is often not available for plasma species.37 The Knudsen number, λ/L, for this system is about 0.1, so continuum mechanics are appropriate for this system and will be used here to allow for more detailed analysis of the plasma chemistry.
2.3.1 AURORA Software Description

AURORA, a CHEMKIN component, was used to model the plasma chemistry inside the source. CHEMKIN is a modular software package that combines gas phase and surface chemistry utilities with thermodynamic and transport libraries in a variety of applications. The available applications include channel flow, plug flow, stagnation flow, diffusion flames, and perfectly stirred tanks. AURORA is the zero dimensional perfectly stirred reactor (PSR) application that is able to handle plasma chemistry. PSR models neglect transport and mixing effects, which requires that the system be adequately described by bulk properties. This is appropriate in most low pressure plasma systems because diffusive transport is much faster than the rate limiting chemical kinetics. PSR models are attractive because their computational efficiency allows the use of detailed chemistry and large reaction mechanisms.

The plasma component of AURORA relies on three basic simplifying assumptions. The first is that power absorption is uniform throughout the system, also meaning that electron diffusion is very fast compared to electron reaction rates. Secondly, the electron energy distribution should be close to Maxwellian since this assumption is implicit in the calculation of the reaction rate coefficients. Thirdly, the model requires that the sheath thickness be much less than the reactor diameter in order to characterize the quasi-neutral bulk plasma.

The average electron speed in a plasma is given by equation 2.3, which gives a speed of $1 \times 10^6$ m/s for an electron temperature of 3 eV. This is very fast and indicates that the first assumption is valid for this reactor. The second assumption requires an electron energy distribution function (EEDF) that follows equation 2.4, known as a
Maxwellian distribution. The EEDF for O₂ plasmas and mixtures of O₂ and Ar with less than 25% Ar are Maxwellian at pressures below 20 mtorr, but deviate to a three temperature structure at higher pressures. The assumption of a Maxwellian EEDF is very rarely accurate for most plasmas, but it is acceptable and frequently used for O₂/Ar plasmas. The thin sheath assumption can be checked by calculating the Debye length \( \lambda_{De} \), given in equation 2.5. The Debye length is commonly considered the characteristic length scale in the plasma, and it is the distance over which potentials near or larger than \( k_B T_e/e \) can occur. It is also approximately equal to the sheath thickness. The Debye length for this system is 0.01 cm, and the reactor diameter is 2.54 cm, so the “thin sheath” assumption is valid. This system satisfies all of the fundamental assumptions of the AURORA model, so the PSR model is a good choice for this application.

\[
f(\varepsilon) = 2\pi \left( \frac{1}{\pi T_e} \right)^{3/2} \varepsilon^{1/2} \exp\left( -\frac{\varepsilon}{T_e} \right)
\]

2.4

Plasma mechanism development is done in the same manner as other gas phase chemistry mechanisms. First, identify the feed gasses and the types of reactions those are likely to undergo. Then, search the literature for kinetic and thermodynamic data at similar temperatures and pressures as the system of interest. The types of gas phase reactions that are important in plasmas are shown in Table 1.1. Low pressure gas phase plasma mechanisms generally contain many electron impact reactions and the fast ion – neutral and neutral- neutral reactions. Third body recombination reactions are rarely
important at these lower pressures. Data for reactions with electrons is often found in the
form of electron impact cross sections. Cross sections for the feed gases are a good
starting point for mechanism development. Then, chemistry such as ionization,
excitation, and dissociation for the electron impact reaction products can be added.\(^{37}\)

A reaction mechanism for \(\text{O}_2/\text{Ar}\) plasmas is available in the literature as a subset
of a mechanism for the production of \(\text{SiO}_2\) from \(\text{SiH}_4, \text{O}_2\) and \(\text{Ar}\) in a high density
plasma.\(^{58}\) This gas phase mechanism is given in Appendix A.2. The authors calculated
rate constants from the available cross section data assuming a Maxwellian EEDF using
equation 2.6. This rate constant was then fit to the modified Arrhenius format used by
CHEMKIN, which is given in equation 2.7.

\[
k_j(T_e) = \left(\frac{8}{m_e\pi}\right)^{1/2}\left(\frac{1}{k_B T_e}\right)^{3/2} \int_0^\infty \epsilon \sigma_j(\epsilon) e^{-\epsilon/k_BT_e} d\epsilon
\]

\[k_j(T_e) = A_j T_e^B e^{C_j/T_e}
\]

Table A.1 in the appendix contains the 36 gas phase reactions used in the model.
A is in units of molecules, B is dimensionless, and E is in Kelvins. All reactions
involving electrons depend on the electron temperature, while the ion and metastable
reactions depend on the gas temperature. The excitation energy for each reaction
generating \(\text{O}^*\) and \(\text{Ar}^*\) was specified directly using the EXCI keyword. The excitation
energy values are given in table two, along with their sources. Most were from literature
data for the specific electronic or vibrational excitation, a few were calculated from the
activation energy because literature data were not readily available. Use of the EXCI
keyword avoids having to declare a separate species and thermodynamic data for each
excited state.
2.3.3 Surface Chemistry Mechanism

Surface relaxation processes are the most important loss mechanisms for excited and ionized species and for recombination of O atoms. The Meeks mechanism does not include surface reactions for O and Ar species, but it does have extensive surface chemistry for SiO₂ deposition, which provides a different sink for these species.

A simple surface reaction mechanism, given in table A.2, was developed to account for these losses. The reactions were specified in terms of sticking coefficients for neutral species and the Bohm criterion for charge species. The sticking coefficients for O* and Ar* were assumed to be one because they are metastable species. The sticking coefficient for the O recombination reactions was fit to experimental data. The Bohm parameter in the table is the ratio of the ion density in the sheath to the ion density in the bulk plasma. It is a correction factor to the calculated speed of the ions towards the wall, and it is determined according to the procedure given in Lieberman for ICP discharges.¹⁵

2.3.4 AURORA Model Input

In addition to the gas phase and surface chemistry input files, a separate AURORA input file is required. This file contains information including reactor pressure, flowrate, input power, geometry, feed gas composition and temperatures, initial guesses for calculated quantities. Simulations were conducted at varying input powers and ICP pressures. The adjustable parameters in this model are the reactor pressure and the sticking coefficients for the O atom surface recombination reactions. The reactor pressure is measured approximately six inches upstream of the ICP tube, so the exact pressure in the plasma is not known. Additionally, there is likely a small pressure gradient down the length of the tube, so this is an average pressure at some point in the
tube. These results were used to quantify the O atom density in the ICP plasma and compared with experimental actinometry data.

2.4 Film Characterization

A variety of ex-situ analysis tools were used to characterize the deposited films. Information from these tools was combined to provide comprehensive knowledge of the structure, composition, electrical properties, optical properties, and morphology of the films.

2.4.1 Variable Angle Spectroscopic Ellipsometry (VASE)

A J. A. Woolam Company WVASE32 (Omaha, NE) was used for ellipsometric measurements of the film thickness and optical constants. Ellipsometry measures the relative phase change in a beam of polarized light reflected from a sample surface. This measurement must then be combined with a model to extract physical information about the film. All films in this work were measured using the Lorentz optical model for semiconductors from spectroscopic measurements ranging from 400-1200 nm. The measurements were performed at a 70° angle of incidence. These measurements were used to extract the film thickness, index of refraction, and extinction coefficient.

2.4.2 Thermopower and the Seebeck Coefficient

The Seebeck effect occurs when a thermal gradient applied to a sample induces a potential difference across it. The potential difference arises from a thermally driven diffusion current of the majority carriers toward the cooler side of the sample. An illustration of this is shown in Figure 2.3. The Seebeck coefficient ($\alpha_s$) can be
Electrons will diffuse towards the cold side in n-type material, to produce a negative $\alpha_s$. In p-type material, holes will accumulate on the cold side to induce a positive voltage and $\alpha_s$. Thermopower measurements were made to determine $\alpha_s$ on a custom built benchtop system consisting of a hot plate, two copper blocks, two thermocouples, and a Keithley 197 microvolt meter. One copper block rested on a room temperature stand adjacent to the hot plate with the other copper block. Thermocouples were taped to each block. The hot plate was set at approximately 70°C to maintain a 45°C temperature gradient. The sample was placed on top of both blocks and held down with a 100g weight. Handheld probes were then used to measure the voltage across the copper blocks. This measurement was repeated at least three times and the average value was used. P- and n-type silicon wafers and n-type SnO$_2$:F were used as references for each measurement.
2.4.3 Hall Effect

Hall effect measurements were performed on a Biorad Hall (HL5500PC) system equipped with a variable temperature controller. As illustrated in Figure 2.4, the Hall effect occurs when a magnetic field is applied perpendicular to a flowing current. This causes a deflection in the drift velocity of the flowing electrons or holes until a transverse electric field strong enough to balance the Lorentz force from the magnetic field is established. The direction of the transverse electric field is determined by the carrier type. The Hall effect was used to measure resistance ($\rho_H$), carrier type (+/-), carrier concentration (n), and mobility ($\mu$) according to equations 2.10a-d. Obtaining Hall effect measurements at varying temperatures enables the determination of fundamental electrical properties of the film such as the scattering mechanism. \(^{62}\)

$$R_H = \frac{E_y}{j_x B}$$ \hspace{1cm} \text{2.10a}^{39}

$$\rho_H = \frac{E_y}{j_x}$$ \hspace{1cm} \text{2.10b}^{39}

$$n = \frac{A_x}{eR_H}$$ \hspace{1cm} \text{2.10c}^{60}
2.4.4 Spectrophotometry

Optical transmittance and reflectance in the ultraviolet, visible, and near-infrared were performed on a Cary 5G spectrophotometer between 250 and 2500 nm. A glass reference was used to determine the baseline measurements. Transmittance and reflectance measurements were used to calculate the absorption coefficient and the optical bandgap using equation 2.11. For semiconductors like ZnO with a direct bandgap, a Tauc plot of \((\hbar \nu \alpha)^2\) vs. \(\hbar \nu\) can be used to determine the bandgap. The bandgap is estimated by extrapolating the linear region of the curve to the x-axis.

\[
\alpha = A (h \nu - E_g)^{1/2}
\]

2.4.5 X-Ray Diffraction (XRD)

XRD is a widely used non-destructive technique for the determination of structural characteristics of bulk and thin film materials. A Seimans Crystalloflex A10 XRD using Cu Kα radiation was used for these studies, which were conducted in the θ-2θ configuration over a range of 20-70° in 2θ. In XRD, X-rays enter the crystal and are scattered by the crystal planes according to Bragg’s Law, given in equation 2.11.

\[
n \lambda = 2d \sin(\Theta)
\]

Diffraction only occurs at specific angles, θ, for each lattice structure and atomic spacing. In Bragg’s Law, n is any whole integer, and is representative of scattering by adjacent
parallel crystal planes. $\lambda$ is the wavelength, and $d$ is the spacing between the crystal planes. However, $n\lambda$ must be less than $2d$ so that $\sin \theta$ remains smaller than one. The location of the diffracted XRD peaks at different values of $2\theta$ is indicative of the basic crystal structure, and these peaks are often used for material and phase identification. Any shift or broadening of the XRD peaks can be used to identify stress or strain in a known material.\(^{64}\)

2.4.6 Atomic Force Microscopy (AFM)

AFM produces a digital image of a thin film, device, or microstructure. It is a type of scanning tunneling microscope that does not require a conducting surface.\(^{65}\) These microscopes yield three dimensional images that can detail features as small as 10 nm across with sub angstrom vertical resolution. They rely on an atomically sharp tip mounted on a flexible cantilever. Repulsive van der Waals forces cause the cantilever to deflect when it comes within a few angstroms of the sample surface. The deflection is measured with a laser and input to a computer to create an image as the tip is scanned across the sample with a piezoelectric transducer. AFM can be used for topographic imaging, surface roughness, electrical property mapping, thermal imaging and many other applications.\(^{66,67}\)

2.4.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS is an ultra-high vacuum technique to study the elemental composition of surfaces. Metals, semiconductors, ceramics, organic materials, polymers, and biological materials can be analyzed with XPS. The technique is extremely surface sensitive, with a penetration depth that varies from 2-20 atomic layers. XPS has an absolute sensitivity that depends on the element, ranging between 0.01-0.3 atomic percent.\(^{66}\) A Kratos XPS
system located at the University of California at Santa Barbara was used in this work to quantify nitrogen incorporation in our ZnO:N films.

XPS works by bombarding a sample with high energy (X-ray) photons which ionize the sample and cause it to eject electrons. These electrons are bound with energy $E_B$ that is specific to each element. The kinetic energy ($E_k$) of the emitted electron is measured, and $E_B$ is determined from equation 2.12, where $h\nu$ is the energy of the X-ray photon. Although each element has specific allowed $E_B$ values, the measured values can be shifted slightly depending on the chemical bonding environment and oxidation state of the atom. These shifts are known for many elements and compounds. They allow for the determination of the element and its bonding state in the material.

$$E_k = h\nu - E_B$$  \hspace{1cm} 2.12

2.4.8 Secondary Ion Mass Spectrometry (SIMS)

SIMS is an extremely sensitive surface analysis technique. Elemental detection limits range from below parts-per-billion (ppb) to parts-per-million; depth resolution can be as good as 2 nm, and lateral resolution ranges from 50 nm-2 μm. SIMS is often used for impurity and dopant detection, and is able to measure down to about $10^{12}$-$10^{16}$ atoms/cm$^3$. Unlike XPS, SIMS can be used for depth profiling.

A beam of highly energized heavy “primary” ions hit the sample surface, creating a mixing zone of the primary ions and displaced ions from the sample. The depth of this mixing zone is the limiting factor in SIMS depth resolution, and it depends on the ion energy, angle of incidence, and the respective masses of the primary ions and the sample. Momentum and energy transfers in the mixing zone cause the ejection of an assortment of particles, including atomic and molecular secondary ions from the sample. In dynamic SIMS, the sample is continually sputtered away by the primary beam. This enables depth profiling. The secondary ions enter a mass spectrometer that is either similar to the QMS
described in section 2.2.2; one that filters mass by time-of-flight (TOF-MS); or one that relies on a magnetic sector.\textsuperscript{66}

The sensitivity of SIMS is highly beneficial to determining doping in semiconductors, but absolute quantification of the material composition can be difficult. It requires a standard, which is often not available for new materials. If a standard analyzed with the same type of primary beam is available, quantification can be as accurate as 2\%. Also, sample charging from the ion beam is a complication on insulating substrates. SIMS samples generally must be small with a very smooth surface. They should not be susceptible to outgassing due to the high vacuum in the instrument.\textsuperscript{66} In our studies, the dynamic SIMS system employing Cs\textsuperscript{+} ions was used to evaluate the nitrogen and carbon content throughout the ZnO:N films.
The following is a reproduction of a paper accepted for publication in the Sept/Oct. 2004 issue of *The Journal of Vacuum Science and Technology A*. This chapter is as submitted except that the section numbers, references, and figure labels were changed to conform to the thesis format.

ZnO Synthesis by High Vacuum Plasma-assisted Chemical Vapor Deposition using Dimethylzinc and Atomic Oxygen

Teresa M. Barnes, Steve Hand, Jackie Leaf, and Colin A. Wolden*
Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401

3.0 Abstract

Zinc oxide thin films were produced by high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) from dimethylzinc (DMZn) and atomic oxygen. HVP-CVD is differentiated from conventional remote plasma-enhanced CVD in that the operating pressures of the inductively coupled plasma (ICP) source and the deposition chamber are decoupled. Both DMZn and atomic oxygen effuse into the deposition chamber under near collisionless conditions. The deposition rate was measured as a function of DMZn and atomic oxygen flux on glass and silicon substrates. Optical emission spectroscopy and quadrupole mass spectrometry (QMS) were used to provide real time analysis of the ICP source and the deposition chamber. The deposition rate was
found to be first order in DMZn pressure and zero order in atomic oxygen density. All films demonstrated excellent transparency and were preferentially orientated along the c-axis. The deposition chemistry occurs exclusively through surface-mediated reactions, since the collision-less transport environment eliminates gas-phase chemistry. QMS analysis revealed that DMZn was almost completely consumed, and desorption of unreacted methyl radicals was greatly accelerated in the presence of atomic oxygen. Negligible zinc was detected in the gas phase, suggesting that Zn was efficiently consumed on the substrate and walls of the reactor.

3.1 Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor that is routinely used as a transparent electrical contact, with many potential applications such as optical waveguides, UV lasers, and short wavelength light emitting diodes (LEDs). ZnO is especially attractive for UV laser applications due to its bandgap of 3.37 eV and high exciton binding energy of 60 meV. The exciton binding energy of ZnO is more than double that of GaN, enabling room temperature lasing and improved photonic device reliability.\textsuperscript{1,2} ZnO blue emitting LEDs\textsuperscript{3}, UV nanolasers\textsuperscript{4}, and quantum pyramids\textsuperscript{5} have already been demonstrated. In addition, doped ZnO is widely used as a transparent contact for amorphous silicon devices, and it is being pursued as a replacement candidate for indium-tin oxide (ITO) in organic LEDs and other applications.\textsuperscript{6-8}

Many experimental techniques have been used to deposit ZnO, including plasma-assisted molecular beam epitaxy (P-MBE)\textsuperscript{47,68-70}, metal-organic chemical vapor deposition (MOCVD)\textsuperscript{50,71-73}, sputtering\textsuperscript{74}, pulsed laser deposition (PLD)\textsuperscript{49}, atomic layer deposition (ALD)\textsuperscript{75}, and plasma-enhanced chemical vapor deposition (PECVD)\textsuperscript{30-33,76,77}. Sophisticated high vacuum techniques like MBE, PLD, and ALD generally produce the highest quality films, but at relatively low growth rates. MOCVD and PECVD provide faster film growth and are more easily scaled for large area deposition.
In this paper, we describe a unique high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) system to study the kinetics of ZnO deposition from atomic oxygen and organometallic precursors. Atomic O is produced by the dissociation of either O\(_2\) or N\(_2\)O using an inductively coupled plasma (ICP) source. Atomic oxygen effuses from the source under near choked flow conditions and is directed towards the substrate. The organometallic precursor, dimethylzinc (DMZn) in this case, was introduced into the background of the high vacuum deposition chamber that operates around 10\(^{-5}\) torr. HVP-CVD is similar to P-MBE except that an organometallic precursor replaces the elemental zinc effusion source. The decoupling of the deposition chamber and ICP source pressures differentiates HVP-CVD from traditional remote plasma-enhanced chemical vapor deposition (RPECVD) systems.\(^7\)\(^8\)

The collisionless HVP-CVD transport environment eliminates atomic oxygen recombination and reaction with DMZn in the gas phase, allowing the surface chemistry to be studied directly. We use this unique system to study the surface kinetics of ZnO deposition from DMZn and atomic O, which is also relevant to both to traditional plasma and thermal CVD production of ZnO. Additionally, this system allows for the exploration of low temperature ZnO synthesis without ion bombardment.

