Fabrication and Characterization of Thin Film Transistors based on Sol-Gel Derived Zinc Oxide Channel Layers

by

Vahid Mirkhani

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Keywords: ZnO, Sol-Gel, Spin-Coating, Characterization, Thin Film Transistors, Gamma Irradiation

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پن باما براه سخن، آسانی ست.
باما براه سخن، آسانی ست؟

تقدیم به:
مریان ترین، شهیرترین بار، اعظم حرمین
صور ترین و ولوز ترین بدر، دادو سرمایی رشی
زیباترین، بالترین، کلا ترین، عزیزترین خوازان،
لیک ، ملک، مرک
ذکار ترین و دفاده ترین سخر، بنا نازنین، مشی وچومن,
ضریر
Abstract

This dissertation aims to explore film and device characteristics of zinc oxide (ZnO) based channel layers fabricated via the sol-gel spin-coating growth technique. ZnO is a wide band gap semiconductor with a wide range of industrial applications and numerous electronic applications such as optoelectronics, flexible transparent electronics and sensors. ZnO films were synthesized with different number of layers by repeating the spin-coating process and then annealed at different temperatures. Micro-Raman, Photoluminescence (PL), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) were used for film characterization and to investigate crystal quality of the films. The results indicated an increase in the magnitude of $E_{2}^{\text{High}}$ Raman shift as well as the near-band-edge PL peak as the annealing temperature increased. This intensification was related to the enlargement of grain size as a result of higher annealing temperature. The area under the curve ratio for UV PL over visible PL, in addition to the intensification of $E_{2}^{\text{High}}$ Raman peak, suggested higher film quality as the annealing temperature increases. However, SEM images revealed that annealing temperatures higher than 800 °C result in the formation of gaps between grains, causing non-continuity in the film. Bottom gate thin film transistors (TFTs) were fabricated and Current-Voltage (I-V) and Capacitance-Voltage (C-V) measurements were implemented to investigate a possible “kink-effect” (also known as the ”hump-effect”) in the multilayer-channel samples, due to the renowned surface oxygen chemisorption in oxide semiconductors. The measurements hint to the possibility of depletion layer formation at the ZnO-ZnO interlayer-interfaces. The kink effect disappeared after high doses of radiation, suggesting the likelihood of
the distortion of the depletion layers due to the displacement damage. After 18 months, the kink effect in unirradiated samples remained existent and in the irradiated samples, it remained absent. Multilayer ZnO TFTs were exposed to a $^{60}$Co radiation source and the robustness of ZnO TFTs against gamma irradiation was verified by comparing the transfer and output characteristics of TFTs and the PL of the channel layers before and after irradiation. By applying High Resolution Digital Optical Microscopy and Atomic Force Microscopy (AFM), it was found that the thickness of the ZnO was drastically influenced by the irradiation. A model was provided to explain the possible etching mechanism. Three effective medium approximations were applied to theoretically investigate the modification of the refractive index of the flexible conductive polymer matrix Poly(3,4-ethylenedioxythiophene) and Poly(styrene sulfonic acid) (PEDOT:PSS) by gallium doped ZnO nanoparticle inclusions, as a function of volume fraction of nanoparticle inclusions. Calculations determined the desired volume fraction of the gallium doped nanoparticles to be between 45% and 71% when gallium dopant concentration varies between 0 and 4 percent.
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<tr>
<td>2DEG</td>
<td>2-Dimensional Electron Gas</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum doped ZnO</td>
</tr>
<tr>
<td>BG</td>
<td>Bruggeman</td>
</tr>
<tr>
<td>BJT</td>
<td>Bipolar Junction Transistors</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CBM</td>
<td>Conductance Band Minimum</td>
</tr>
<tr>
<td>CM</td>
<td>Center of Mass</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance-Voltage</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DAP</td>
<td>Donor-Acceptor Pairs</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>ECR MBE</td>
<td>Electron Cyclotron Resonance Assisted Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective Medium Approximations</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
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<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close-Packed</td>
</tr>
<tr>
<td>HF LCAO</td>
<td>Hartree-Fock Linear Combination of Atomic Orbitals Method</td>
</tr>
<tr>
<td>HEMT</td>
<td>High Electron Mobility Transistor</td>
</tr>
<tr>
<td>Ga-ZnO</td>
<td>Gallium doped Zinc Oxide</td>
</tr>
<tr>
<td>GGA</td>
<td>General Gradient Approximation</td>
</tr>
<tr>
<td>IGZO</td>
<td>Indium Gallium Zinc Oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>IZO</td>
<td>Indium Zinc Oxide</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid Crystal Displays</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>LL</td>
<td>Lorentz-Lorenz</td>
</tr>
<tr>
<td>LO</td>
<td>Longitudinal Optical</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MESFET</td>
<td>Metal Semiconductor Field Effect Transistor</td>
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<tr>
<td>MG</td>
<td>Maxwell-Garnet</td>
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<tr>
<td>MOCVD</td>
<td>Metalorganic Chemical Vapor Deposition</td>
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<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>MOVPE</td>
<td>Metalorganic Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>MS</td>
<td>Magnetron Sputtering</td>
</tr>
<tr>
<td>NBE</td>
<td>Near Band Edge</td>
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<tr>
<td>NC</td>
<td>Nanocrystalline</td>
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<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OMVPE</td>
<td>Organometallic Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>OSC</td>
<td>Organic Solar Cells</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke- Ernzerhof</td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma-Enhanced Atomic Layer Deposition</td>
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<tr>
<td>PECVD</td>
<td>Plasma-Enhanced Chemical Vapor Deposition</td>
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<td>PEDOT:PSS</td>
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<td>PLD</td>
<td>Pulsed laser deposition</td>
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<td>PP LDA</td>
<td>Pseudopotential Local Density Approximation</td>
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<tr>
<td>QHO</td>
<td>Quantum Harmonic Oscillator</td>
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<tr>
<td>rf</td>
<td>Radio Frequency</td>
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<tr>
<td>RHEED</td>
<td>Reflected High Energy Electron Diffraction</td>
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<td>RMS</td>
<td>Reactive Magnetron Sputtering</td>
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<td>Description</td>
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<td>-----------------------------------------</td>
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<tr>
<td>RTA</td>
<td>Rapid Thermal Annealing</td>
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<tr>
<td>RTM</td>
<td>Repeated Temperature Modulation</td>
</tr>
<tr>
<td>SCVT</td>
<td>Seeded Chemical Vapor Transport</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SHO</td>
<td>Simple Harmonic Oscillator</td>
</tr>
<tr>
<td>SIC PP LDA</td>
<td>Self-Interaction Corrected Pseudopotential Local Density Approximation</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SS</td>
<td>Subthreshold Swing</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin Film Transistor</td>
</tr>
<tr>
<td>TO</td>
<td>Transverse Optical</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>VPE</td>
<td>Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>VTD</td>
<td>Vapor Transport Deposition</td>
</tr>
<tr>
<td>WBGS</td>
<td>Wide Band Gap Semiconductor</td>
</tr>
<tr>
<td>WZ</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ZB</td>
<td>Zinc Blende</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