### 3.2 Experimental Techniques

The HVP-CVD chamber is a unique tool for the production of metal oxides. It allows for the synthesis of high quality material and real time observation of the deposition chemistry.

#### 3.2.1 Deposition Chamber and Diagnostics

Figure 3.1 shows a schematic cross section of the HVP-CVD system used in this work. The reactor was a custom vacuum grade stainless steel chamber (HPS
Instruments) exhausted by an Edwards diffusion pump to a base pressure of \(10^{-7}\) torr. The ICP source was a one inch diameter Pyrex tube, surrounded by a six turn water-cooled copper coil. The ICP tube was supplied by ultra-high purity \(O_2\) and \(N_2\)O, and industrial grade Ar. The Ar flowrate was 0.1 sccm for all experiments, while the total oxidizer flowrate (\(O_2 + N_2\)O) was 0.65 sccm. All flowrates were controlled by Unit electronic mass flow controllers. The plasma was ignited with a 500 W RF Power Products power supply operating at 13.56 MHz. It was coupled to the deposition system through an Advanced Energy AM5 automatic match network. Reactive products effuse from a 0.125 inch hole directed towards the substrate under near choked flow conditions. DMZn (95% purity, Strem) was introduced without carrier gas directly into the chamber through a port in the top of the reactor using a calibrated metering valve. The pressure in the plasma tube was measured by an upstream convection gauge (\(P_1\)), and the pressure in the film growth chamber was measured by an ionization gauge (\(P_2\)). Under typical growth conditions the plasma pressure was \(P_1 \sim 100\) mtorr and the deposition chamber was \(P_2 \sim 10^{-5}\) torr. The substantial pressure difference (\(P_1 / P_2 > 10^3\)) between the tube and deposition chamber ensures that the two regimes were effectively decoupled.

The ICP source performance and the composition in the deposition chamber were

![Figure 3.1. Top view schematic of HVP-CVD reactor.](image-url)
monitored in real time using optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS). Emission from the plasma was collected by a fiber optic externally mounted on a window and directed at the center of the source. The light was analyzed using an Ocean Optics S2000 optical emission spectrometer operating over the extended visible regime ($300 < \lambda < 900$ nm) with a resolution of $\sim 1.5$ nm. A Stanford Research Systems RGA300 was used to analyze the gas composition in the film deposition chamber. The QMS has a range of 2–300 amu and a resolution of 0.1 amu. The QMS was mounted on a port directly opposite of the OES window. The QMS analyzed the chamber composition directly, so its values were not complicated by issues related to sampling and differential pumping. The ICP source was encircled by a grounded Faraday gauge made of copper mesh, which allowed simultaneous operation of the plasma and the QMS with minimal interference. However, it was observed that the intensity of all QMS signals varied slightly (20%) when the ICP source was turned on due to residual RF leakage. To account for this the QMS spectra were normalized with respect to the argon signal at $m/z = 40$, since the argon flowrate and partial pressure were held constant throughout all experiments.

The DMZn density was calibrated using both the ion gauge ($P_2$) and the QMS. A linear correlation was observed between $P_2$ and all the major DMZn fragments. As work proceeded, the integrity of the ion gauge became compromised due to carbon deposition, while the QMS signals remained stable. Because of this phenomenon, the DMZn partial pressure was set using the QMS-recorded intensity of the largest DMZn fragment at $m/z=79$ ($\text{ZnCH}_3^+$). However, in the figures of this paper we report the total DMZn partial pressure that was obtained using the original ion gauge correlation.

ZnO films were deposited on Corning 1737 glass and p-type silicon (001) substrates. The substrates were clamped to a resistively heated susceptor whose temperature was maintained by a PID controller that responded to a thermocouple mounted on the backside of the susceptor. Calibrations were performed between the control thermocouple and thermocouples that were taped to the surfaces of the respective
substrates. All films discussed here were grown at a calibrated surface temperature of 500 K.

The structural, optical, and electrical properties of the deposited films were characterized. Film thickness was measured using a Woolam WVASE32 variable angle spectroscopic ellipsometer. The ellipsometry measurements were confirmed by comparison with thickness data obtained by step profilometry after etching in a 2M HCl solution. Crystal orientation and quality were examined using X-ray diffraction (XRD) over angles of incidence that ranged from 20 - 70°. Optical transmission and reflection were measured using a Cary 5G UV-Vis-NIR spectrophotometer for films deposited on glass.

3.2.2 Characterization of ICP Source

Both OES and QMS were used to characterize the ICP performance in-situ as a function of rf power and gas composition. These techniques were combined with plasma modeling to estimate the degree of oxygen dissociation in the plasma. The rf power was varied from 60-140 W for O\textsubscript{2}/Ar and N\textsubscript{2}O/Ar plasmas. The influence of gas composition was studied by incrementally substituting N\textsubscript{2}O for O\textsubscript{2} over a range of 0 – 100% N\textsubscript{2}O at a constant power input of 100 W.

OES is a widely used diagnostic that provides information on the species present in the plasma. Figure 3.2 shows representative OES spectra obtained from (a) O\textsubscript{2}/Ar and (b) N\textsubscript{2}O/Ar plasmas. The strong emission lines at 777 and 844 nm indicate that substantial amounts of atomic oxygen are present in both cases. The primary difference between the two sources is the presence of strong emission bands associated with molecular N\textsubscript{2} that occur between 500-750 nm in the case of N\textsubscript{2}O.

Actinometry is a common technique used with OES to quantify the relative density of ground state species in the plasma as described by Equation 3.1.\textsuperscript{53}
It requires a known amount of inert gas, such as Ar, in the plasma, and relies on the ratio of the emission intensities of the species of interest and the inert gas. Choosing appropriate peaks for equation 3.1 can be difficult, but O atom actinometry with Ar has been extensively studied. It has been found that actinometry results using the O\textsubscript{844} and the Ar\textsubscript{750} emission lines are in good agreement with absolute measurements obtained by laser induced fluorescence.\textsuperscript{53-55} Unfortunately, the Ar\textsubscript{750} peak was somewhat obscured by N\textsubscript{2} bands in the case of N\textsubscript{2}O – containing plasmas. The Ar emission line at 811 nm was used instead as the actinometer since it was a prominent signal that was not compromised by the N\textsubscript{2} bands. Good agreement was observed between the data evaluated with the Ar\textsubscript{750} and Ar\textsubscript{811} lines in O\textsubscript{2}/Ar plasmas. Figure 3.3 shows actinometry evaluation of the O atom density in the plasma as a function of (a) rf power in O\textsubscript{2}/Ar and (b) percentage N\textsubscript{2}O at 100 watts. The O atom density increased linearly with power, doubling as the power was
increased from 60 to 140 watts. The O atom density decreased linearly by 30% as N\textsubscript{2}O replaced O\textsubscript{2}.

The plasma chemistry in the ICP source was modeled for the O\textsubscript{2}/Ar system using the AURORA component of CHEMKIN\textsuperscript{57}. The plasma model consisted of 36 reactions and 11 species that were a subset of a mechanism that was validated for SiO\textsubscript{2} deposition in an ICP system\textsuperscript{58}. The model suggests that the primary production pathway for O atom is electron impact dissociation of O\textsubscript{2}, given in equation 3.2.

\[
e^- + O_2 \rightarrow O^+ + O + e^-
\] (3.2)

The modeling results, also shown on Figure 3.3a, indicate that the O atom mole fraction in the ICP source doubles from 0.15 to 0.30 as the rf power increases from 60-140 W. Very good agreement between model predictions and actinometry measurements was observed, indicating that the model can reliably quantify the O atom density for O\textsubscript{2}/Ar mixtures in our ICP source.
The mass spectra from both (a) O$_2$/Ar and (b) N$_2$O/Ar mixtures with and without plasma operation are given in Figure 3.4. The production of atomic oxygen is demonstrated in Figure 3.4a by the significant decrease in the molecular oxygen m/z=32 signal and an increase in atomic oxygen at m/z=16 observed in the O$_2$/Ar case upon plasma activation. The spectrum also reveals peaks for water, CO, and CO$_2$, which are commonly formed in oxygen plasmas from atomic oxygen reacting with hydrocarbon contaminants on the chamber walls. Figure 3.5 presents the ratio of the O$^+$/O$_2^+$ peaks as a function of rf power in the O$_2$/Ar plasma. The linear increase observed in this ratio agrees quantitatively with both the OES data and modeling predictions shown in Figure 3.3a. Note that while the model suggests O atom mole fractions of 15-30% in the ICP source, the QMS data suggests that the value in the chamber is about half of that. This is consistent with the observation of substantial amounts of CO and CO$_2$ in the QMS, which are formed by the reaction of O atom with material on the walls.
The N\textsubscript{2}O/Ar mass spectra shown in Figure 3.4b is somewhat more complicated with significant peaks at m/z = 14(N\textsubscript{2}\textsuperscript{+}), 16(O\textsuperscript{+}), 28(N\textsubscript{2}\textsuperscript{+}/CO\textsuperscript{+}), 30(NO\textsuperscript{+}), 32(O\textsubscript{2}\textsuperscript{+}), and 44(N\textsubscript{2}O\textsuperscript{+}/CO\textsubscript{2}\textsuperscript{+}). The m/z=44 peak observed during plasma operation can be attributed to CO\textsubscript{2}\textsuperscript{+}, based on comparison with Figure 3.4a and previous experience with N\textsubscript{2}O plasmas. Literature data\textsuperscript{34,44,79} shows that N\textsubscript{2}O is highly dissociated at powers densities (<0.5 W/cm\textsuperscript{3}) far less than the operating range of used here (2–6 W/cm\textsuperscript{3}). With N\textsubscript{2}O completely dissociated in the ICP source, the primary products observed are N\textsubscript{2}, NO, O, and O\textsubscript{2}. Although a complete plasma reaction mechanism has not been validated for N\textsubscript{2}O, much is known about its behavior. N\textsubscript{2}O is widely used for production of atomic oxygen in SiO\textsubscript{2} PECVD, and it has been studied with OES and QMS.\textsuperscript{34,44,79} The literature suggests that the primary pathway for O production from N\textsubscript{2}O is also electron impact dissociation.

\[ N_2O + e^- \rightarrow N_2 + O + e^- \quad (3.3) \]
This pathway is also supported by the QMS data showing a large increase in N₂ for the N₂O plasma compared with the baseline N₂O mass spectrum. The dominant pathway for NO formation occurs through a two step mechanism\(^{34}\)

\[
e^- + O \rightarrow O^* + e^- \tag{3.4}
\]

\[
O^* + N_2O \rightarrow NO + NO \tag{3.5}
\]

where O\(^*\) is an electronically excited state. NO does not exhibit any OES peaks in the visible range, but the QMS indicates that it is produced in significant quantities as shown in Figure 3.4b.

### 3.3 Results - Deposition Kinetics

The ZnO deposition rate was measured as a function of DMZn pressure (P\(_{DMZn}\)) and atomic O density with the substrate temperature fixed at T\(_s\) = 500 K. Figure 3.6 plots the measured growth rate on silicon as a function of DMZn partial pressure. The linear relationship between growth rate and P\(_{DMZn}\) indicates that under these conditions the kinetics are first order in DMZn. The two lines in Figure 3.6 represent the predicted ZnO growth rate that would be obtained assuming a DMZn sticking coefficient of \(\gamma = 0.2\) and 1. The experimental data is bound between these two points, demonstrating that the conversion of DMZn to ZnO is highly efficient. The growth rate approaches the collisional limit within the uncertainty of the DMZn pressure measurement. In contrast, the growth rate was found to be independent of the amount of available atomic O in the chamber. The growth rate as a function of the O atom density is shown in Figure 3.7. The x-axis values were determined from actinometry results.
Figure 3.6: Growth rate as a function of DMZn partial pressure. The lines indicate the ZnO growth rate that would result assuming DMZn sticking probabilities of $\gamma = 1$ (solid) and $\gamma = 0.2$ (dashed), respectively.

Figure 3.7: Growth rate as a function of O atom density.
The films were characterized by XRD, Hall effect, and UV-VIS-IR spectrophotometry. Substrates were approximately 3 x 3 cm square, and were highly uniform in nature. A more complete description of film properties as a function of substrate temperature and nitrogen doping will be discussed in future publications. Here, we simply note that the intrinsic HVP-CVD films have extremely high quality as evidenced by their crystal structure and transparency. Representative XRD patterns obtained on Si and glass for films are shown in Figure 3.8. All of the films deposited for this study were highly (002) oriented, with no other peaks visible in the pattern. Examples of optical transmission spectra are presented in Figure 3.9 as a function of N\(_2\)O percentage in the oxidizer. All films were between 200-250 nm thick and have transmittance greater than 85% in the visible range. Increasing the N\(_2\)O content was found to shift the band gap absorption only slightly towards the visible. All films were observed to be highly insulating, indicating that oxygen vacancies were suppressed. This is in agreement with the growth data, which indicated that under these conditions atomic oxygen was supplied in excess as the rate was independent of atomic O density (Figure 3.7).

3.4 Deposition Chemistry

A great advantage of HVP-CVD over conventional CVD techniques is the ability to directly interrogate the surface chemistry with high vacuum diagnostics. We again stress that the changes observed in the spectra below are predominantly due to chemistry occurring at surfaces. The collision frequency and residence time in the deposition chamber are comparable, and gas-phase collisions are simply precluded. Further evidence for this assertion is presented below.

Figure 3.10 compares the mass spectra obtained by the QMS with and without plasma operation for (a) O\(_2\)/Ar/DMZn and (b) N\(_2\)O/Ar/DMZn mixtures. No chemistry is observed without plasma operation. The DMZn cracking pattern, with isotopic groups
appearing around m/z = 64 (Zn⁺), 79 (Zn(CH₃)⁺), and 94 (Zn(CH₃)₂⁺), was unchanged by the addition of either O₂ or N₂O. In addition, no ZnO deposition was observed on either glass or Si without plasma operation after a 30 minute exposure to these mixtures at 500 K. The substrates were removed in pristine condition. However, it was observed that DMZn was nearly completely consumed (~95%) when the plasma was ignited for both oxidizers. This observation is supported by the measured deposition rates shown in Figure 3.6. The rates are consistent with a DMZn surface reaction probability that is approaching unity. Film growth is weakly activated, and high deposition rates have been obtained at room temperature. As such, the bulk of the reactor interior is also expected to behave as a substrate for consumption of DMZn.

A comparison of Figures 3.10 and 3.4 show that spectra obtained during plasma operation with and without DMZn are very similar in both oxidizers. The only significant difference observed upon the addition of DMZn is the substantial increase in the signal at m/z = 15. This peak is attributed to CH₃⁺ that is believed to desorb from the
surface in an unreacted state. The spectra obtained with O$_2$ and N$_2$O with DMZn both show similar behavior. In the case of O$_2$ there is a doublet at 15 and 16, which is attributed to CH$_3^+$ and O$^+$. In the case of N$_2$O there is a triplet caused by the presence of N$_2^{++}$ at 14.

We cannot completely rule out the presence of methane, whose cracking pattern yields strong peaks at both 16 and 15. A small amount of CH$_4$ was evident in the Ar/DMZn spectra due to cracking and impurities in the DMZn. However, the m/z=15 signal increased by nearly a factor of ten when the plasma was turned on, which is commensurate with the drop in the organometallic signals. Unlike the m/z=15 signal, the CO$^+$ and CO$_2^+$ signals remained similar to those observed in the O$_2$/Ar plasma. If methane were desorbing, it would be produced by reactions between absorbed methyl groups. However, surface science experiments revealed that these reactions do not begin to occur until temperatures $> 700$ K.$^{80}$ In addition, if methane desorption was a significant product channel one would also expect to see significant amounts of species such as H$_2$, H$_2$O, CO, or CO$_2$ to account for the remaining CH$_x$ left on the surface. Again, a comparison of Figures 3.4 and 3.10 indicate that all of these signals are nearly unchanged by the addition of DMZn. The insensitivity of the CO$^+$ and CO$_2^+$ signals to the addition of DMZn indicates that they are due only to the reaction of O with contaminants on the walls, and not from combustion of DMZn.

The presence of significant amounts of CH$_3$ and the relatively low amounts of O in the system imply that DMZn is not decomposing through combustion. Plasma modeling and actinometry results presented in Figure 3.3 gives an O atom mole fraction in the plasma of 0.2 at 100W, and the QMS results suggest that half of this is consumed by reaction on the chamber walls. Based on these data it was estimated that the upper limit for atomic oxygen partial pressure in the chamber under deposition conditions is $\sim 2 \times 10^{-5}$ torr. The DMZn pressures examined ranged from $5 \times 10^{-6}$ to $1 \times 10^{-5}$ torr. At maximum deposition rates the highest O/DMZn flux ratio would be no greater than 2.
Figure 3.10: The QMS spectra obtained with and without plasma operation for (a) O$_2$/Ar/DMZn and (b) N$_2$O/Ar/DMZn mixtures. All spectra were normalized to the Ar 40 signal and offset for clarity.
Complete combustion of DMZn by atomic oxygen would require an O/DMZn flux ratio of 11, and there is clearly insufficient atomic oxygen available for this to occur.

It is of interest to contrast the surface chemistry of DMZ observed in the HVP-CVD system with conventional thermal pyrolysis. The results of a surface science investigation of DMZ decomposition on silicon performed by Rueter and Vohs are illustrated in Figure 3.11a. They observed that DMZ dissociatively absorbs at temperatures < 400 K, producing atomic zinc and methyl groups. Upon heating Zn desorbed first, leaving only methyl groups on the surface by T = 600 K. Dehydrogenation reactions were observed to commence at T > 700 K, resulting in methane and hydrogen desorption, with some residual carbon left on the surface. The strong methyl signal shown in Figure 3.10, which was obtained at T = 500 K, indicates that the behavior is very different in the presence of atomic oxygen. The contrast between the surface chemistry occurring during HVP-CVD and thermal decomposition is illustrated in Figure 3.11. It is assumed that the first step in HVP-CVD remains dissociative absorption. However, the presence of atomic oxygen results in ZnO synthesis and accelerates methyl desorption without further reaction. No carbon incorporation was observed in the films, as evidenced by the extremely high transmission shown in Figure 3.9. We note that the ability of a reactive gas to alter surface chemistry has been observed before. In high vacuum studies of trimethyl gallium decomposition it was observed that the presence of arsine greatly accelerated methyl desorption as well.

3.5 Conclusions

A novel HVP-CVD process was described for metal oxide thin film formation from atomic oxygen and organometallic precursors. Gas-phase chemistry is precluded in this system by the absence of collisions. Highly oriented and transparent ZnO was produced by HVP-CVD using DMZn. The ICP source used to generate atomic oxygen was
successfully characterized with a combination of diagnostics and kinetic modeling. The film growth rate was found to be first order in DMZn and zero order in atomic O over the range studied. Deposition rates approaching the collisional limit indicate that deposition proceeds exclusively through surface reactions. QMS measurements provide further support, showing that the presence of atomic O accelerates desorption of unreacted methyl groups and facilitates ZnO formation.

3.5 Acknowledgments

The authors gratefully acknowledge financial support from the National Science Foundation through CAREER Award No. CTS-0093611.
CHAPTER FOUR
LOW TEMPERATURE DEPOSITION OF HIGHLY ORIENTED ZnO

The following is a reproduction of a paper submitted to The Journal of Crystal Growth in June of 2004. This chapter is as submitted, except that section numbers, figure labels, and references have been changed to conform to the thesis format.

Room Temperature Chemical Vapor Deposition of c-axis ZnO

Teresa. M. Barnes, Jacquelyn Leaf, Cassandra Fry, and Colin A. Wolden*
Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401

4.0 Abstract

Highly (002) oriented ZnO films have been deposited at temperatures between 25 – 230 ºC by high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) on glass and silicon substrates. The HVP-CVD process was found to be weakly activated with an apparent activation energy of ~0.1 eV, allowing room temperature synthesis. Films deposited on both substrates displayed a preferential c-axis texture over the entire temperature range. Films grown on glass demonstrated high optical transparency throughout the visible and near infrared.

Keywords: A3. Metalorganic chemical vapor deposition; B1. Oxides; B1. Zinc compounds; A1. X-ray diffraction; B2. Semiconducting II-VI materials
4.1 Introduction

Zinc oxide (ZnO) is a versatile wide band-gap semiconductor with an array of uses including transparent conductors, piezoelectrics, and short wavelength light emitting devices. ZnO is especially attractive for UV laser applications due to its band gap of 3.3 eV and high exciton binding energy of 60 meV. The exciton binding energy of ZnO is more than double that of GaN, enabling room temperature lasing and improved photonic device reliability. Blue emitting LEDs and UV lasing at room temperature have already been demonstrated. Doped ZnO is widely used as a transparent contact for amorphous silicon devices, and it is being pursued as a replacement candidate for indium-tin oxide (ITO) in organic LEDs and other applications.

In the device applications cited above, zinc oxide synthesis was accomplished at high processing temperatures (>500 ºC). Fabrication of high quality ZnO at lower temperature would enable the production of devices and contacts on polymer substrates and on temperature sensitive components. The c-axis orientation is preferred for nearly all device applications. ZnO synthesis by thermal chemical vapor deposition (CVD) typically requires temperatures in excess of 350 ºC order to achieve (002) preferentially oriented films. Plasma enhanced chemical vapor deposition (PECVD) has allowed temperature requirements to be reduced substantially, with many groups obtaining dominant c-axis orientation at substrate temperatures around ~200 ºC. Further reduction in substrate temperature resulted in either randomly oriented or amorphous film structures.

ZnO has been deposited on unheated substrates by both sputtering and pulsed laser deposition. The sputtered films exhibited excellent optical and electrical characteristics for transparent electrical contacts, but they were randomly oriented. ZnO films with an (002) texture were deposited by oxygen radical assisted pulsed laser deposition at room temperature. However, both of these techniques utilize a ZnO target. We have recently developed a new technique for metal oxide deposition that is described as high vacuum
plasma-assisted chemical vapor deposition (HVP-CVD). The unique feature of this process is that gas-phase chemistry is eliminated by the collisionless environment, restricting the process chemistry to surface-mediated routes. In this paper, we present the synthesis of highly (002) oriented ZnO by HVP-CVD at low temperatures using dimethyl zinc and atomic oxygen as precursors.

4.2 Experimental Methods

The films presented in this work were deposited in a HVP-CVD system that is described in detail elsewhere. The HVP-CVD reactor shares similarities with plasma-assisted molecular beam epitaxy (P-MBE), with the exception that the metal source is a volatile organometallic precursor instead of elemental zinc. In this case, atomic oxygen and dimethyl zinc (DMZn) effuse into a high vacuum chamber, where they subsequently react on a temperature-controlled substrate. The organometallic precursor was stored in an ice bath, and introduced without carrier gas into the background of the high vacuum chamber using a calibrated needle valve. Atomic oxygen was generated using an inductively coupled plasma (ICP) source supplied with 0.65 sccm of O₂ (99.999%). A small amount of argon (0.1 sccm) was also added to the plasma for diagnostic purposes, with both gas flow rates maintained by electronic mass flow controllers. The RF power was coupled to the ICP source using an automated match network and held constant at 80 W. Reactive products effused from a ~2 mm orifice at the end of the ICP source and directed toward the substrate. Detailed characterization of ICP source performance is detailed elsewhere. A PID-controlled resistive heater mounted on the back of the susceptor maintained the desired temperature. The substrate surface temperature was calibrated using a thermocouple mounted on the surface of both glass and silicon prior to deposition experiments. The total pressure in the deposition chamber was ~7.5 *10⁻⁵ torr.
for all experiments. Films were deposited on to Corning 1737 glass and p-type (100) silicon wafers.

Variable angle spectroscopic ellipsometry (VASE, J. A. Woollam Company) was used to measure the film thickness. Film composition was studied with secondary ion mass spectrometry (SIMS, Phi 6650) using a Cs$^+$ ion beam to monitor impurity incorporation. The crystal structure was evaluated using X-Ray diffraction using Cu K$\alpha$ radiation (XRD, Siemens). The optical transmission of films on glass was measured using a Cary5 spectrophotometer using the glass transmission as a baseline. The morphology of the films was observed with a Nanoscope III atomic force microscope (AFM, Digital Instruments).

4.3 Results and Discussion

Zinc oxide thin films were deposited over a temperature range of 25 – 230 ºC on both silicon and glass substrates. All conditions were the same with the exception that the DMZn pressure was 25% greater for the silicon samples in order to yield thicker films that are more convenient for characterization. It was previously observed that the deposition rate is first order in DMZn and independent of O for this range of conditions. Figure 4.1 presents Arrhenius plots of the ZnO growth rate on glass and silicon substrates in the HVP-CVD system. Linear fits to the data yielded apparent activation energies of 0.1 and 0.06 eV for glass and silicon, respectively. The small differences in activation energy on glass and silicon are within the expected experimental error and are likely insignificant. ZnO growth should be similar on both substrates after the first ZnO monolayers are formed.

XRD patterns obtained on silicon and glass are presented in Figure 4.2. All films demonstrate a strong preferential orientation in the (002) direction. We note that the highest temperature employed here (230 ºC) was well below those used in many other
In the case of silicon, the patterns remain nearly unchanged between 60 and 230 ºC (Figure 4.2a). At room temperature, the full width half maximum (FWHM) increases and peaks attributed to the (101) and (100) orientations appear, but remain small compared to the (002) peak.

Figure 4.2b shows the XRD patterns from the films grown on glass substrates. For glass substrates it was observed that the XRD patterns improved with increasing substrate temperature. This results from a combination of two factors, crystal quality and sample thickness. The thicknesses of the films grown at 200 ºC and above were on the order of 200 nm, while the films grown below 150 ºC were on the order of 100 nm thick. As the film thickness decreased the background increased due to interactions of the X-rays with the underlying amorphous substrate material. Films deposited on glass at temperatures below 100 ºC displayed a more random orientation, with significant peak broadening and the appearance of the (100) peak. However, it was found that the c-axis orientation could be restored by controlling the DMZn flux. The bottom XRD pattern in Figure 4.2b was obtained from a film grown at room temperature with the DMZn partial pressure reduced by one third relative to standard conditions. The exclusive (002)
Figure 4.2: XRD patterns as a function of deposition temperature obtained from (a) silicon and (b) glass substrates.
orientation and narrow linewidth were restored by reducing both the growth rate and the DMZn/O ratio.

AFM images of films grown on silicon at selected substrate temperatures are shown in Figure 4.3. Films grown between 60 and 230 °C were characterized by a well-defined nanocrystalline morphology as displayed in Figure 4.3a and 4.3b. The typical grain size was ~ 50 nm and the crystallites were distinct and densely packed. The AFM results were consistent with XRD, in that no changes were observed over this temperature range. The morphology of the film grown at room temperature (Figure 4.3c) was distinct in that well-defined crystallites were not observed. The poorly defined structure was again consistent with XRD (Figure 4.2a), which displayed multiple crystal orientations as well as amorphous content. AFM imaging of films grown on glass were consistent with the

![AFM images](image)

Figure 4.3: AFM images obtained in tapping mode of ZnO grown on silicon at (a) 230 °C, (b) 60 °C, and (c) 25 °C.
features illustrated in Figure 4.2. Distinct nanocrystalline morphologies were observed for films with the preferred (002) orientation, while the more ambiguous surface were observed in films with random orientations and/or amorphous components.

All of the films deposited on glass demonstrated exceptional optical transparency throughout the entire visible range. Figure 4.4 plots the percent transmission versus wavelength for selected films. All films display transparency in excess of 85% throughout the visible range. These intrinsic films were all found to be highly insulating, as they were grown under conditions where atomic oxygen was supplied in excess. As such the films remain transparent in the infrared region as well. The optical band gap was determined from the intercepts of plots of \((h\nu^2\alpha^2)\) vs. \(E\). It was found that the optical band gap increased slightly with decreasing deposition temperature. At 230°C the optical band gap was 3.28 eV, and it increases to 3.33 eV at room temperature. It is noted that these small changes are not viewed as significant. It is well known that the ZnO band gap is particularly sensitive to small changes in carrier concentration, grain boundary

![Figure 4.4: Optical transmission spectra of selected films deposited on glass at different substrate temperatures.](image)
configuration, and film stress. The low activation energy enabled room temperature ZnO synthesis on both substrates. The energetics observed in HVP-CVD were unique with respect to other ZnO deposition systems. In thermal CVD with DMZn activation energies around 0.7 eV were observed, which helps to explain the difficulty of low temperature ZnO deposition in non-plasma systems. The apparent activation energy reported for PECVD systems was actually lower, around 0.02 eV. However, these films were grown with diethylzinc, and as noted above, it was not possible to maintain crystal orientation in PECVD systems at temperatures significantly below 200 ºC. In P-MBE studies it was found that the activation energy was negative, as the rate-limiting step was attributed to Zn absorption. It should be noted that all of these cases were studied at much higher temperature regimes (200 – 600 ºC) than the work presented here.

The apparent activation energy observed on both the glass and silicon substrates suggest a surface mediated reaction to form ZnO. It is known that dimethyl zinc readily absorbs on silicon at low temperature, dissociating into atomic zinc and methyl groups. Upon heating in vacuum it has been observed that atomic zinc desorbs first, followed by decomposition and desorption of the remaining methyl groups. The surface chemistry behavior in is very different in the HVP-CVD system. The flux of atomic oxygen facilitates methyl desorption and subsequent ZnO formation.

The mechanism suggested above raises the possibility of carbon incorporation. For device consideration it is important to minimize the density of such impurities. Although the optical transparency was good in all cases, SIMS was employed to measure the relative density of carbon impurities in the films. Absolute standards were not available for quantification, so the ratio of the $^{12}\text{C}/^{83}\text{ZnO}$ was used for all samples. The results are plotted in an Arrhenius format in Figure 4.5 for films grown on silicon. The carbon concentration increased exponentially with decreasing temperature. The apparent activation energy is negative 0.1 eV. The film deposited at room temperature also showed significant accumulation of carbon at the ZnO/Si interface. The temperature dependence
of the C/ZnO ratio mirrors that of the growth rate (Figure 4.1). It is postulated that desorption of methyl groups is the key rate-limiting step for both growth and carbon incorporation. It is likely that the decline in crystalline properties observed at low temperatures is due to carbon contamination. Work is underway to minimize carbon incorporation by varying the atomic oxygen density, controlling the deposition rate, and exploring alternative organometallic precursors.

4.4 Conclusions

ZnO thin films with a dominant c-axis texture were deposited by chemical vapor deposition at temperatures between 25°C and 230°C on both glass and silicon substrates. Film growth in the HVP-CVD system was weakly activated, and shows only a slight dependence on substrate type. The high quality of the material was verified by XRD,
AFM, and optical transmission. At room temperature the film orientation may be controlled by appropriate adjustment of the DMZn flux, to lower the growth rate and reduce the DMZn/O ratio in the growth environment. The density of carbon impurities in the films was found to mirror the growth rate dependence on temperature, suggesting that desorption of methyl groups was the rate-limiting step. The HVP-CVD technique is quite promising for reducing the processing temperatures needed for fabrication of ZnO-based devices.

4.5 Acknowledgements

The authors gratefully acknowledge financial support from the National Science Foundation through CAREER Award No. CTS-0093611. We also thank Dr. Tom Mates for assistance with SIMS, which was performed at the University of California Santa Barbara using the MRL Central Facilities supported by the MRSEC Program of the National Science Foundation under award No. DMR00-80034.
A high vacuum plasma-assisted chemical vapor deposition system was used to systematically study ZnO:N thin film synthesis. Nitrogen doping was achieved by mixing either N$_2$O or N$_2$ with O$_2$ in a high density inductively coupled plasma (ICP) source. In-situ diagnostics showed that the ICP composition was predominantly a function of the elemental oxygen to nitrogen ratio, and relatively insensitive to the choice of N$_2$ or N$_2$O as the molecular precursor. Nitrogen incorporation was measured by both XPS and SIMS, and was found to increase monotonically with both N$_2$O and N$_2$ addition. Nitrogen doping was correlated with systematic shifts in lattice spacing, electrical conductivity, and optical absorption. Quantitative comparisons between film properties and gas composition suggest that atomic nitrogen is the primary precursor for doping in this system.
5.1 Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor that is regularly used as a transparent electrical contact, with many potential applications such as optical waveguides, UV lasers, and short wavelength light emitting diodes (LEDs). ZnO is especially attractive for UV laser applications due to its bandgap of 3.3 eV and high exciton binding energy of 60 meV. The exciton binding energy of ZnO is more than double that of GaN, enabling room temperature lasing and improved photonic device reliability.1,2 ZnO blue emitting LEDs3, UV nanolasers4, and quantum pyramids5 have already been demonstrated.

ZnO is unique among the commonly used transparent conducting materials in that it can be doped p-type, most often with nitrogen. P-type ZnO:N was first proposed by Kobayashi in 198310, but experimental work has proven that it is difficult to produce. Challenges arise from an asymmetric doping limitation that strongly favors n-type conductivity.11,12 Theoretical calculations suggest that the nitrogen solubility in ZnO is strongly affected by the nitrogen source.13 Potential nitrogen dopant sources include N2O, N2, N, and NO. It has been proposed that NO is the most thermodynamically attractive nitrogen acceptor source.13,14 Despite the extensive theoretical calculations, relatively little experimental work has been done to study the mechanism of N doping or to determine the doping precursor species.

Nitrogen doped ZnO has been synthesized by a variety of techniques including plasma-assisted molecular beam epitaxy (P-MBE), pulsed laser deposition (PLD), and metalorganic chemical vapor deposition (MOCVD). P-MBE processes have produced ZnO:N from the reaction of elemental Zn with active O and N containing species generated from an N2/O2 plasma source. A film fabricated in this manner was characterized as p-type by Look et al.2, while those grown by Iwata and coworkers47 were
not. PLD relies on irradiating a ZnO target in the presence of an N$_2$O plasma, but only a small fraction of these films exhibit p-type conductivity. A MOCVD process combined diethyl zinc and NO in a thermally driven reaction to form ZnO:N, again identifying a narrow processing window for p-type conductivity. None of these reports provided information about the gas composition in the growth environment. There has been little discussion of the nitrogen-containing species responsible for ZnO:N formation, or an explanation for the wide disparity in nitrogen doping results. A recent study compared ZnO:N synthesis by PLD using three plasma-activated sources (N$_2$, N$_2$O, and NO). All three sources provided a high level of N incorporation as determined by SIMS, but all films remained n-type. Using a very qualitative assessment of emission spectra, these authors suggest that both vibrationally excited N$_2^*$ and NO were potential origins of nitrogen incorporation.

In this paper, we describe a unique high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) system used to synthesize ZnO:N from dimethyl zinc and plasma activated mixtures of O$_2$/N$_2$O or O$_2$/N$_2$. In particular, we directly compare the efficacy of N$_2$O and N$_2$/O$_2$ plasmas for the production of ZnO:N. Oxygen mixed with either N$_2$O or N$_2$ was dissociated in an inductively coupled plasma (ICP) source. The dissociation products were monitored and tracked in-situ with optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS). Controlled nitrogen doping was confirmed by XPS and SIMS, and its impact on structural, electrical, and optical properties is discussed. Quantitative evaluation of N, O, N$_2^*$ and NO densities are compared with resulting film properties to provide insight into the doping mechanism.

5.2 Experimental Methods

The deposition system used in this work is described in detail elsewhere. It is similar in many ways to P-MBE, except that the elemental zinc source is replaced with an organometallic precursor. Briefly, a Pyrex ICP source was supplied by mixtures
of semiconductor grade N\textsubscript{2}O, ultra high purity O\textsubscript{2} and N\textsubscript{2}, and industrial grade Ar. The Ar flowrate was 0.1 sccm for all experiments, while the total oxidizer and dopant flowrate (O\textsubscript{2} + N\textsubscript{2}O/N\textsubscript{2}) was 0.65 sccm. All gas flows were controlled by Unit electronic mass flow controllers. The plasma was ignited by powering a 6 turn water-cooled copper coil operating at 13.56 MHz with an Advanced Energy AM5 automatic match network. The ICP power was varied over the range of 50-100 W. Reactive products effuse from a 0.125 inch hole directed towards the substrate under near choked flow conditions. DMZn (95% purity, Strem) was introduced without a carrier gas into the chamber directly through a port in the top of the reactor using a calibrated metering valve. The DMZn density was calibrated using a cold cathode pressure gauge and the QMS. Under typical growth conditions the ICP source pressure was \( \sim 100 \) mtorr and the deposition chamber was \( \sim 4 - 8 \times 10^{-5} \) torr. The substantial pressure difference ( \( >10^3 \)) between the tube and deposition chamber ensures that the two regimes were effectively decoupled.

The ICP source performance and the composition in the deposition chamber were monitored in real time using OES and QMS. Light emission from the plasma was analyzed using an Ocean Optics S2000 optical emission spectrometer over a wavelength range of 300 – 900 nm. A Stanford Research Systems RGA300 was used to analyze the gas composition in the film deposition chamber. The QMS has a range of 2 – 300 amu and a resolution of 0.1 amu. The QMS was mounted on a port directly opposite of the OES window. The QMS analyzed the high vacuum chamber composition directly, so its values were not complicated by issues related to sampling and differential pumping.

ZnO films were deposited on Corning 1737 glass and p-type silicon (100) substrates. A PID-controlled resistive heater mounted on the back of the susceptor maintained the substrate temperature at 230 °C for all experiments described here. The deposited films were extensively characterized to evaluate their composition, structural, optical, and electrical properties. Film thickness was measured using a Woollam WVASE32 variable angle spectroscopic ellipsometer and confirmed by profilometry. The film composition was studied with X-ray photoelectron spectroscopy (XPS, Kratos) and secondary ion
mass spectrometry (SIMS, Phi 6650). The SIMS employed a Cs\(^+\) beam, and the secondary ion intensity of the \(^{30}\text{NO}\) was used for nitrogen detection. Crystal orientation and quality were examined using X-ray diffraction (XRD, Rigaku) over a 20 - 70° angle of incidence range using Cu Kα radiation. Optical transmission and reflection were measured using a Cary 5G UV-Vis-NIR spectrophotometer for films deposited on glass. A 4-point probe was used to measure sheet resistance, and a BioRad HL5500PC Hall system was used to confirm resistivity and to determine the Hall mobility, carrier type, and the carrier concentration of the films deposited on glass. Additional confirmation of the carrier type was obtained from Seebeck coefficient measurements made on a custom built system.