During the last three decades the interest in zinc oxide (ZnO) research as a semiconductor has been uplifted, despite the compound being exploited in industry for more than 150 years. In the realm of semiconductors, various compounds such as arsenides, phosphates, tellurides and selenides are toxic and often, a comprehensive discretion must be exercised during the fabrication process. ZnO is an odorless, non-toxic and ultra-violet (UV) absorbent mineral with various convenient growth methods. Furthermore, it has antibacterial behavior, making it ideal for rampant medical, cosmetic and nutrition applications in an industrial scale. Whereas the optical studies on this II-VI compound was initialized more than a century ago, various properties of ZnO such as the band structure, phonon dispersion, irradiation damage and donor/acceptor impurity behavior were investigated in 1950s and 1960s. ZnO has been recently scrutinized as a prominent candidate for numerous electronic applications such as transparent electrodes, varistors, solar cells, gas sensors, biosensors, piezo-phototronic and optoelectronic devices and etc. ZnO has been studied along organic conductors as well. Recently, ZnO-PEDOT nanowires with a core-shell structure were fabricated via hydrothermal growth, indicating fast switching rates and high efficiencies suitable for transparent displays. Silicon is the dominant semiconductor implemented in electronics. Yet, the relatively small indirect band gap (\(~1.12\) eV) of the
semiconductor imposes limitations on the electronic properties such as their operation temperature. This is where the wide band gap semiconductors (> 2eV) come into play. Wide band gap semiconductors (WBGS) can be utilized in power electronics and the efficiency of the devices are more advanced compared to the silicon-based devices. Another property of the WBGS such as zinc oxide (ZnO), gallium nitride (GaN), silicon carbide (SiC), titanium dioxide (TiO₂) and n-diamond is their transparency. Transparent electronics are far from being a mere ambition. Fully transparent screens are available due to the transmittive property of each device structure. On the contrary, the aforementioned WBGS are UV absorbent, as their band gap energy’s corresponding wavelength lies between 400nm and 200nm. The UV absorption property along with non-toxicity of ZnO and TiO₂ qualifies them to be in medical products such as sunscreen and cosmetics, as well as UV sensors. The UV absorption is not without consequences. The interacting photons produce electrons and holes which, as a result, contribute to the conductivity. In some crystals, such as ZnO and GaN, this conductivity amplification endures, even after the light source is removed and hence, the persistent photoconductivity effect.¹⁴

This work further explores the properties of thin film transistors fabricated via the sol-gel spin-coating growth method. Chapter 2 introduces the basic properties of ZnO and surveys the background research performed on different aspects of the direct WBGS such as its band structure, doping with elements from different groups, recent transactions on p-type doping of ZnO, ZnO High Electron Mobility Transistors (HEMT), different growth techniques, and etc.