5.3 Results – ICP Source Characterization

The ICP source performance was characterized using both OES and QMS to examine the dissociation of \(\text{N}_2\text{O}/\text{N}_2/\text{O}_2\) mixtures to determine the production of radicals such as O, NO, and N. OES was used to monitor the reactive species density in the plasma, and the QMS was used to directly monitor the composition in the high vacuum growth chamber. These tools enable the detection of the active oxidizer and doping precursor(s) in the HVP-CVD system.

Figure 5.1 compares QMS patterns obtained from plasma activation of pure \(\text{N}_2\text{O}\) with a 2:1 \(\text{N}_2:\text{O}_2\) mixture at 100 W. The spectra obtained from these two mixtures were nearly identical, indicating that the reactive gas composition produced by an \(\text{N}_2\text{O}\) plasma and an elementally equivalent mixture of \(\text{N}_2\) and \(\text{O}_2\) are quite similar. Both show significant amounts of O, N, \(\text{N}_2\), NO, and \(\text{O}_2\) are present in the plasma. \(\text{N}_2\text{O}\) is completely dissociated in the plasma at these power densities, and the signal at \(m/z=44\) due to \(\text{CO}_2^+\) formed from the reaction of atomic oxygen with residual carbon on the walls of the reactor chamber. The patterns shown in Figure 5.1 were only weakly impacted by
power over the range studied. Signals from atomic species (O$^+$/N$^+$) increased slightly with power at the expense of their molecular parents (O$_2^+$/N$_2^+$). The density of NO$^+$ remained essentially constant.

Figure 5.2 compares OES spectra obtained from the same N$_2$O and N$_2$/O$_2$ plasmas, which were again strikingly similar. Both spectra consist of sharp peaks from atomic O and Ar, and large bands associated with electronically and vibrationally excited N$_2^*$. In this paper, electronically excited states of N$_2$ will be described using the following notation: N$_2$(A) refers to the lowest lying A$^3\Sigma_u^+$ excited states that are 6-7 eV above ground; N$_2$(B) denotes the B$^3\Pi_g$ states that are 7-8 eV above ground; and N$_2$(C) represents the high energy C$^3\Pi_u$ states that are 11-12 eV above ground. Vibrationally excited ground state N$_2$ is noted as N$_2$(X,$\nu$). The notation N$_2^*$ will be used to refer generically to all excited states.

In Figure 5.2, the band at 500-760 nm is the first positive band that is due to N$_2$(B) to N$_2$(A) transitions, and the second positive band at 300-500 nm is caused by
N\textsubscript{2}(C) to N\textsubscript{2}(B) transitions. Some peaks in the region between 300 and 500 nm may be caused by the first negative system of the N\textsubscript{2}B\textsuperscript{2}\Sigma\textsuperscript{+}\textsubscript{u} to N\textsubscript{2}\textsuperscript{+}(X\textsuperscript{2}\Sigma\textsuperscript{+}\textsubscript{g}) transition.\textsuperscript{96} Each spectra also shows a small peak at 821 nm that is attributed to atomic N.\textsuperscript{97} No emission from NO was detected in this system. NO emits primarily in the deep UV, but peaks from a second order diffraction of the \gamma \text{ system appearing in the visible range from 420-550 nm are reported in the literature.}\textsuperscript{79} This region was somewhat noisy in these spectra, and there were no distinct signals that could be clearly resolved from the N\textsubscript{2} bands.\textsuperscript{96} The similarities in reactive the gas composition produced by the two mixtures illustrates that both might be equally successful for p-type ZnO:N production.

Key reactive species that were monitored during ZnO:N production include O, N, and NO and excited N\textsubscript{2}\textsuperscript{+}. Quantification of the gas composition from the QMS and OES spectra described above can be quite difficult. However we take advantage of the complementary nature of OES and QMS to ensure a self-consistent analysis. First, an important distinction is that OES reflects the composition in the ICP source, while QMS...
measures the composition in the high vacuum deposition environment. Although gas-phase chemistry is precluded by the low operating pressure, surface reactions including recombination and relaxation can significantly alter the composition. Atomic oxygen, nitrogen, and excited states are particularly impacted by these processes. For example, the atomic O is prominent in the OES spectra but quite weak in the QMS patterns. In our previous work on intrinsic ZnO synthesis, it was shown that the mole fraction of atomic oxygen in the deposition chamber was less than half that in the ICP source due to production of CO and CO$_2$ from carbonaceous contaminants.\textsuperscript{90} In contrast, information on NO density cannot be extracted from the OES, but it is clearly resolved in the QMS. The relative density of NO was determined using the QMS signal at m/z = 30 normalized with respect to the argon signal at m/z = 40, since the argon density was constant for all experiments.

Actinometry was employed to quantitatively interpret the OES spectra.\textsuperscript{53} Actinometry has been used extensively for absolute and relative measurements of atomic oxygen.\textsuperscript{54,55} The argon emission line at 750 nm is most often used as the actinometer, however in most of these spectra this peak is compromised by overlapping emission from the N$_2$ first positive series. The argon emission line at 811 nm was used instead. The O$_{844}$/Ar$_{811}$ actinometry pair is also well studied and has been validated for determination of atomic O density in O$_2$-N$_2$ plasmas.\textsuperscript{98} The Ar 811 peak and the atomic N line at 821 nm were used to quantify the atomic nitrogen density. The relative densities of N$_2$(B) and N$_2$(C) were determined using the 646 nm line and the 357 nm line respectively, with the Ar 811 nm peak as the actinometer. To summarize, the relative density of these five species were evaluated experimentally using the following relations:

$$[NO]_{QMS} \propto \frac{I_{30}}{I_{40}} \quad (5.1)$$

$$[O]_{OES} \propto \frac{I_{844}}{I_{811}} \quad (5.2)$$
The relative changes in O, N, N2(B, C), and NO density as a function of the percentage N2O or N2 in an O2 plasma are shown in Figure 5.3. Figure 5.3(a) shows that the O atom density decreases linearly with increasing percentages of N2O or N2 in the feed gas. N2O is known as a prolific source of O atom for oxide growth, and the O atom density decreases only ~35% when O2 is completely replaced by N2O. In contrast, the O atom density drops off sharply to zero as O2 is replaced by N2. Modeling studies of the discharge suggest that the O atom mole fraction in the ICP device is between 0.2 and 0.3 for the pure O2/Ar plasma.90 O is predominantly produced from electron impact dissociation of O2 or N2O. A second electron may then excite the O to O(1D)44,58, which is an important reactant for the formation of N and NO as discussed below.

Atomic nitrogen density for both N2O/O2 and N2/O2 plasmas is shown in Figure 5.3(b). In the case of N2O, [N] initially increases sharply. As the N2O fraction increases above 60%, the [N] density saturates. The response is somewhat similar in the case of N2, although [N] reaches a distinct maximum at 80% N2 before declining. The dominant N production pathway is likely electron impact excitation of N2, with a smaller contribution from relaxations of higher N2 excited states.97,99-101 The maximum in N density when using N2 suggests that oxygen is involved in an important N production channel. The absolute density of N atom is smaller than O atom, but its concentration is high enough to be chemically significant. The electron temperature, calculated according to the procedure in Lieberman and Lichtenberg, in this ICP device is approximately 3 eV
Figure 5.3: Plots of the changes in relative density of (a) [O], (b) [N], (c) [N$_2^*$], and (d) [NO] as a function of % N$_2$ (solid symbols) or % N$_2$O (open symbols) in the ICP source.
at 100 W.\(^{15}\) Experimental data from ICP plasmas indicates that about 4% of the available \(\text{N}_2\) is dissociated into \(\text{N}\) atoms under these plasma conditions.\(^{102}\)

The electronically excited \(\text{N}_2(\text{B and C})\) densities are shown in Figure 5.3(c). The behavior of both states is similar in \(\text{N}_2\text{O}\) and \(\text{N}_2\) mixtures, and both \(\text{N}_2(\text{B})\) and \(\text{N}_2(\text{C})\) exhibit similar trends with nitrogen addition. \(\text{N}_2(\text{A})\) is not measurable by OES due to its long radiative lifetime, but it is present at much larger densities than \(\text{N}_2(\text{B})\).\(^{99,103}\) A variety of sources report that atomic \(\text{N}\) concentration is between two to four orders of magnitude greater than any of the electronically excited \(\text{N}_2(\text{A, B, or C})\) states.\(^{35,99,103}\) Despite their prominence in the OES spectra, the impact of electronically excited \(\text{N}_2\) on the deposition process may be relatively minor.

Excited vibrational modes of ground state \(\text{N}_2(\text{X,v})\) are not directly measurable by our OES setup. The bands present in Figure 5.2 show the different vibrational states of the \(\text{N}_2(\text{B and C})\) in the plasma, but yield no information on the ground state vibrational distribution. However, this is a non-equilibrium plasma, with a gas temperature on the order of 500 K. At these low temperatures, the vibrational distribution function is heavily skewed towards the lowest vibrational states.\(^{104}\) In addition, studies of \(\text{N}_2/\text{O}_2\) mixtures show that the presence of just a few percent atomic oxygen effectively quenches the higher order vibrational states.\(^{105}\) Only these higher order states would have sufficient energy to be chemically reactive at the low substrate temperature employed here.

Figure 5.3(d) illustrates the relationship between NO production and the \(\text{N}_2\text{O}\) or \(\text{N}_2\) feed fraction. In the case of \(\text{N}_2\text{O}\), the NO density rises sharply as the feed fraction increases from 0 to 60%. The density then plateaus between 60 and 80% before decreasing slightly at 100% \(\text{N}_2\text{O}\). In contrast, the NO density profile in the \(\text{N}_2/\text{O}_2\) mixtures is parabolic in shape, with a maximum near 50% \(\text{N}_2\). If the data in Figure 5.3(d) were plotted as a function of elemental nitrogen, the points from \(\text{N}_2\text{O}\) and \(\text{N}_2\) are in perfect agreement. Therefore, the similarities between the two mixtures demonstrated in Figures 5.1 and 5.2 are maintained across the entire composition range.
The most common reaction pathways discussed in the literature for plasma formation of NO are presented in reactions 5.6-8. Reaction 5.6 is important in low power density discharges where N$_2$O is not completely dissociated. However, at the high power densities (3-7 W/cm$^3$) employed in this system, all of the N$_2$O is dissociated by electron impact. Two alternative pathways for NO formation that are expected to be more dominant in the high density plasma are given in reactions 5.7 and 5.8.$^{105}$

\begin{equation}
N_2O + O(\overset{1}{D}) \rightarrow NO + NO \tag{5.6}
\end{equation}

\begin{equation}
N + O_2 \rightarrow O + NO \tag{5.7}
\end{equation}

\begin{equation}
N_2 * + O \rightarrow NO + N(\overset{2}{D}) \tag{5.8}
\end{equation}

Reaction 5.7 will occur much more readily than reaction 5.8, but the atomic nitrogen density is generally low compared to the atomic O density. Both reactions are likely to contribute to NO production, with the dominant pathway dependent on the elemental N/O ratio in the mixture. NO generation is dependent in both atomic N and O, so an optimum is expected in mixture with an elemental oxygen to nitrogen ratio of one. Both reactions become oxygen (nitrogen) limited at high N$_2$ (O$_2$) feed fractions, and the maximum in NO density seen here between 40 and 60% N$_2$ is consistent with literature observations.$^{105}$ This limitation is less pronounced in the N$_2$O/O$_2$ mixtures because O is always abundant. Reaction 5.8 also relies on N$_2*$, implying that the excited N$_2$ species are important for the production of NO. The reduction in N density observed in the pure N$_2$ plasma shown in Figure 5.3(b) indicates that reaction 5.8 is important for N production.
5.4 Results - ZnO Film Properties

ZnO:N films were synthesized by mixing both N\(_2\) and N\(_2\)O with O\(_2\) in the ICP source. For all films the background partial pressure of DMZn was fixed at 8.0 *10\(^{-5}\) torr, the substrate temperature was 230 °C, and the ICP power was 100 W unless otherwise noted. Nitrogen incorporation in ZnO was measured by both XPS and SIMS as a function of the percentage of N\(_2\)O or N\(_2\) in the feed gas. The two techniques are complementary as the XPS is surface sensitive and SIMS provides depth profiles.

XPS survey scans of ZnO films as a function of N\(_2\)O percentage revealed the presence of Zn, O, N and C present on the surface of all films. The binding energies were calibrated by centering the aliphatic carbon peak at 285 eV. High resolution XPS scans revealed two distinct forms of nitrogen as shown in Figure 5.4. First, a peak centered at ~402 eV was present in all films at nearly the same intensity. This peak is located between the expected peak positions for NH\(_3\) and NH\(_4\)NO\(_3\).\(^{106}\) This peak is attributed to nitrogen bound to adventitious carbon. A second peak centered at ~398 eV was only found in films with N\(_2\)O, and is attributed to a nitrogen bound to zinc.\(^{106}\) The 398 eV peak was not present in the 0% N\(_2\)O film, but it appeared and increased monotonically as N\(_2\)O was added to the plasma source as shown in Figure 5.4.

The presence of the N peak at 398 eV is indicative of successful incorporation of N in the ZnO lattice, as this peak is often ascribed to Zn-N bonding.\(^{107,109}\) Two N 1s peaks have been observed in the ZnO:N literature. The Zn-N bonding state shown in Figure 5.4, and a second peak that appears at higher binding energies (405 - 407 eV) that is attributed to N bonded to O. This N-O form of nitrogen was not observed in any of our films. We note that the presence of the Zn-N form and the absence of the N-O form has been correlated with p-type conductivity in the literature.\(^{108,110}\)

XPS can provide quantitative evaluation of the elemental composition of the films. The XPS spectra shown in Figure 5.4 were deconvolved using the two peaks centered at 402 eV (N-C) and 398 eV (N-Zn). The individual contributions and the
Figure 5.4: High resolution XPS scans of nitrogen in the ZnO lattice for films grown at (a) 0% N$_2$O, (b) 60% N$_2$O, and (c) 100% N$_2$O.
overall fit are shown in Figure 5.4 (b and c). The nitrogen content was evaluated by using only the Zn-N component at 398 eV. Figure 5.5 shows the atomic percentage of nitrogen in the ZnO:N films, measured by XPS, as a function of the percentage N\textsubscript{2}O in the feed gas. The nitrogen percentage in the films increased linearly with N\textsubscript{2}O to a maximum of 1.6% in the film grown at 100% N\textsubscript{2}O. This is just below the threshold seen for p-type conductivity in thermally grown ZnO:N of two atomic percent nitrogen\textsuperscript{111}. SIMS results confirmed the presence of N in the ZnO:N films. The m/z=30 signal (\textsuperscript{14}N\textsubscript{16}O) was used to monitor N, as is common practice for ZnO:N\textsuperscript{51,112}. Contributions of minor signals such as \textsuperscript{30}Si and \textsuperscript{30}CO were accounted for using the intensity measured in intrinsic films. Depth profiling showed that nitrogen was distributed uniformly throughout the films. An absolute standard was unavailable, so in all cases the \textsuperscript{30}NO signal was normalized by the \textsuperscript{83}ZnO signal that was used to track the film matrix. SIMS was used to study ZnO:N films deposited on silicon from N\textsubscript{2}O, and films on glass using
N\textsubscript{2}. The use of an electron beam was required to reduce charging for films deposited on glass.

Figure 5.6 shows the relative nitrogen incorporation as measured by SIMS as a function of the elemental nitrogen in the ICP source for both N\textsubscript{2}O and N\textsubscript{2} mixtures. In the case of N\textsubscript{2}O and low N\textsubscript{2} feed, (< 50%), the nitrogen content increased linearly in the films, consistent with the XPS results. For high N\textsubscript{2} feed concentrations (>60%), the nitrogen incorporation was significantly higher. The higher nitrogen incorporation observed at high N\textsubscript{2} fractions is directly coupled to the decreased amount of oxygen in these mixtures. PLD experiments have shown that nitrogen incorporation decreases linearly with increasing oxygen dilution\textsuperscript{51,111,112} As shown in Figure 5.3(a), the amount of atomic O in the N\textsubscript{2}/O\textsubscript{2} mixtures at high nitrogen fractions is far lower than in N\textsubscript{2}O/O\textsubscript{2} mixtures. Unlike PLD, atomic oxygen in the HVP-CVD system is consumed by the growing film, and it is central to the desorption of methyl groups\textsuperscript{90}. All of the N\textsubscript{2}O films and the low percentage N\textsubscript{2} films were deposited under conditions where the growth
kinetics were observed to be independent of the O atom density.\textsuperscript{90} However, the growth rate was found to decrease substantially for the high N\textsubscript{2} percentage films, indicating that atomic oxygen was rate limiting. Correspondingly, the levels of carbon impurities in these two films were an order of magnitude higher than in the other films. Thus, the disproportionately high nitrogen in these films is a consequence of the oxygen-limited kinetic regime and the films are of poor quality.

XRD patterns presented in Figure 5.7(a) and (b) show that all of the ZnO and ZnO:N films were preferentially oriented in the (002) direction. No other peaks were observed in the patterns. All of the films shown in Figure 5.7 were grown on glass at varying percentages of N\textsubscript{2}O or N\textsubscript{2}. Both dopant sources systematically shift the position of the (002) peak to higher angles with increasing nitrogen content. The maximum shift of about 0.3° is observed in the case of 100% N\textsubscript{2}O. This shift was stable through annealing at 450°C in air, and it occurred in films deposited on both glass and Si substrates. The full-width at half-maximum (FWHM) also increased about 50% with nitrogen incorporation. FWHM is strongly affected by strain in the films and changes in

![Figure 5.7: XRD patterns of ZnO films as a function of (a) N\textsubscript{2}O and (b) N\textsubscript{2} addition.](image-url)
The combination of the peak shift and increase in FWHM is consistent with both a uniform compressive macrostrain and a non-uniform microstrain caused by nitrogen incorporation.\textsuperscript{64} The shift to higher angles is opposite of the behavior observed in oxynitride alloys (ZnO\textsubscript{x}N\textsubscript{y}). ZnO\textsubscript{x}N\textsubscript{y} films show a diffraction peak whose position varies with nitrogen content between the (222) peak of Zn\textsubscript{3}N\textsubscript{2} at 31.6° and the (002) peak of ZnO at 34.4°.\textsuperscript{109,113} The consistent shift to higher angles with nitrogen incorporation demonstrates that no nitride phase or oxynitride alloy formation occurs in the films discussed here. Despite the relatively high nitrogen concentration, these films remain ZnO with a high strain induced by nitrogen incorporation. Little has been reported on the influence of N-doping on XRD lineshapes. In MOCVD, ZnO:N films were observed to become randomly oriented at high nitrogen incorporation.\textsuperscript{111} However, the XRD shift with nitrogen incorporation shown in Figure 5.7 has not been previously reported.