In Chapter 3, the growth method applied for ZnO thin film deposition used as the active layer is discussed. The films are characterized by Raman spectroscopy, photoluminescence and Scanning Electron Microscopy (SEM) in order to investigate the crystal quality of the films.
Chapter 4 investigates the possibility of the formation of depletion layers at the ZnO-ZnO interlayer-interfaces during film deposition. In addition to film characterization methods such as X-ray Diffraction (XRD), Current-Voltage (I-V) and Capacitance-Voltage (C-V) measurements are conducted on TFTs. The measurements indicated a likelihood of depletion regions being present inside the ZnO bulk.

ZnO TFTs with 2 different thicknesses were fabricated and irradiated with gamma rays. After device measurements, the samples were additionally irradiated to a higher dose to examine the consequences of irradiation on the thicker sample. The results are presented in Chapter 5. Although the transistors with different thicknesses displayed different traits, measurements after additional irradiation resulted in an apparent trend as the thickness of the channel layer was lessened, due to displacement damage occurred to the surface atoms.

In Chapter 6, in an attempt to match the refractive index of the organic conductive layer (PEDOT:PSS) with the emissive layer, effective medium approaches were applied to increase the refractive index of the conductive layer with doped ZnO nanoparticle inclusions. Gallium doped ZnO nanoparticles with different doping concentrations and therefore, different refractive indices were used to obtain a range for the volume fraction of nanoparticle inclusions inside the conductive layer.
References


Chapter 2

Literature Review

Wurtzite ZnO is a direct wide band gap semiconductor (3.37 eV at room temperature) with a relatively high free exciton binding energy (60 meV)\(^1\), appointing ZnO an exemplary candidate for excitonic emission applications, such as light emitting devices. This is due to its high device efficiency at room temperature (\(k_B T = 26\) meV) among other direct band gap semiconductors’ exciton binding energies such as GaAs (4.8 meV), CdTe (10 meV), 4H-SiC (20 meV), GaN (25 meV) and ZnSe (22 meV).\(^2\)\(^3\)\(^4\)

ZnO has been compared to GaN due to their crystal structure, lattice constants and other various similarities due to the proximity of oxygen (zinc) with nitrogen (gallium). In addition to high free exciton binding energy, ZnO has several advantages, over GaN such as the possibility of wet etching and more resistance to irradiation.\(^5\) Tables 2.1 and 2.2 represent the fundamental and the mechanical properties of wurtzite ZnO, respectively.
Table 2.1 Fundamental properties of wurtzite zinc oxide [6]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>3.2495 Å</td>
</tr>
<tr>
<td>$c$</td>
<td>5.2069 Å</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.602</td>
</tr>
<tr>
<td>$u$</td>
<td>0.380</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g.cm$^{-3}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6 – 1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient ($/^{\circ}$C)</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>$6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>$c$</td>
<td>$3.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008 – 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Carrier concentration</td>
<td></td>
</tr>
<tr>
<td>Intrinsic (electrons)</td>
<td>$&lt; 10^6$ cm$^{-3}$</td>
</tr>
<tr>
<td>Max n-type doping (electrons)</td>
<td>$&gt; 10^{20}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Max p-type doping (holes)</td>
<td>$&lt; 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass ($m_e^*$)</td>
<td>0.24 $m_0$</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for n-type</td>
<td>200 cm$^2$.V$^{-1}$.s$^{-1}$</td>
</tr>
<tr>
<td>Hole effective mass ($m_h^*$)</td>
<td>0.59 $m_0$</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for p-type</td>
<td>5 – 50 cm$^2$.V$^{-1}$.s$^{-1}$</td>
</tr>
</tbody>
</table>
Table 2.2 Mechanical properties of wurtzite zinc oxide acquired by experimental techniques [7,8,9,10]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11} (GPa)</td>
<td>157</td>
</tr>
<tr>
<td>C_{12} (GPa)</td>
<td>89</td>
</tr>
<tr>
<td>C_{13} (GPa)</td>
<td>83</td>
</tr>
<tr>
<td>C_{33} (GPa)</td>
<td>208</td>
</tr>
<tr>
<td>C_{44} (GPa)</td>
<td>38</td>
</tr>
<tr>
<td>C_{66} (GPa)</td>
<td>34</td>
</tr>
<tr>
<td>e_{31} (C.m(^{-2}))</td>
<td>– 0.51</td>
</tr>
<tr>
<td>e_{33} (C.m(^{-2}))</td>
<td>1.22</td>
</tr>
<tr>
<td>e_{15} (C.m(^{-2}))</td>
<td>– 0.45</td>
</tr>
<tr>
<td>Bulk modulus, B (GPA)</td>
<td>183</td>
</tr>
<tr>
<td>dB/dP</td>
<td>4.0</td>
</tr>
<tr>
<td>Young’s modulus, E (GPa)</td>
<td>111.2</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

ZnO is among the many II-VI compound semiconductors which have recently been attracting attention. Due to its distinct properties, ZnO is one the most important metal oxide semiconductors. ZnO may crystalize in structures such as hexagonal wurtzite (WZ) (P6\(_3\)mc), zinc blende (ZB) and rock salt (RS) structures. Figure 2.1 indicates the aforementioned structures. The space group of these structures (WZ, ZB and RS) reside in P6\(_3\)mc, F\(^{\bar{4}}\)3m and Fm\(^{\bar{3}}\)m in the Hermann-Mauguin notation, respectively; and in C\(^{\bar{4}}\)\(_6\)\(_v\), T\(_d\)\(^2\) and O\(_h\)\(^5\) in the Schoenflies notation, respectively. The hexagonal wurtzite is the most stable structure of ZnO in the ambient temperature and the ambient pressure. The unit cell of this structure has two lattice constants \(a\) and \(c\) and the ideal ratio of \(\frac{c}{a} = \sqrt{8/3}\). Experimental values for lattice constants are obtainable via X-ray
diffraction analysis (XRD). It can be indicated that the spacing $d_{hkl}$ between reticular planes with Miller indices $hkl$ for a crystal structure can be obtained from its relationship with the reciprocal space vector $\vec{N}_{hkl}$

$$\vec{N}_{hkl} \cdot \vec{d}_{hkl} = 1.$$  

In hexagonal wurtzite structures, Bragg’s relation $2d_{hkl} \sin \theta_{hkl} = n\lambda$ can be used to extract the lattice parameters, where $n$ is the order of diffraction and $\lambda$ is the wavelength of incident ray.$^{11}$

$$\theta_{hkl} = \sin^{-1} \left\{ \frac{n\lambda}{2d_{hkl}} \right\} = \sin^{-1} \left\{ \frac{n\lambda}{2} \sqrt{\frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2}} \right\}$$

For ZnO, the $a$ parameter may vary from 3.2475 Å to 3.2501 Å and the $c$ parameter may vary from 5.2042 Å to 5.2075 Å. The definition of the lattice constant $u$ is defined as the length of oxygen-zinc bond along the c-axis by $u = \frac{1}{3} \times (\frac{c}{e})^2 + \frac{1}{4}$. The $\frac{c}{a}$ ratio, which is influenced by the electronegativities of oxygen and zinc, varies between 1.593 to 1.6035 and the lattice constant $u$ varies between 0.3817 to 0.3856.$^{12,13}$ The aforementioned empirical ratio values are in agreement with the ideal hexagonal wurtzite structure ratio values. The wurtzite structure can be formed by inserting two parallel hexagonal closed packed (HCP) structures into one another, one with zinc constituents and the other with oxygen atoms, with the separation lattice-constant $u$ (Figure 2.2 (b)). Figure 2.2 (a) shows the Brillouin zone in reciprocal lattice. The high symmetry points of the Brillouin zone are $\Gamma = (0, 0, 0)$, $A = \frac{2\pi}{c} \left( 0, 0, \frac{1}{2} \right)$, $K = \frac{2\pi}{a} \left( \frac{\sqrt{3}}{3}, \frac{1}{3}, 0 \right)$, $M = \frac{2\pi}{a} \left( \frac{\sqrt{3}}{3}, 0, 0 \right)$, $H = \frac{2\pi}{c} \left( \frac{\sqrt{3}}{3}, \frac{1}{3}, \frac{a}{2c} \right)$, $L = \frac{2\pi}{a} \left( \frac{\sqrt{3}}{3}, 0, \frac{a}{2c} \right)$.  