The optical transmission of selected films is shown in Figure 5.8 as a function of nitrogen incorporation for both nitrogen sources. The thickness of these films was approximately 200 nm. Figure 5.8(a) shows that the optical transparency in the visible is generally quite high, but decreases as the N\textsubscript{2}O feed fraction is increased. The optical bandgap increases slightly with nitrogen incorporation in these films, possibly due to stress in the film.\textsuperscript{38} Similarly, the films grown with N\textsubscript{2} show a decline in visible transparency in Figure 5.8(b). There is a softening of the absorption edge at high N\textsubscript{2} fractions that is much greater than the softening seen in the N\textsubscript{2}O films. This is consistent with the higher N content seen in these films with SIMS in Figure 5.6. Additionally, these films contained high levels of carbon impurities, which would also contribute to the decline in optical properties.
Film resistivity, mobility, and carrier type were examined using a 4-point probe and a Hall effect measurement. A thermopower measurement was used to confirm the carrier type. All films were highly resistive, and Hall effect measurements were generally unreliable. The sheet resistance increased from $2 \times 10^5$ Ω/sq to $1 \times 10^6$ Ω/sq as N$_2$O was increased from 0 to 100% of the plasma feed. Films grown with N$_2$ became too resistive to be measured for films with >40% N$_2$ feed. The elevated carbon levels in these films is expected to be detrimental to electrical performance. The thermopower measurements indicated a negative Seebeck coefficient for the undoped films, and became unreliable due to high sheet resistances at high nitrogen incorporation. All of the ZnO:N films were either n-type or too resistive to clearly identify the carrier type.

5.5 Discussion

In this work, we have compared plasma activated N$_2$O/O$_2$ and N$_2$/O$_2$ mixtures for synthesis of ZnO:N by HVP-CVD. Both precursors have been used with and without

Figure 5.8: Optical transparency of films deposited on glass as a function of (a) N$_2$O and (b) N$_2$ addition.
success in the literature for the production of p-type ZnO. Here, we seek to illuminate the mechanism of nitrogen incorporation. Figures 5.1 and 5.2 illustrate the striking similarities in the plasma composition of the two mixtures. In this high density source, the plasma composition is largely independent of the molecular sources employed. Instead, the composition is dictated by the elemental N to O ratio. Both N₂-O₂ and N₂O produce significant amounts of N, O, NO, O₂, N₂, and N₂⁺. Previous experimental work has argued that either NO, NH, N, or N₂⁺ must be responsible for N incorporation in ZnO. NH is not present in this system. Because we can detect NO, N, and N₂⁺ in this system, we are able to systematically study the relationship between the availability of these active species and nitrogen incorporation in ZnO films.

Most reports of ZnO:N involve a limited number of films, and systematic control of nitrogen doping has not been demonstrated. All of the experimental data presented here indicate that nitrogen incorporation increases steadily as the N₂ or N₂O feed fraction rises. The XPS and SIMS results show this directly for both feed gasses. XRD patterns show a systematic shift in the (002) peak position as N₂ or N₂O was added to the plasma. The optical data demonstrate a considerable softening of the absorption edge as nitrogen is incorporated. Where measurable, the electrical data show the n-type conductivity is reduced with increasing nitrogen content. The poor electrical quality is attributed to the insulating nature of the films, and is an indication of being near the transition between n-type and p-type conductivity. In addition, films grown at high N₂ fractions (> 50%) contained much larger amounts of carbon than the films grown at low N₂ fractions or with N₂O. This degraded their optical, electrical, and structural characteristics.

Of the two potential nitrogen sources, N₂O was found to be the superior nitrogen source for higher levels of doping. In the case of small nitrogen addition (< 50%), the differences in film properties between films grown with N₂O and films grown with N₂ were quite minor. However at higher fractions (> 50%), films deposited with N₂O had superior optical, structural and electrical properties. This is primarily attributed to its ability to maintain copious amounts of atomic O. As shown in Figure 5.3 (a), the density
of [O] in the ICP source with 100% N$_2$O is about the same as a 40% N$_2$/60% O$_2$ mixture. At higher N$_2$ fractions [O] continues to drop which leads to detrimental carbon incorporation.

A second question to be addressed is what nitrogen-containing molecule/atom leads to nitrogen incorporation. The two leading candidates are NO and atomic nitrogen. The QMS data in Figure 5.3(d) indicates that the NO density is maximized at approximately 50% N$_2$ and ~70% N$_2$O, respectively. Nitrogen incorporation continues to increase at N$_2$O and N$_2$ feed fractions well past the NO maxima. This behavior suggests that although NO may contribute to nitrogen doping, its composition profile is not consistent with the nitrogen content in the films. NO has been identified as the nitrogen precursor in MOCVD and PLD systems. In MOCVD, the substrate temperature was 400 °C and the NO density was more than six orders of magnitude greater than the amount present here.$^{111}$ The high density and elevated temperature are necessary to overcome the 6.6 eV bond dissociation energy. PLD also employs high temperatures$^{48}$, and photo-dissociation of NO is also likely. The low temperature and density in the HVP-CVD system make it unlikely that NO is a leading contributor to nitrogen doping.

Unlike NO, both atomic N and N$_2^*$ continue to increase steadily as the N$_2$ or N$_2$O feed fraction increases, as shown in Figures 5.3 (b) and (c). This is consistent with literature observations that both N$_2^*$ and N are produced primarily by electron impact reactions of N$_2$. The concentrations of the specific N$_2^*$ states and atomic N are highly coupled. N$_2$(B) is readily formed by the two step recombination reaction represented in equation 5.9$^{115}$.

\[ N(^4S) + N(^4S) + M \rightarrow N_2(B^3\Pi_g) + M \]  

(5.9)

Conversely, reaction 5.8 shows that N$_2^*$ is an important precursor for N production in the presence of atomic oxygen. Information on the absolute densities of these species is required to decouple their contributions to the deposition process. Reasonable estimates of the magnitudes of these species may be obtained from the extensive number of
fundamental studies on low pressure nitrogen plasmas.\textsuperscript{99,103,104,116,117} First, N$_2$(C) undergoes rapid radiative decay (40 ns) to N$_2$(B), which ensures that the N$_2$(C) concentration is very small.\textsuperscript{117} N$_2$(C) will be neglected as an important nitrogen dopant source due to its small concentration. The radiative lifetime for N$_2$(B) is longer, but on the order of microseconds.\textsuperscript{116} Under the ballistic transport conditions in the deposition reactor, the mean time for travel between the ICP source and substrate is on the order of $10^{-4}$-10$^{-5}$ s. As was mentioned earlier, the density the excited N$_2^*$ species is expected to be 2-4 orders of magnitude lower than the N density in the plasma. The relatively long transport time to the substrate will further reduce the flux at the deposition surface. The electronic excited states are important intermediates for N production and consumption, but they probably do not directly contribute much to film growth due to their low concentration. Higher energy vibrational states N$_2$(X, $\nu$>12) could be important nitrogen contributors. As discussed earlier, N$_2$(X,$\nu$>1) molecules are also expected to exist only in small concentrations due to the low temperature and high density of atomic oxygen in the ICP source. Therefore, N$_2$(X, $\nu$) and N$_2$(A, B, and C) excited states are not expected to be significant nitrogen dopant sources due to their low densities.

Unlike excited N$_2^*$, N is present in significant quantities in high density plasmas and it is not subject to radiative decay. The relative density measured by OES correlates well with nitrogen incorporation measured by SIMS and XPS. Based on abundance, reactivity, and correspondence to nitrogen content, atomic N is the most plausible candidate for the nitrogen dopant source. Excited N$_2^*$ and NO may contribute, but all of the data presented here are consistent with N as the primary dopant.

This result may be linked to the same thermodynamic arguments used to support NO as a superior dopant over N$_2$ or N$_2$O.\textsuperscript{13,14,118} These arguments are based on the difficulty of breaking the 9.6 eV N-N triple bond. High temperature electrons in the ICP source can easily break that bond and generate significant quantities of N atoms. The N atoms are also energetically more favorable for incorporation than NO. This is likely
responsible for the successful p-type ZnO:N production from both N₂O and N₂-O₂ with an ECR source²,⁴⁸, and the consistent failure to obtain p-type results from these precursors without one.⁴⁸,¹⁰⁸ In keeping with theoretical expectations, these films are not p-type. Nitrogen is present in relatively large concentrations that are stable over time and mild annealing conditions, but there is not enough active N to produce reasonable p-type conductivity. This is likely a product of many factors, including insufficient N, carbon impurities, and the relatively low substrate temperature.

5.6 Conclusions

We have demonstrated systematic control of N incorporation by manipulation of precursor feed fractions using both N₂-O₂ and N₂O-O₂ mixtures. An ICP device was used to dissociate both mixtures into active species for ZnO:N production. The ICP composition was determined primarily by the elemental N/O ratio, and not strongly dependent on the molecular source used. Atomic nitrogen generated in the ICP source is identified as the dominant precursor responsible for N doping in the HVP-CVD process. Nitrogen incorporation in the films can be reliably detected with XRD, SIMS, and XPS. The shift in the (002) peak of the XRD pattern provides a convenient screening tool for nitrogen incorporation. Work is ongoing to increase the nitrogen content through the manipulation of process variables and achieve reproducible p-type conductivity in ZnO:N.

5.7 Acknowledgements

The authors gratefully acknowledge financial support from the National Science Foundation through CAREER Award No. CTS-0093611. One of us (C.A.W.) would like to thank Professor Eray Aydil for his kind support during a sabbatical stay at the University of California at Santa Barbara. We also thank Dr. Tom Mates for assistance
with XPS and SIMS, which were performed at UCSB using the MRL Central Facilities supported by the MRSEC Program of the National Science Foundation under award No. DMR00-80034.
CHAPTER SIX

STABILITY OF P-TYPE CONDUCTIVITY IN ZNO:N

This manuscript is in preparation for submission to Applied Physics Letters

6.0 Abstract

Acceptable reproducibility of p-type conductivity in ZnO has yet to be demonstrated. The behavior of nitrogen in ZnO thin films grown by high vacuum plasma-assisted chemical vapor deposition is examined. Highly oriented (002) films doped with 0–2 at. % N were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, Seebeck, and Hall measurements. XRD measurements revealed that the zinc oxide lattice constant decreased systematically with nitrogen doping. The as-deposited films were p-type at high doping levels, as confirmed by both Seebeck and Hall measurements. However, it was observed that hole conduction decreased and films reverted to n-type conductivity in a period of several days. This change was accompanied by a simultaneous increase in the lattice constant. The transient electrical behavior may be explained by compensation caused either by hydrogen donors or through defect formation processes common to analogous II-VI semiconductors.
6.1 Introduction

Zinc oxide is a wide band gap semiconductor that possesses a versatile combination of unique optical, electrical, and magnetic properties. Pearton and co-workers\textsuperscript{119} provided an excellent review of zinc oxide’s status, and recent progress toward its incorporation in numerous device applications including light emission, spintronics, and gas sensors. Of these applications, perhaps the most tantalizing is the possibility of blue/UV lasers and light emitting diodes (LEDs). Zinc oxide shares the same crystal structure as the AlInGaN system, a comparable band gap (3.3 eV), and its exciton binding energy is more than double that of GaN. Other advantages for ZnO include the availability of bulk crystal substrates\textsuperscript{120} and the low thermal budget required for thin film deposition.\textsuperscript{121} Despite these attributes, full realization of its optoelectronic potential requires robust control of \textit{p}-type doping, which has proven to be elusive. In this letter we report on the structural and electronic properties of nitrogen doped zinc oxide. Using X-ray diffraction we show that the ZnO lattice is systematically compressed with the addition of nitrogen. For films doped with > 1.5 at. % N \textit{p}-type conductivity was observed and confirmed by both Seebeck and Hall measurements. However, \textit{p}-type conductivity was not found to be stable, reverting back to \textit{n}-type conductivity within a matter of days. The changes in conductivity were observed to coincide with lattice relaxation. The behavior of ZnO is discussed in relation to analogous Zn-VI semiconductors, in particular ZnSe.
Active semiconductor devices require both $n$- and $p$-type doping, which is often controlled and achieved through the addition of an extrinsic dopant. For ZnO, $n$-type conductivity is relatively well-understood and commonly realized through the substitution of a group III element (Al, Ga, In) on a zinc site. As is the case in many wide band gap semiconductors (GaN, ZnSe), realization of $p$-type doping has proven to be much more challenging. Specific challenges include compensation, the formation of nitrogen donor states, limited solubility, and relatively deep acceptor levels. Further compounding the problem is the role of hydrogen, which has been predicted and experimentally confirmed to behave exclusively as an electron donor in bulk ZnO crystals.

The possibility of forming $p$-type ZnO by introducing a group V atom on an oxygen site was first proposed by Kobayashi and coworkers in 1983. Their calculation predicted that substitutional nitrogen occupying an oxygen site ($N_O$) would be an ideal $p$-type dopant. The $N_O$ site is thought to be tetrahedrally bonded to four Zn atoms. The formation of this defect is thermodynamically favorable, but the bonds contain excess energy when compared to intrinsic ZnO indicating that the $N_O$ acceptor may be metastable. There are several different mechanisms proposed to relieve this excess energy, and the dominant process depends on the positions of nitrogen in the lattice and the energy barriers to form each defect.

Many synthesis methods, including molecular beam epitaxy (MBE), chemical vapor deposition (CVD), and pulsed laser deposition (PLD) have been explored
to form $p$-type ZnO using group V atoms. Reports claiming successful hole conduction cite either a single sample$^{2,49,114}$ or a small fraction of samples.$^{50}$ Systematic studies of $p$-type conductivity have not been reported, and there is limited data available on either the nitrogen content or structure of these $p$-type films. Many groups have also reported that group V doping was unsuccessful using nominally identical deposition techniques.$^{47,51,124}$ It was also recently noted that $p$-type conductivity may not be stable, and that films revert to $n$-type conductivity over time.$^{14}$

Nitrogen-doped ZnO films for this study were produced by high vacuum plasma assisted chemical vapor deposition (HVP-CVD). Briefly, the HVP-CVD technique combines a high density plasma source with a high vacuum film growth environment. Details of the system are provided elsewhere.$^{90}$ Mixtures of ultra high purity oxygen and semiconductor grade N$_2$O were dissociated in a high density inductively coupled plasma (ICP) source. The plasma products then effuse through a small orifice into a high vacuum deposition environment containing a background pressure of $\sim10^{-5}$torr of dimethylzinc (DMZn). Polycrystalline ZnO films were deposited at 500 K on both silicon and glass substrates. X-ray diffraction (Seimans, Crystalloflex A10) revealed that all films were highly oriented in the (002) direction, and no other diffraction peaks were observed. Nitrogen incorporation was systematically controlled by varying the N$_2$O: O$_2$ ratio supplied to the ICP source.$^{125}$ The nitrogen content in the films was found to increase linearly with the fraction of N$_2$O. Absolute quantities were determined by X-ray photoelectron spectroscopy (XPS, Kratos). The results were confirmed by secondary ion
mass spectrometry (SIMS, Phi 6650), which also showed that nitrogen was distributed uniformly throughout the films.\textsuperscript{125}

### 6.2 Results and Discussion

A series of films was deposited with controlled nitrogen doping, and the structural and electrical properties were examined. The first significant observation was that the position of the (002) diffraction peak shifted toward higher angles as nitrogen incorporation increased.\textsuperscript{125} Fig. 6.1 illustrates the monotonic correlation between the $c$-axis lattice constant extracted from XRD, and the percentage of nitrogen incorporated in

![Graph showing the monotonic correlation between lattice constant and atomic percentage of nitrogen](image)

**Figure 6.1:** Lattice constant measured by XRD vs. the percentage of nitrogen in the ZnO:N film measured by XPS
the film, as measured by XPS. Undoped films displayed a \( c \)-axis lattice constant that is close to the literature value of 5.2069 Å.\(^{119}\) The lattice constant decreased linearly with nitrogen content to 5.157 Å for the highest doping level. This behavior was intrinsic to the films, as ZnO:N samples deposited on both silicon and glass display very similar shifts. One reason for the decrease is that Zn-N bond lengths are somewhat shorter than Zn-O bond lengths.\(^{126}\) However, the difference is relatively small, and it is concluded that compressive stress is the main reason for the reduction in the lattice constant. Excessive nitrogen, randomly distributed in the lattice, and an additional collapse of Zn tetrahedrons around N\(_{o}\) may contribute to the stress. Similar behavior is observed for ZnSe, where the lattice constant shift with nitrogen doping is also greater than what can be explained by shorter Zn-N bond lengths.\(^{127}\)

We note that the films shown in Fig. 6.1 were all either \( n \)-type, or too insulating to be accurately measured.\(^{125}\)

In order to reproducibly achieve \( p \)-type conductivity, additional films were grown under similar conditions, with the exception that the deposition rate was reduced by a factor of four by decreasing the DMZn partial pressure. The ICP source was operated identically as before with 100% N\(_2\)O. The goals were to reduce the amount of compressive stress in the films, and increase the nitrogen content by increasing the flux ratio of N:Zn arriving at the deposition surfaces. The lattice shift remained, but was reduced significantly. For films deposited with 100% N\(_2\)O the shift was reduced 40% from 0.05 Å in the high rate films to ~0.03 Å. This supports the assertion that stress was responsible for a substantial portion of the shift in lattice constant.
Seebeck coefficient (α₀) measurements were conducted on a custom built system consisting of two temperature controlled copper blocks and a Keithley 197 Microvolt meter. All measurements were performed between room temperature and 70°C, and the performance of the setup was confirmed using both p- and n-type silicon wafers. Hall effect measurements were performed using a Biorad Hall HL5500PC system operating in the Van der Pauw configuration at room temperature. Seebeck and Hall measurements both confirmed p-type conductivity in some samples, but the results were erratic. After evaluating numerous films, it was observed that the electrical results were highly correlated with the elapsed time between deposition and performing the measurements. To further clarify this phenomenon we began to evaluate films on a daily basis after deposition. Both the Seebeck and Hall measurements showed p-type conductivity on the day of deposition and within a few days after. However, when the same films were measured a week later, both techniques indicated either n-type or highly insulating behavior.

Fig. 6.2 plots the transient nature of α₀ for five ZnO:N films deposited at nominally identical conditions. The amount of scatter in our values for α₀ reflects the p-type ZnO:N literature, as α₀ is sensitive to the carrier concentration in the film and measurement temperature. Initial Hall measurements confirmed their p-type conductivity, with typical carrier concentrations of 6±4 x 10¹⁷/cm³ and mobilities between 0.5 – 1 cm²/V*s. These Hall data are consistent with published results for p-type ZnO:N. Only ~0.1% of the incorporated N is electrically active in these films, and scattering processes
involving the excess N may account for the low mobility values. It was difficult to obtain reliable Hall coefficient measurements after the films reverted to \( n \)-type conductivity.

Having established the transient nature of the electrical properties, we performed time-dependent measurements of structural and optical properties to see if there were additional changes. It was found that there was an abrupt shift in the lattice constant that coincided with the change in carrier type. Fig. 6.3 displays the value of the lattice constant of several ZnO:N films over time. The lattice constants shown in Fig. 6.3 are initially much less than the literature value. After a few days, the lattice constants relax back to a value approaching intrinsic HVP-CVD grown films. Nitrogen does not leave
the film, as XPS and SIMS data taken months after deposition confirm that high levels of nitrogen remain. After the initial relaxation, the film structure appears to be quite stable. XRD measurements performed several months after deposition indicate that no further changes occur.

The transient $p$-type behavior observed by us and noted by others\textsuperscript{14} can be explained by either the addition of free electrons or the creation of compensating defects. Both are plausible explanations. As noted previously, hydrogen behaves exclusively as a donor in ZnO.\textsuperscript{122,123} We recently demonstrated that a few seconds of atomic hydrogen exposure at room temperature can increase the free electron density by $>10^{10}$ cm$^{-3}$ in polycrystalline

![Figure 6.3: Lattice constant as a function of time after deposition for films D, E, and F. The open symbols represent p-type films, and the filled symbols indicate n-type films as determined from the sign of the Seebeck Coefficient.](image)
ZnO thin films. In addition, the hydrogen-generated donors are mobile at room temperature, with both short term (s) and long term (days) transients being observed. In the case of our \( p \)-type ZnO, the addition of only \( \sim 10^{17} \text{ cm}^{-3} \) donors would be sufficient to alter the electrical properties. It is conceivable that either water or other ambient impurities could supply hydrogen and be responsible for the observed electrical behavior.

Structural changes were also observed (Fig. 6.3), and the second explanation relates to the loss of electronically active acceptor states. Although interest in \( p \)-type ZnO is fairly recent, \( p \)-type conductivity in analogous Zn-VI semiconductors has been of interest for some time. ZnTe is easily doped \( p \)-type, but acceptor formation becomes increasingly more difficult as one moves up the group VI column. With respect to the group V elements, nitrogen is the most suitable candidate and \( p \)-type doping becomes more difficult as one descends the periodic column to P and As. Like ZnO, ZnSe has been vigorously pursued for wide bandgap optoelectronic devices. Stable \( p \)-type doping remains the critical issue in this material system, and a primary reason why commercial efforts in blue/UV light emission have turned from II-VI compounds to III-V nitride semiconductors.

Interstitial N, oxygen vacancies, AX centers, and substitutional N\(_2\) on an O site (N\(_2\)O) may all potentially compensate or trap holes. Of particular concern is the formation of AX centers, which are formed by breaking two Zn-V bonds and the release of four electrons. AX centers are predicted to be stable for ZnS:N, ZnO:P, and ZnO:As. Recent experimental observations of highly conductive \( n \)-type ZnO:P may be a result
of this mechanism. However, AX centers are not predicted to be stable in either ZnSe:N or ZnO:N. Nevertheless, other lattice rearrangements and distortions are thought to strongly affect the potential \( p \)-type conductivity of all II-VI materials.\(^{130}\) In the case of ZnSe, XRD\(^{127}\) and electric field gradient\(^{133}\) measurements suggest that a significant density of point defects are generated at high nitrogen concentrations. Recent calculations suggest a possible mechanism for point defect generation in ZnSe:N that may be applicable to ZnO:N.\(^{134}\) An acceptor is formed in ZnSe when nitrogen substitutionally occupies a selenium site (\( N_{\text{Se}} \)). However, an interstitial nitrogen (\( N_i \)) paired with a Se vacancy (\( V_{\text{Se}} \)) is thermodynamically more favorable. Transient \( p \)-type behavior can be explained if nitrogen is first incorporated substitutionally, then migrates to an interstitial site to create the \( N_i - V_{\text{Se}} \) pair. This migration involves breaking several Zn-N bonds, and the estimated barrier of \( \sim 2.5 \) eV is comparable to the energy of photons generated in a ZnSe laser diode.\(^{134}\) Similarly, the formation of \( N_i - V_{o} \) pair is a plausible explanation for the transient \( p \)-type conductivity seen in ZnO:N. The barrier energy for this process is not known, but must be small if it occurs at room temperature. The process could be aided by film stress or the excess energy present in the \( \text{Zn}_4 \)-N bonds. It is possible that the lattice expansion observed after deposition may be related to this type of bond rearrangement.
6.3 Conclusions

In summary, we have shown that the zinc oxide lattice constant is systematically reduced with nitrogen doping. This decrease is much greater than expected from bond length arguments, and it is inferred that substantial compressive stress is present in the as-deposited films. By reducing the deposition rate, $p$-type conductivity was reproducibly achieved and verified by both Seebeck and Hall measurements. However it was observed that the hole conductivity was unstable, and films converted to insulating or $n$-type behavior within a period of several days. Concurrent measurements of structural properties showed that this shift coincided with a relaxation of the lattice constant. Plausible explanations include both hydrogen-related donors and defect formation analogous to other II-VI semiconductors. The observed transient behavior may be responsible for some of inconsistencies that have been reported for ZnO:N in the literature.

6.4 Acknowledgements

The authors gratefully acknowledge the National Science Foundation for support of this work through grant #CTS-0093611. We also acknowledge Dr. V. Kaydanov of the Colorado School of Mines for helpful discussions regarding the Seebeck apparatus.
CHAPTER SEVEN

ORGANOMETALLIC PRECURSOR SELECTION FOR HVP-CVD

7.1 Introduction To Organometallics

Metal oxide film growth by HVP-CVD relies on a surface mediated reaction between an organometallic precursor and atomic oxygen. Several different classes of organometallic compounds are available as precursors, and their properties vary widely. Important selection criteria for an organometallic precursor include its vapor pressure, chemical reactivity, available purity, toxicity, ease of handling, and cost. Metal-alkyls, alicyclics, aryls, alkoxides, carbonyls, and acetylacetonates are all commercially available and widely used in industrial and research deposition applications. Figure 7.1 illustrates generic structures for each type of precursors. Due to their toxicity and cost, it is important to choose the proper precursor for a given application. Unfortunately, little is known about organometallic reactivity under deposition conditions. HVP-CVD can be used to study organometallic surface chemistry, and that data can be used to aid future workers in precursor selection. Metal oxide films commonly deposited by CVD processes include Al₂O₃, Cr₂O₃, Ga₂O₃, HfO₂, Fe₂O₃, SiO₂, Ta₂O₅, SnO₂, TiO₂, ZnO, ZrO₂, PbTiO₃, SrTiO₂, and YBa₂Cu₃O₇. These materials are used or have potential applications as transparent electrical contacts, gas sensors, diffusion barriers, gate dielectrics in integrated circuit components, and refractory materials. In this chapter, we compare two commonly used zinc precursors and use the end results to develop criteria for precursor selection in HVP-CVD processes.
7.2 Organometallic Zinc Precursors

We chose to demonstrate the usefulness of the HVP-CVD technique for metal-oxide deposition by producing ZnO. ZnO is a wide band-gap semiconductor that is often used as a transparent electrical contact and has the potential for use in short wavelength optoelectronic devices. These devices require the availability of both p- and n-type ZnO, and the reliable production of p-type material has proved problematic. HVP-CVD was used to elucidate both the reaction kinetics of dimethylzinc (DMZn) with O and the nitrogen species responsible for doping in ZnO:N. Here, we consider alternative organometallic Zn sources for ZnO production using HVP-CVD.
The two most widely used organometallic Zn compounds for ZnO CVD are DMZn\textsuperscript{71,137-140} and diethylzinc (DEZn)\textsuperscript{31,73,76,87,88,141}. A comparison of the basic properties of the two precursors is presented in Table 7.1. ZnO is also deposited from zincacetylacetonate\textsuperscript{30,72}.

Table 7.1: Physical properties of DMZn and DEZn

<table>
<thead>
<tr>
<th>Property</th>
<th>DMZn</th>
<th>DEZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure at 0(^{\circ})C</td>
<td>123 mm Hg\textsuperscript{142}</td>
<td>3.6 mm Hg\textsuperscript{142}</td>
</tr>
<tr>
<td>Vapor Pressure at 20(^{\circ})C</td>
<td>300 mm Hg\textsuperscript{142}</td>
<td>12 mm Hg\textsuperscript{142}</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>46 (^{\circ})C\textsuperscript{27}</td>
<td>118 (^{\circ})C\textsuperscript{27}</td>
</tr>
<tr>
<td>Hazardous Reactions</td>
<td>Pyrophoric</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Ingestion or inhalation can lead to zinc fume fever, hypothermia, and irritation\textsuperscript{142}</td>
<td>Ingestion or inhalation can lead to zinc fume fever, hypothermia, and irritation</td>
</tr>
<tr>
<td>State at room temperature</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Cost</td>
<td>~$1000/100g, 95% purity</td>
<td>~$200/100g, 95% purity</td>
</tr>
<tr>
<td>Energy Barrier for Pyrolysis</td>
<td>54 kcal/mol\textsuperscript{143}</td>
<td>49.08 kcal/mol\textsuperscript{144}</td>
</tr>
</tbody>
</table>

(Zn-AcAc). Zn-AcAc was not experimentally tested in this study because it is a solid at room temperature,\textsuperscript{27} which presents additional precursor delivery challenges. The comparison of DMZn and DEZn was initiated as an attempt to reduce carbon contamination in the ZnO films. Ethyl precursors are generally preferred over their methyl analogs for the reduction of carbon incorporation in compound semiconductor CVD processes. For example, triethylgallium has now displaced trimethylgallium for high quality GaN and GaAs production due to lower carbon incorporation.\textsuperscript{145}
Differences in the surface mediated decomposition processes of the methyl and ethyl precursors are likely responsible for the reduced carbon incorporation when using the ethyl precursors.

Carbon incorporation is thought to occur through two mechanisms, and it is important because carbon degrades the optical and electrical properties of the films. The first is incomplete desorption of the organic ligands. The second process involves dehydrogenation reactions between adsorbed alkyl groups that yield a mixture of volatile species and non-volatile residual carbon. With DMZn, the adsorbed methyl groups undergo dehydrogenation at temperatures around 700 K to form methane, hydrogen, and residual carbon.\textsuperscript{146} The ethyl groups in DEZn undergo similar reaction processes, but form only volatile products such as ethylene and hydrogen.\textsuperscript{147} The in-situ diagnostic capabilities of HVP-CVD permit the rapid evaluation of precursor decomposition mechanisms, and therefore organometallic precursor suitability for metal oxide deposition.

7.2.1 Dimethylzinc

DMZn was initially selected as the Zn precursor for this study due to its high vapor pressure and slightly lower gas phase reactivity suggested by the higher energy barrier for pyrolysis. The high vapor pressure was thought be desirable for direct delivery to the chamber without a carrier gas. The lower gas phase reactivity was attractive due to concerns over stability and the potential for prereaction with oxygen. Additionally, the organic ligands are typically oxidized to form CO, CO\textsubscript{2}, and H\textsubscript{2}O in most MOCVD metal oxide deposition processes. DMZn would be preferred over higher alkyls because it requires less oxygen for combustion. Chapters 3-6 of this thesis present clear evidence that DMZn was a suitable Zn precursor for this process. However, a means of reducing carbon incorporation through precursor optimization is highly desirable.
Experimental results discussed in Chapter 3 demonstrate that DMZn and O react solely through a surface mediated pathway. No evidence was found for gas phase combustion of DMZn. DMZn was also found to be unreactive with either O$_2$ or N$_2$O under HVP-CVD conditions, and deposition only occurred when the plasma generated atomic O. The reaction between O and DMZn appears to proceed through O atom attack on adsorbed DMZn, followed by methyl desorption. Further results given in Chapter 4 show an activation energy of 0.1 eV for this process. This data also shows carbon incorporation increases in the films as the substrate temperature decreases. Films in the nitrogen doping study described in Chapter 5 also exhibited a trend of increasing carbon contamination as the atomic O density was reduced in the chamber.

The data presented in Chapters 3-5 suggest several options for reducing carbon incorporation in the films. One is to increase the O atom density. Plasma chemistry modeling and actinometry data predict that O atom density increases linearly with power. This may have an undesirable side effect for the nitrogen doped films as nitrogen incorporation is inhibited by the presence of oxygen.$^{111,112}$ Increasing the substrate temperature should also accelerate methyl desorption and reduce the carbon levels. Work is underway to install a substrate heater capable of reaching higher temperatures. However, increased temperature may also increase undesirable dehydrogenation reactions, requiring an optimization of the substrate temperature. The third option is to pursue and alternative zinc precursor whose decomposition products would more readily desorb from the surface.

Surface reactivity data may provide clues to discovering an optimal Zn precursor. Our precursor of choice, DMZn, dissociates on silicon at approximately 400 K, leaving methyl groups behind as the Zn desorbs below 600 K. The methyl groups desorb along with acetylene at 825-850 K.$^{80}$ On GaAs, DMZn decomposes at 275 K. Zn again desorbs first between 400 and 600 K. Methyl radicals either desorb at 625 K, or react to form gaseous methane and residual carbon which incorporates into the GaAs at 700K.$^{146}$ These results indicate that the methyl groups form a relatively strong bond to different
surfaces, and react to form non-volatile carbon species. A precursor with ligands that form only volatile dehydrogenation products would likely reduce carbon incorporation. Diethylzinc is the next logical precursor to pursue.

### 7.2.2 Diethylzinc

Diethylzinc is the most widely used organometallic precursor for the CVD of ZnO. Its low vapor pressure enables high precision control, and it is much more economical than DMZn for most applications. DEZn decomposes more easily in the gas phase than DMZn, and an evaluation of its surface reactivity may provide guidance on whether or not it will be a more effective Zn precursor for HVP-CVD. Like DMZn, DEZn absorbs dissociatively on GaAs with the Zn desorbing around 530K. But, DEZn dissociates well below room temperature. Dissociative adsorption has been observed at temperatures as low as 222 K on Pd, with the Zn desorbing much more slowly than the hydrocarbon groups. On GaAs, ethyl groups react at temperature above 500 K to form ethylene, ethane, and hydrogen. Remaining ethyl groups can react with surface Ga like the methyls from DMZn, but these compounds desorb without leaving residual carbon. These results indicate that DEZn should dissociate completely at room temperature, and that the carbon incorporation will depend strongly on the interactions between the adsorbed species and the growing film. From a simple comparison of DEZn and DMZn behavior on GaAs, films grown from DEZn should contain less residual carbon than those grown with DMZn.

One important difference between conventional MOCVD and HVP-CVD is the operating pressure. MOCVD processes generally run in the range of 10 mtorr to several hundred torr, while deposition in HVP-CVD occurs at $10^{-5}$ torr. This is an advantage for introducing precursors with low volatility. However a consequence of the low operating pressure in HVP-CVD is that the precursor will collide with the reactor walls before
reaching the substrate surface. An example mass spectrum from one of our best attempts to introduce DEZn into the HVP-CVD chamber is shown in Figure 7.2. The spectrum from DMZn is included in the figure to demonstrate the dramatic differences between the two precursors. First, the spectrum for DMZn shows that the precursor remains largely intact. The dominant peak in the DMZn cracking pattern is mono-methylzinc with large peaks for both Zn, and DMZn. The cluster of peaks in these signals reflects the natural isotopic distribution of zinc. The carbon peaks from CH\textsubscript{x} and C\textsubscript{2}H\textsubscript{x} groups are nearly 20 times smaller than the largest MMZn peak. In contrast, DEZn appears to have decomposed almost completely in either the gas lines or on the chamber walls due to its high surface reactivity. The DEZn mass spectrum shows a large peak around 26 m/z that is more than one hundred times larger than any of the zinc containing peaks. Not surprisingly, all attempts to produce ZnO from DEZn resulted in negligible growth rates.

Figure 7.2: A comparison of DMZn and DEZn mass spectra, illustrating the surface decomposition of DEZn before reaching the QMS.
Due to the problems with DEZn, another precursor such as Zn-AcAc should be investigated for the reduction of carbon in ZnO. Unfortunately, neither surface nor gas phase kinetic data is available for this compound, and the difficulties in delivering a solid source are substantial. The precursor delivery lines and all reactor surfaces would need to be heated to prevent condensation. As is the case with DEZn, the solid precursors would also collide with the walls. Instead of decomposing, they would simply condense out. Condensable solid sources are workable for conventional MOCVD processes because precursors are insulated from the reactor walls by using high carrier gas flow rates and relatively high pressures. Therefore, a usable precursor for HVP-CVD must not react or condense on the reactor walls at room temperature, and must become surface reactive at somewhat elevated temperatures. The optimum temperature would depend on both decomposition and desorption behavior. Substrate selection and device operation may impose additional thermal constraints.

7.3 Precursors for New Metal-Oxides

Based on our guidelines from the previous section, we will now attempt to determine criteria to select optimal precursors a priori. We will use the examples of Al$_2$O$_3$ and Ga$_2$O$_3$ for this. Al$_2$O$_3$ is being pursued as a high-$\kappa$ gate dielectric$^{136}$, and Ga$_2$O$_3$ is of interest for wide bandgap optoelectronic applications$^{149,150}$. Both materials are often deposited from metal alkyls such as trimethyl-Ga/Al and triethyl-Ga/Al. A similar analysis of the surface reactivity of these precursors may provide guidance on which might be compatible with the HVP-CVD system. The surface chemistry of both trimethylgallium (TMG) and trimethylaluminum (TMA) has been studied on a number of substrates.

TMA exists in the gas phase primarily as the Al$_2$(CH$_3$)$_6$ dimer at room temperature, which will dissociate on a surface at a temperature of 570 K. The rate of TMA dissociation is dependent on the availability of electron donors at the surface. The
energy barrier for methyl desorption was found to be about 13 kcal/mol (373 K). Aluminum desorption occurs only at very high temperatures. Methyl desorption is slow at temperatures below 600 K. Dehydrogenation and organic radical recombination reactions are found to occur as secondary gas phase reactions and not on the surface for a variety of substrates. These reactions are unlikely to occur in the HVP-CVD chamber due to its low pressure.\textsuperscript{151} The presence of hydrogen on the substrate surface strongly affects the decomposition mechanism of TMA on Si, but theoretical calculations predict that the direct deposition of methyl groups on the Si surface is unlikely to occur. The dominant surface reaction yields adsorbed dimethylaluminum and gas phase methane on a hydrogen passivated surface.\textsuperscript{152} The lower tendency of TMA ligands to undergo dehydrogenation on the surface may result in lower amounts of residual carbon depositing on the surface. Based on volatility and surface reactivity considerations, TMA appears to be a suitable candidate for HVP-CVD. Its use may require higher substrate temperatures than those employed for ZnO deposition (500K), unless O atom enhances TMA decomposition through a similar mechanism as is seen with DMZn. On silicon, TMG decomposes at 290 K on the (111) face, and 550 K on the (100) face. On both Si and GaAs, the methyl groups desorb at temperatures above 650 K, while the Ga remains on the surface.\textsuperscript{153} TMG dissociates on GaN into monomethyl- and dimethylgallium at temperatures between 250 and 300 K. These species can desorb readily at between 300 and 450 K. Methyl radicals also desorb unreacted at 600 K at low surface coverage. At high surface coverage, dehydrogenation and methane desorption dominate methyl desorption at temperatures above 600 K. This process is expected to dominate under the high surface coverage conditions experienced in MOCVD.\textsuperscript{154} However, the presence of arsine accelerates methyl desorption for TMG adsorbed on GaAs. No methane is seen when arsine is present.\textsuperscript{155} This is similar to what we have observed when O atom reacts with DMZn, accelerating methyl desorption.

Comparisons of semiconductor growth with TMG or triethylgallium (TEG) have demonstrated that films grown with TEG have orders of magnitude lower carbon
contamination than films grown from TMG. Both precursors chemisorb dissociatively on the GaAs surface to produce an ethyl/ methyl radicals and dimethyl- /diethylgallium. The desorption rates of the organometallic radical are strongly dependent on the surface coverage, and only the high coverage limit will be discussed here since it is most similar to HVP-CVD conditions. A typical HVP-CVD growth rate deposits a nanometer of metal oxide film every 5 seconds. At our most frequently used substrate temperature of 500 K, DEG remains on the surface for 0.01 seconds, while DMG remains for about 0.1 seconds. However, these species must further dissociate to yield a Ga for deposition. The C₂H₅ ligand can undergo rapid β-hydride elimination to form C₂H₄ and H₂. This leads to a C₂H₅ surface lifetime that is three orders of magnitude shorter than the CH₃ surface lifetime.¹⁴⁵

It is also reported that carbon contamination is lower in GaAs produced from TMG and AsH₃ by MOCVD than for material produced by atomic layer deposition (ALD). In the ALD process, TMG and AsH₃ are introduced in alternating steps to the reactor. The simultaneous addition of the precursors in MOCVD is thought to provide the hydrogen needed to volatize residual CH₂ on the surface.¹⁵⁶ This result suggests that the addition of small amounts of hydrogen may reduce carbon incorporation for non-oxides. Careful study is required to determine the effects of hydrogen on the electrical and optical properties of the film.

7.4 Ideal Precursor Attributes for HVP-CVD

HVP-CVD requires a unique set of attributes in organometallic precursors for metal-oxide synthesis due to its low pressure and surface mediated deposition pathways. Unlike conventional MOCVD, gas phase reaction kinetics are not important to the HVP-CVD deposition process, but may provide some guidance on the precursor reactivity if surface data is not available. An ideal precursor for HVP-CVD will have its surface reactivity well characterized on a variety of substrates. Often low precursor volatility is a
serious limitation in MOCVD, but this constraint is nearly eliminated in HVP-CVD. At an operating pressure of 10^{-5} \text{ torr}, even many solid sources will have adequate vapor pressure for introduction to the growth chamber.

Judging from our experience with the Zn precursors, experimental data from the surface reactivity literature appears to be most relevant for organometallic precursor selection for HVP-CVD. The precursor should be resistant to dissociative adsorption at room temperature, and preferably slightly above. DMZn may be an ideal precursor in this regard, as it is stable enough to arrive at the surface intact, yet reactive enough in the presence of atomic oxygen to yield films at room temperature. The temperature at which a precursor dissociates on a surface is often readily available in the literature.

In addition to affecting volatility and the dissociation temperature, the ligands comprising the organometallic strongly affect its reactivity and the formation of undesirable byproducts such as non-volatile carbon. The studies of zinc and gallium compounds with methyl or ethyl ligands presented above illustrate a trend of higher reactivity, lower dissociation temperature, and lower carbon incorporation with the ethyl compounds. These data also suggest that this reactivity is relatively insensitive to the substrate material. In contrast, TMA decomposition is sensitive to the conductivity of the substrate and affected by the presence of a hydrogenated surface. Unlike Zn and Ga alkyls, methyl groups from TMA do not undergo extensive dehydrogenation on the substrate surface to create non-volatile carbon. This group of well studied and fairly simple metal alkyl compounds illustrate the potential and the limitations of general predictions of precursor suitability. Namely, the metal component of the precursor may cause compounds that appear similar to react quite differently.

In general, deposition of group III metal compounds from organometallic precursors relies almost exclusively on metal-alkyl precursors. The ideal metal alkyl precursor will have an organic ligand, such as ethyl or t-butyl, that can undergo β-hydrogen elimination to yield a metal hydride and a volatile organic component. In contrast, alkoxide precursors are widely used for the deposition of transition metal
oxides. These precursors tend to polymerize unless bulky alkoxide groups, such as t-butyl, are used. Copper, yttrium, and lanthanum tert-butoxides have substantially improved volatility if the alkoxy group is fluorinated. Aryloxo derivatives of a few transition metals tend to produce carbides. Alkoxide precursors do not have a direct metal to carbon bond, making them generally less likely to lead to carbon incorporation, especially through the formation of a carbide phase. Broadly speaking, the alkoxide compounds are often the optimal precursor for oxide deposition. Some of these derivatives can present challenges due to low volatility, polymerization, or low reactivity, but there are many alternative ligand groups that can be used to manipulate these properties. Alkoxides can be used even without oxygen to yield metal-oxide films, and should reduce carbon contamination in the deposited films.

7.5 Conclusions

Suitable metal precursor selection is essential for the synthesis of high quality material by chemical vapor deposition. The basic precursor selection criteria of vapor pressure, ease of handling, safety, stability, and cost are quite useful for the preliminary determination of the suitability of a precursor for a process. Due to its unique attributes, the precursor selection criteria for HVP-CVD are somewhat different than for MOCVD. For example, vapor pressure is much less of a concern for HVP-CVD processing than for conventional MOCVD processes due to the low pressures employed here. Likewise, gas phase chemistry is also unimportant. However, when available, gas phase chemical reactivity data can provide general clues to precursor suitability. Since HVP-CVD film synthesis proceeds through surface mediated criteria, there are different constraints on the precursor selection process. Key data can be found in the surface science literature on the reactivity of these precursors. Most surface science studies are conducted only in vacuum, and these data appear to be extremely useful for comparing potential precursors for HVP-CVD. Precursor reactivity may be quite different in a reactive environment, but
the surface science literature provides helpful guidance on which precursors may succeed in HVP-CVD. HVP-CVD operates at extremely low pressures, and no carrier gas is used for organometallic precursor delivery. This puts the precursor in intimate contact with the gas lines and reactor walls, requiring that the precursor be unreactive on those surfaces at room temperature. An optimal precursor for HVP-CVD is unreactive with stainless steel at room temperature. This precursor should be reactive at slightly elevated temperatures, with organic ligands that desorb more readily than the metal and form entirely volatile reaction products.
CHAPTER EIGHT
CONCLUSIONS AND FUTURE WORK

8.1 Major Results and Conclusions

In this thesis, we have described the development of high vacuum plasma-assisted chemical vapor deposition (HVP-CVD) for metal oxide thin film synthesis. We have demonstrated the utility of HVP-CVD for both film deposition and kinetic analysis. First, we described the deposition of high quality semiconducting ZnO. Significant achievements of HVP-CVD synthesis of ZnO include room temperature deposition of highly oriented material and systematic control of nitrogen doping. The second aspect of HVP-CVD is its utility for detailed investigations of deposition kinetics. Using a combination of in-situ diagnostics and ex-situ film characterization, the surface reaction mechanism for ZnO growth from DMZn and O was determined and the precursor for nitrogen doping was identified.

High quality (002) oriented ZnO was deposited at temperatures between 25 and 230°C. The reaction is a surface mediated process consisting of an O atom attack on dissociatively adsorbed DMZn. The presence of atomic O accelerates desorption of methyl groups and leads to formation of ZnO. The growth rate of these films was first order in DMZn, and showed a weak Arrhenius dependence on the substrate temperature. For undoped films, the growth rate was independent of the atomic oxygen density. Electrical measurements revealed these films to be highly insulating, and optical characterization demonstrated their high transparency. Carbon incorporation increased as the substrate temperature was reduced. The Arrhenius dependence of carbon
incorporation mirrored the growth rate, suggesting that methyl desorption or interference from residual carbon limited film growth.

Nitrogen incorporation was systematically controlled by the addition of either N$_2$O or N$_2$ to the plasma source. The amount of nitrogen incorporation increased linearly with the fraction of total nitrogen introduced to the plasma, and was unaffected by the choice of nitrogen precursor. In-situ OES and QMS studies were combined with ex-situ measurements of nitrogen content using XPS and SIMS. A comparison of these data indicates that atomic N is the primary source for incorporated N in the deposited films. These data also showed that nitrogen incorporation is enhanced under low oxygen conditions, under which detrimental carbon incorporation also increases.

The electrical and structural properties of the nitrogen doped films were studied as a function of time. It was found that the lattice constant of the as-deposited films decreased linearly with nitrogen incorporation. This decrease is attributed to lattice strain due to shorter Zn-N bond lengths and compressive stresses. For films with [N] greater than 1.5 atomic percent, both Seebeck and Hall measurements confirmed that the films exhibited $p$-type conductivity. However, it was observed that the conductivity reverted to $n$-type or semi-insulating behavior after a maximum of 5-7 days. The conversion to $n$-type conductivity was found to coincide with a slight increase in the lattice constant. This suggests the formation of lattice relaxation induced compensation centers.

In order to further reduce carbon incorporation, we attempted to use DEZn to produce higher quality films. However, DEZn was found to decompose on the reactor surfaces at room temperature. Thus, it could not be successfully introduced to the HVP-CVD chamber. It is suggested that another zinc precursor or higher quality DMZn be used to reduce carbon contamination combined, perhaps using a higher substrate temperature.
8.2 Recommendations for Future Work

Despite great progress on ZnO and ZnO:N synthesis, many opportunities still exist for improvement. The two most important issues are carbon incorporation and compressive stress in the films. A substrate heater capable of higher temperatures may help to accelerate the methyl desorption and therefore reduce the carbon incorporation. Higher temperatures would also enhance the surface mobility of the adsorbed species, and therefore potentially reduce film stress. Stress reduction is especially important for developing an improved understanding of the transient lattice relaxation processes leading to $n$-type conductivity. An investigation of the stability of $p$-type conductivity should be repeated with films grown at higher temperatures. Possibly, higher purity DMZn should be used to further reduce carbon contamination. An alternative precursor may also be warranted, but DMZn appears to be the best commercially available precursor for HVP-CVD.

The low temperature deposition capabilities of HVP-CVD may be exploited for many applications. It may be especially useful for deposition on polymer substrates and for temperature sensitive device fabrication steps. Often, applications for MOCVD processes are limited by their high temperatures. Lower deposition temperatures are desirable for transparent electrical contacts, dielectrics, diffusion barriers, and optoelectronic device components.

Expansion of the in-situ diagnostic capabilities of HVP-CVD would allow for more detailed studies of organometallic surface reactions and for analysis of other material systems. The addition of in-situ Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy to HVP-CVD would enable the precise determination of surface species. FTIR is widely used to observe polar hydrocarbon entities, and Raman is able to detect non-polar species. FTIR would be the most useful of the two due to its capabilities for the determination of organometallic decomposition processes. It may be used to observe the reaction and desorption products evolving in the gas phase right at the
surface. The addition of FTIR would require the addition of carefully aligned optical ports with IR transparent windows to the HVP-CVD chamber, which would entail a significant structural modification or replacement of the deposition chamber itself. Raman spectroscopy can be used to study nitrogen incorporation in metal oxide deposition in-situ, although it is generally used for ex-situ characterization. Due to the complicated laser alignment, it would be more practical to use it ex-situ to study the effects of nitrogen doping or varying growth conditions on the films. Photoluminescence spectroscopy would be an extremely valuable tool for ex-situ film characterization. It is widely used in the analysis of p-type ZnO and other optoelectronic materials. Its use for wide band gap semiconductors is complicated by the requirement for a short wavelength laser.

These additional diagnostics would make the HVP-CVD chamber ideal for the analysis of the surface reactivity of metal precursors in vacuum and various reactive environments. Combined with the high temperature heating capabilities and QMS, detailed studies could be carried out on novel precursors under reactive, inert, or vacuum conditions. This would allow for the direct comparison of several precursors in the same reactor, and would be very helpful in assessing new precursors. For example, if we wish to examine a novel Zn precursor, we could compare its reactivity with the behavior of DMZn at different environments and temperatures. This would provide a useful assessment of novel precursors that are not well characterized but meet our basic requirements for volatility and room temperature stability before extensive deposition experiments are conducted.

The utility of HVP-CVD as a tool to explore surface reaction chemistry for metal-oxide deposition should be further explored. Al₂O₃ and Ga₂O₃ are both of interest for advanced dielectrics and optoelectronics, and both can be deposited from simple metal alkyl precursors. Trimethylgallium and trimethylaluminum are both readily available, and have been well characterized. The surface reactivity data suggests that both are suitable precursors for HVP-CVD, and the knowledge gained about their behavior in the
presence of O atom would be beneficial for the development of improved CVD processes for both materials. Additionally, both Al and Ga can be used as dopants for \( n \)-type ZnO, and possibly as codopants for \( p \)-type ZnO. An improved understanding of TMA and TMG behavior under HVP-CVD conditions may facilitate their use as dopants for higher conductivity ZnO.

HVP-CVD is quite capable of dissociating nitrogen for the production of nitrides and oxynitride films. III-V nitrides such as GaN, AlN, and InN and their alloys are of interest for electronic and optoelectronic applications\(^{27} \), and there are still fundamental questions about their ideal growth conditions and optimal precursors.\(^{159-161} \) Carbon and oxygen defects can severely affect III-V device performance, and the diagnostic capabilities of HVP-CVD may be useful in reducing these impurities. \( \text{Si}_3\text{N}_4 \) is an excellent diffusion barrier, widely used in integrated circuit applications.\(^{27} \) Silicon oxynitride compounds are also of interest to replace \( \text{SiO}_2 \) as a dielectric and diffusion barrier as feature sizes shrink.\(^{162} \) These materials are often thermally grown, but their deposition by various CVD techniques is being explored.\(^{79} \) HVP-CVD has a demonstrated ability to control nitrogen incorporation in ZnO that may be useful for the formation of oxynitrides.

Extremely thin interfacial layers of many oxide and nitride materials are desirable for optoelectronics and integrated circuits. Ternary and quaternary alloys are often employed to manipulate material bandgaps and optical properties. The low pressure and growth rates in HVP-CVD compared to MOCVD suggest that it is superior for applications requiring either a thin film or precise composition control. Oxide growth rates in HVP-CVD are controlled solely by the organometallic partial pressure in the chamber, which can be controlled down to the low \( 10^{-6} \) torr levels. With DMZn and O, this would yield ZnO growth rates well below 1 nm/min. Gate oxides and diffusion barriers in integrated circuit devices are moving towards thicknesses of several nanometers\(^{136} \), which HVP-CVD is well suited for. Additionally, HVP-CVD can produce high quality materials at lower temperatures than MOCVD. Alloy deposition would be substantially more difficult, but the high level of control offered by HVP-CVD
should make it a promising avenue for these tasks. Additionally, the diagnostic capabilities allow the observation of ligand exchange reactions and other interactions between the organometallics that can affect growth.

We have demonstrated the potential of HVP-CVD for the analysis of complex CVD chemistry through the example of ZnO:N. There are similar questions about the synthesis of other materials, such as carbon nanotubes. Carbon nanotubes have unique and extraordinary electronic and mechanical properties, and have generated enormous attention recently. PECVD has shown promise for the growth of vertically aligned nanotubes, but relatively little is understood about the growth processes. Nanotube growth by PECVD requires a transition metal catalyst, and the produce properties are highly dependent on the surface conditions, hydrocarbon feedstock, diluent gas fraction, and electric field at the substrate. HVP-CVD with the above mentioned diagnostics and a substrate biasing capability may be able to answer crucial questions regarding the PECVD growth of nanotubes. These questions include determining the species responsible for growth; the role of atomic hydrogen, radicals, ions, and diluents; the possibility of lower temperature growth; how to reduce amorphous carbon incorporation; and the determination of an ideal feedstock for a given catalyst. Gas phase dissociation of the hydrocarbon precursor is detrimental to nanotube properties, and excessive carbon inhibits their growth through catalyst poisoning. Atomic H may preferentially etch amorphous carbon, leading to faster growth of higher quality tubes. HVP-CVD could be used to directly compare CO with hydrocarbon precursors such as methane, acetylene, ethylene, and propane with different diluents such as H$_2$, Ar, and NH$_3$. A unique capability of HVP-CVD is the ability to introduce the carbon feedstock either through the plasma or directly to the deposition chamber. A comparison of results for these two scenarios would elucidate the role of gas phase chemistry in the PECVD of nanotubes. HVP-CVD may also provide insights for reducing the growth temperature of nanotubes.

HVP-CVD has two broad applications. The first is for the synthesis of a wide array of thin films using plasma generated radicals and reactive species. This can be
done at low temperature, and yields high quality material. Deposition is enabled by a high density plasma source can dissociate most molecular precursors, and the collisionless deposition environment ensures delivery of these active species to the substrate. The second application is for the analysis of thin film deposition chemistry. Both organometallic reactivity and real time deposition chemistry can be studied with HVP-CVD through direct observation of the plasma and deposition environment. We combined these abilities to study ZnO:N deposition, and this combination could be equally useful in many materials systems. ZnO:N may have tremendous potential as a wide bandgap semiconductor, but very little was known about its synthesis and basic properties. The truly unique aspect of HVP-CVD is that its capability for real time study of the deposition of high quality films over a wide range of temperatures and with a variety of precursors.
GLOSSARY

Actinometry: Technique used to quantify OES data by measuring relative intensities of a peak of interest and an inert gas peak.

AFM: Atomic Force Microscopy – A physical measurement of the film morphology and grain structure with nanometer resolution that is obtained by passing an atomically sharp cantilever over the film surface.

CCP: Capacitively Coupled Plasma – A plasma source in which the power is coupled to the source gas directly between a set of parallel plates.

CHEMKIN: A reactive flow modeling package that is capable of simulating gas and surface reactions in a zero dimensional plasma process.

E_g: Band gap – the distance between the conduction and valence bands in a semiconductor.

Ellipsometry: An optical technique for measuring the film thickness and basic optical properties n and k of the films.

ICP: Inductively Coupled Plasma – A plasma source in which the power is coupled from the coil to the gas through a dielectric window.

Hall Effect: An electrical measurement of the films relying on the motion of carriers in a magnetic field that is used to determine the resistivity, carrier type, carrier density, and mobility.

MOCVD: Metal-Organic Chemical Vapor Deposition – Thin film growth process in which an organometallic precursor(s) is reacted thermally with O2 or similar molecular feedstock.

MBE: Molecular Beam Epitaxy – Thin film growth process in which evaporated metal is combined with other reactants in a high vacuum environment to form an epitaxial thin film.

OES: Optical Emission Spectroscopy, the observation of light emission from excited state species in the plasma.
PECVD: Plasma-assisted Chemical Vapor Deposition – A thin film growth process in which the some or all of the reactants are dissociated in a plasma source.

P-MBE: Plasma-assisted Molecular Beam Epitaxy – Similar to regular MBE except that some or all of the molecular precursors are dissociated in a plasma source.

Profilmety: Physical measurement of film thickness determined by running a probe over a clean step from the film to the substrate.

PLD: Pulsed Laser Deposition – Thin film growth process in which a target of the desired film is ablated with a laser either in vacuum or in a low pressure reactive environment.

QMS: Quadrupole Mass Spectrometry – used to determine the composition of the deposition environment.

R-PECVD: Remote Plasma-assisted Chemical Vapor Deposition – A PECVD process in which the plasma source is separate from the film growth region.

Seebeck Effect: An electrical measurement relying on the motion of carriers through a thermal gradient used to detect the carrier type.

SIMS: Secondary Ion Mass Spectrometry – highly sensitive surface analysis technique used to determine the composition of a sample.

Spectrophotometry: Measurement of the optical transmittance and reflectance of the films that can be used to determine the optical bandgap.

T_e: Electron temperature – the temperature of electrons in a non-equilibrium plasma, usually of the order of 10,000 K, compared to an overall gas temperature of 500 K.

XPS: X-Ray Photoelectron Spectroscopy – surface analysis technique used to determine the atomic composition of a sample.

XRD: X-Ray Diffraction: Used to determine the crystal structure of the deposited films
REFERENCES CITED


C. G. Van de Walle, phys. stat. sol. (b) 229 (1), 221 (2002).


73 TH. Gruber, C. Kirchner, K. Thonke, R. Sauer, and A. Waag, phys. stat. sol. (a) **192** (1), 166 (2002).


APPENDIX

A.1 Standard Operating Procedure for the Deposition of ZnO by HVP-CVD

1) Record Base Pressure, should be $6 \times 10^{-7}$ or below
2) Turn on chiller (set to 15°C), fill DMZn bath with ice, and open ZS1 if it is closed, start RGA P vs. T scan
3) Wait 30 minutes for the RGA to warm up and chiller and DMZn to cool down
4) Calibrate DMZn flow when pressure has returned to base value
   4a) Turn off RGA filament
   4b) Set M1 to desired value.
   4c) Open ZS1 and ZSS and restart RGA P vs. T scan
      Record pressure as a function of time and M1 setting for 3-4 minutes or until it is stable.
   4d) Close ZSS and ZS2
      * Let the system pump out to the low $10^{-6}$ torr range again before exposing it to any O$_2$
5) When the chiller has reached 15°C, turn on the substrate heater to the desired setting.
     See the calibration plot for the corresponding inside temp
     Allow the heater to come up to temperature, then sit at temperature for at least 45 mins
6) When the system is back to $10^{-6}$ range after DMZn calibration, purge the gas lines you will need to use.
   6a) Stop RGA, turn off filament. Save file as ascii data
   6b) Close ZS1
   6c) Open Ar1 and O$_2$1, set MFCs to 100%, wait 5 mins
   6d) Also, make sure tanks are closed, and pump through the bypass during the purge
      Turn on pump
      Open O$_2$ BP and Ar BP
      Close O$_2$ BP and Ar BP before setting flows
   6e) Open S1, wait another 5 mins
   6f) Close off bypass and set gas flow to correct values for recipe
7) Set the gas flow, start RGA P-T scan and allow the flow to stabilize 30 mins while the heater is equilibrating. Record pressure
8) Once gas flow is stable, open SS and S2 for 5 minutes to recalibrate DMZn flow.
9) Close SS and S2, wait 20 minutes for DMZn to pump out. Stop RGA, save ascii data.
    Record pressure
10) Turn on plasma for 5 minutes
    10a) Record pressure again
    10b) Save OES spectra
11) Open ZS2, ZSS, start timer
   11a) After 5 mins, record pressure and save OES data
   11b) Repeat every 5-10 minutes for the length of the deposition
12) At the end of deposition time
   12a) Close ZS2,Z SS, turn off heater
   12b) Wait 30 sec, turn off plasma power
   12c) Let the substrate cool to 100 or below

**SHUT DOWN**
1) Allow the chamber to cool 40 minutes if it is hot
2) Turn off RGA filament!
3) Turn off Ar and O\textsubscript{2} MFCs, close tanks and AR\textsubscript{2} and O\textsubscript{2}2 valves.
4) Purge DMZn by opening M1 all the way with ZS2 and ZSS closed. Allow system to return to 10\textsuperscript{-7} torr range.
5) Close ZS1
6) Pump out Ar and O\textsubscript{2} through MFC to Ar/O\textsubscript{2} 2, turn off MFC and close Ar/O\textsubscript{2} 1 when P<7E-7 torr, while also pumping through the bypass
7) Turn off the chiller if T<75 (hot substrate is difficult to handle with gloves on)
8) Close gate valve, vent chamber through pressure relief valve
9) Disconnect cooling lines and remove heater from substrate holder
10) Remove holder and substrate, replace with clean substrate
11) Label substrate film side up with sample name
12) Remount new substrate and substrate holder
13) Close gas bypass lines, turn off bypass pump
14) Start pumping down
15) Reconnect cooling lines, remount heater and thermocouple
16) Make sure pressure is going down before you leave!
17) Also, empty DMZn cooling water before you leave (otherwise, it gets rusty)

**Emergency Shutdown – assumes we lost power or a pump failed NOT during a deposition**
1) Check pressure gauges. If cold cathode gauge is above 10\textsuperscript{-6}, or the ICP gauge reads above 100 mtorr, then there is a problem
2) Turn off the cold cathode gauge and RGA main power
3) Make sure all of the gas and DMZ line valves are closed
4) Close the gate valve
5) Turn off the diffusion pump with the white switch on the front panel
6) Check to see if there is cooling water to the diff pump, if we lost power, and/or if the mechanical pump died
7) Find Teresa or Dr. Wolden to determine restart or repair procedure.
A.2 CHEMKIN Equations and Background

AURORA and Equations

AURORA combines an overall mass balance, a species mass balance, a gas energy balance, and an electron energy balance to calculate the electron temperature and density. The overall mass balance is given in equation A.1a, and the species balance is given in equation A.1b. In these equations, \( m \) is a mass flow rate, \( V \) is the reactor volume and \( p \) is the density. \( A \) is the surface area of each given material and \( s \) is the molar surface production rate. \( W \) is the molecular weight of each species, \( w \) is the gas phase production rate, and \( Y \) is the mass fraction.

The electron energy equation is given in equation A.2, and the plasma adjusted gas energy equation is given in equation A.3. The subscript “e” indicates electron

\[
\frac{d(V \rho)}{dt} = m_i - m + \sum_{m=1}^{M} A_m \sum_{k=1}^{K} s_{k,m} W_k \quad A.1a
\]

\[
V \rho \frac{dY_e}{dt} = m \left( Y_e' - Y_e \right) + w W_e V + \sum_{m=1}^{M} A_m \sum_{j=1}^{J} s_{j,m} W_j - Y_e \left( \sum_{m=1}^{M} A_m \sum_{j=1}^{J} s_{j,m} W_j + V \rho \left( \frac{1}{T} \frac{dT}{dt} - \frac{1}{W} \frac{dW}{dt} \right) \right) \quad A.1b
\]

density. The overall mass balance is given in equation A.1a, and the species balance is given in equation A.1b. In these equations, \( m \) is a mass flow rate, \( V \) is the reactor volume and \( p \) is the density. \( A \) is the surface area of each given material and \( s \) is the molar surface production rate. \( W \) is the molecular weight of each species, \( w \) is the gas phase production rate, and \( Y \) is the mass fraction.

The electron energy equation is given in equation A.2, and the plasma adjusted gas energy equation is given in equation A.3. The subscript “e” indicates electron

\[
\frac{d(\rho V Y_e)}{dt} = m Y_e h_e - m Y_e h_e \dot{\omega} W_e V + \sum_{m=1}^{M} s_{m,n} W_e h_e A_m - Q_{el}^{\text{ion}} - Q_{el}^{\text{ion}} + Q_{\text{source}} \quad A.2
\]

\[
\rho V \left( c_r (1 - Y_e) \frac{dT}{dt} + \frac{R}{W_e} \frac{d(Y_e)}{dt} \right) = \quad A.3
\]

\[
m \sum_{k=1}^{K} Y_k' (h_k' - h_k) - V \sum_{k=1}^{K} h_k w_k W_k - w W V h_e - \sum_{m=1}^{M} A_m \sum_{k=1}^{K} s_{k,m} W_k - Q_{\text{ion}} + Q_{\text{ion}} + Q_{\text{ion}} + Q_{\text{sheath}}
\]
specific properties, and the “i” indicates an inlet property. The species enthalpy is given by $h$, and the tilde (\(\sim\)) represents electrons that are just formed in the gas phase. The electron internal energy is shown as $u_e$. In the gas energy equation, $c_p$ is the specific heat. The $Q$ terms are the various heat exchange mechanisms in the plasma. Equation A.2 includes terms for heat losses due to elastic and inelastic collisions, and a $Q'$ term for the source that is the initial heat in minus that lost to ions in the sheath and bulk plasma.
### Table A.1 – Gas Phase Aurora Mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>B</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $E + O \Rightarrow E + O^*$</td>
<td>1.67E-09</td>
<td>0.0</td>
<td>1.46940E+05</td>
</tr>
<tr>
<td>2. $E + O \Rightarrow E + O^*$</td>
<td>4.36E-09</td>
<td>0.0</td>
<td>1.10150E+05</td>
</tr>
<tr>
<td>3. $E + O \Rightarrow E + O^*$</td>
<td>1.93E-15</td>
<td>1.1</td>
<td>5.30780E+05</td>
</tr>
<tr>
<td>4. $E + O \Rightarrow 2E + O^+$</td>
<td>1.95E-11</td>
<td>0.6</td>
<td>1.65410E+05</td>
</tr>
<tr>
<td>5. $E + O^* \Rightarrow 2E + O^+$</td>
<td>1.95E-11</td>
<td>0.6</td>
<td>1.40000E+05</td>
</tr>
<tr>
<td>6. $E + O^* \Rightarrow 2E + O^+$</td>
<td>2.1E-10</td>
<td>0.5</td>
<td>3.9434E+04</td>
</tr>
<tr>
<td>7. $E + E + O \Rightarrow E + O^-$</td>
<td>1.00E-30</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8. $AR^* + AR^* \Rightarrow AR + AR + E$</td>
<td>6.20E-10</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9. $O^+ + O_2^+ \Rightarrow O + O_2$</td>
<td>2.80E-07</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10. $O^+ + O^+ \Rightarrow 2O$</td>
<td>2.80E-07</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>11. $O^+ + O \Rightarrow O_2 + E$</td>
<td>1.40E-10</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>12. $O^+ + AR \Rightarrow O + AR$</td>
<td>2.80E-10</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>13. $O^+ + O_2 \Rightarrow O + O_2^+$</td>
<td>2.10E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14. $O_2^+ + AR \Rightarrow AR^+ + O_2$</td>
<td>5.50E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>15. $AR^* + O_2 \Rightarrow AR + O_2^+$</td>
<td>4.60E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>16. $AR^+ + O \Rightarrow AR + O^+$</td>
<td>4.60E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>17. $O^* + O_2 \Rightarrow O + O_2$</td>
<td>3.20E-11</td>
<td>0.0</td>
<td>-67.0</td>
</tr>
<tr>
<td>18. $O^* + O \Rightarrow O + O$</td>
<td>4.00E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>19. $O^* + AR \Rightarrow O + AR$</td>
<td>4.00E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>20. $O + AR^* \Rightarrow O + AR$</td>
<td>4.00E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>21. $O^* + AR^* \Rightarrow O + AR$</td>
<td>4.00E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>22. $AR^* + O_2 \Rightarrow AR + O_2$</td>
<td>4.00E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>23. $O + O + M \Rightarrow O_2 + M$</td>
<td>5.21E-35</td>
<td>0.0</td>
<td>-900.0</td>
</tr>
<tr>
<td>24. $E + AR \Rightarrow E + AR^*$</td>
<td>1.17E-08</td>
<td>0.0</td>
<td>1.38560E+05</td>
</tr>
<tr>
<td>25. $E + AR \Rightarrow AR^+ + 2E$</td>
<td>7.07E-11</td>
<td>0.6</td>
<td>1.87120E+05</td>
</tr>
<tr>
<td>26. $E + AR^* \Rightarrow AR^+ + 2E$</td>
<td>1.25E-07</td>
<td>0.1</td>
<td>6.0524E+04</td>
</tr>
<tr>
<td>27. $E + O_2 \Rightarrow E + O_2$</td>
<td>1.41E-04</td>
<td>-1.5</td>
<td>1.1594E+04</td>
</tr>
<tr>
<td>28. $E + O_2 \Rightarrow O_2 + E$</td>
<td>2.41E-04</td>
<td>-0.9</td>
<td>7.6827E+04</td>
</tr>
<tr>
<td>29. $E + O_2 \Rightarrow O_2 + E$</td>
<td>7.13E-8</td>
<td>-0.1</td>
<td>3.0812E+04</td>
</tr>
<tr>
<td>30. $E + O_2 \Rightarrow O_2 + E$</td>
<td>2.75E-10</td>
<td>0.0</td>
<td>3.0656E+04</td>
</tr>
<tr>
<td>31. $E + O_2 \Rightarrow O_2 + E$</td>
<td>2.29E-10</td>
<td>0.4</td>
<td>6.8652E+04</td>
</tr>
<tr>
<td>32. $E + O_2 \Rightarrow E + O^* + O$</td>
<td>4.52E-13</td>
<td>0.9</td>
<td>5.1069E+04</td>
</tr>
<tr>
<td>33. $E + O_2 \Rightarrow E + E + O_2^+$</td>
<td>3.99E-14</td>
<td>1.1</td>
<td>1.37580E+05</td>
</tr>
<tr>
<td>34. $E + O_2 \Rightarrow O + O^*$</td>
<td>3.60E-08</td>
<td>-0.5</td>
<td>5.7440E+04</td>
</tr>
<tr>
<td>35. $E + O_2 \Rightarrow E + O^*$</td>
<td>4.30E-07</td>
<td>-0.3</td>
<td>3.8431E+04</td>
</tr>
<tr>
<td>36. $E + O \Rightarrow E + O^*$</td>
<td>1.24E-09</td>
<td>0.0</td>
<td>6.0440E+04</td>
</tr>
</tbody>
</table>
Table A.2 – Surface Reaction Mechanism

<table>
<thead>
<tr>
<th>Surface Reactions</th>
<th>Sticking Coefficient</th>
<th>Bohm Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AR* =&gt; AR</td>
<td>1. STICK</td>
<td></td>
</tr>
<tr>
<td>2. O* =&gt; O</td>
<td>1. STICK</td>
<td></td>
</tr>
<tr>
<td>3. O + WL(S) =&gt; WLO(S)</td>
<td>1.0E-10 0.0 0.0</td>
<td></td>
</tr>
<tr>
<td>4. O + WLO(S) =&gt; WL(S) + O₂</td>
<td>1.0E-10 0.0 0.0</td>
<td></td>
</tr>
<tr>
<td>5. O⁺ + E =&gt; O</td>
<td>0.4 BOHM</td>
<td></td>
</tr>
<tr>
<td>6. O₂⁺ + E =&gt; O₂</td>
<td>0.4 BOHM</td>
<td></td>
</tr>
<tr>
<td>7. AR⁺ + E =&gt; AR</td>
<td>0.4 BOHM</td>
<td></td>
</tr>
</tbody>
</table>
Table A.3- Aurora input

! This is a steady-state plasma simulation for an Ar O2 plasma, based on sample and real operating conditions in run D5
! plasma.
! Try instead setting initial guesses close to operating conditions, starting with very low power, and continuing to higher powers to get convergence.
! steady-state
STST
!
! number of PSR’s to be considered in series
NPSR 1
!

INLET CONDITIONS

! the total flow rate in cm/sec
SCCM 0.75
!
! mole fraction of reactants
REAC O2 0.87
REAC AR 0.13
!
! inlet temperature; only used when ENRG is specified
TINL 300
! inlet electron temperature; only used when ENRG is given
TEIN 300
!

REACTOR CONDITIONS

!
! either calculate the temperature or keep the temp fixed
!ENRG
TGIV
!
! either calculate the electron temperature or keep fixed
ENGE
! try fixed electron temperature to get convergence. set ETEMP to 500K to make all thermal reactions
!TEGV
!
! do not solve the fixed-temperature problem
NOFT
!
! specify estimate of ion temperature in gas
TION 5800.
! power deposition in watts (use PWRE for ergs, PWRC for calories)
PWRW 10.
!
! ion energy gain across the sheath in kTe
ELSH MATERIAL1 14.
! assert Bohm condition on ion fluxes, corrected for presence
! of negative ions if necessary. Use value as multiplier to
! account for Ni_sheath < Ni_plasmabulk
BOHM MATERIAL1 0.4
! elastic collision x-section for electrons and species k
XSEK O2 1.68E-16 !Itikawa from GAPHYOR
XSEK AR 2.57E-16 !Weibel, Hain, and Curtiss
! default value for x-section if not given for a species
XSDF 1.0e-15
! heat transfer coeff to ambient (cal/s-cm2-K) and ambient temp (K)
! [the conversion from ergs to calories is 2.389e-8]
QLOS 0.0
!HTRN MATERIAL1 1.89e-4 298.15
! Do you expect to be etching the bulk?
!ETCH BULK1
! temperature (guess) of the reactor in Kelvin
TEMP 600.
! electron temperature (guess) of the reactor in Kelvin
ETMP 30000.
! Pressure of reactor in mtorr
PRMT 100
! volume of the reactor in cm**3
VOL 32.16
! area in cm**2
AREA 50.65
! INITIAL GUESS AT SOLUTION
!
! estimation of gas phase composition
XEST O+ 5.e-3
XEST O* 2.e-3
XEST E 1.e-2
XEST O2+ 5.e-4
XEST O 0.7
XEST O2 .15
XEST AR* 1E-3
XEST AR .12
XEST AR+ 5.e-4
XEST O- 1.e-5
! estimation of the surface site fractions
!SURF WLCL(S) 0.9
TWOPNT PARAMETERS

amount of printing to be done
PRNT 1
relative and absolute error tolerances for the solution
RTOL 1.e-5
ATOL 1.0E-20
number of time steps and value of time step
TIM1 10 1.E-6
TIM2 100 3.E-8
number of time steps before retiring time-step size
IRET 200
lower bounds for the compositional solution variables
SFLR -1.0E-4
parameters for the calculation of numerical differences
ABSL 1.0E-15
RELT 1.e-5

DO YOU WANT TO DO ANOTHER PROBLEM AFTER THIS ONE ?
CNTN
END OF INPUT PARAMETERS FOR CURRENT PROBLEM
END
PWRW 10
CNTN
END
PWRW 20
CNTN
END
PWRW 30
CNTN
END
PWRW 40
CNTN
END
PWRW 50
CNTN
END
PWRW 60
CNTN
END