9
Figure 2.1: Ball and stick presentation of zinc oxide crystal structures: (a) cubic rock salt (B1), (b) cubic zinc blende (B3), (c) hexagonal wurtzite (B4). The structures were generated by VESTA.\textsuperscript{14}

Figure 2.2: (a) The Brillouin zone in reciprocal lattice. (b) Wurtzitic ZnO structure with lattice constants \( a \) (basal plane) and \( c \) (basal direction); \( u \) parameter (0.375 for an ideal crystal) obtained by dividing the bond length (nearest-neighbor distance) \( b \) by \( c \); and equal bond angles \( \alpha \) and \( \beta \) (109.47° for an ideal crystal).
Along the c-axis, each basal plane consists of either Zn$^{2+}$ or O$^{2-}$ ions. The polar plane terminating with oxygen atoms (the (000\bar{1}) plane) is negatively charged while the polar plane terminating with zinc atoms (the (0001) plane) is positively charged. Every oxygen (zinc) atom is surrounded by four zinc (oxygen) atoms at the corners of a tetrahedron. The Zn-O bonds in the tetrahedron have an indication of sp$^3$ bonding (hybridization of zinc 3d and oxygen 2p orbitals) and yet, they possess a very strong ionic character as well. This ionic character tends to widen the band gap compared to the band gap expected from the purely covalent bonding. Due to ZnO crystal structure being deficient in any inversion symmetry, a spontaneous c-axis oriented electric dipole moment exists in every tetrahedron. The electromechanical coupling and the strong polarization along the c-axis, result in the pyroelectricity$^{15}$ and piezoelectricity$^{16}$ of ZnO, respectively. The layer growth advances along the c-axis (0001). Fujimura et al. grew ZnO via radio frequency (RF) magnetron sputtering with various conditions and Ar:O$_2$ compositions in order to manipulate the growth orientation of the films. Growth occurred along the (10\bar{1}0) and (11\bar{2}0) (a-axis) and (0001) (c-axis) orientations. The calculated values for the surface energy densities of the aforementioned orientations were 0.209 eV/Å$^2$, 0.123 eV/Å$^2$ and 0.099 eV/Å$^2$, respectively.$^{17}$ Due to the surface energy density along the c-axis being minimum, growth along this orientation is the most stable. The maximal growth rate of ZnO nanostructures is normally along the (0001) orientation. Jin et al. grew ZnO via PLD, on sapphire (001), and confirmed the disappearance of the corresponding (1000) orientation XRD peak and the development of the (0002) XRD peak of ZnO subsequent to an increase in the growth temperature.$^{18}$

A stable zinc blende ZnO structure can only be realized via growth on cubic substrates while the rocksalt ZnO structure requires high pressure. Under 9 GPa, the rocksalt ZnO can be formed and the stability can be maintained under pressures as high as 209 GPa, indicating the
feasibility of the use of ZnO in an internal pressure standard at high pressures. Jaffe and Hess implemented periodic Hartree-Fock linear combination of atomic orbitals method (HF LCAO) to calculate the ground state total energy of ZnO phases, as a function of unit cell volume, by addition of an isolated neutral Zn and an O atom energies after reoptimization of outer orbitals. Later, Jaffe et al. calculated $E_0$ via the local density approximation (LDA) and general gradient approximation (GGA) for the three aforementioned phases in addition to a previously predicted B4 phase by Liu and Basset where under an extremely high pressure the B1 phase (cubic NaCl) reconstructs into the B4 phase (cubic CsCl). The rough estimated base of the total cohesive energy ($E_0$) for each phase is summarized in Table 2.3 Whereas the GGA results in the closest result to the wurtzite ZnO experimental value -7.52 eV extracted from experimental Zn heat of vaporization, O$_2$ binding energy and ZnO enthalpy of formation, all methods confirm the higher stability of the hexagonal wurtzite structure with respect to other phases.

Electronic band structure of ZnO has been investigated by various groups via different experimental and theoretical approximation methods. Varshni proposed a temperature dependent universal function for band gap ($E_g$) variation, based on experimental data for several semiconductors:

$$E_g(T) \approx E_g(T = 0) - \frac{\alpha T^2}{\beta + T}$$

where $\alpha$ and $\beta$ are constants. $\beta$ is proportional to $\theta_D$ (Debye temperature). Wang and Giles used temperature-dependent photoluminescence to determine $\alpha$, $\beta$, $\theta_D$ and $\theta_E$ (Einstein temperature) values. They reported 700 K and 240 K as the Debye temperature and the Einstein temperature, respectively.
Table 2.3 Cohesive energies for B4 (wurtzite), B3 (zinc blende), B1 (rocksalt), and B2 (CsCl) phases of ZnO. All extensive quantities are per ZnO formula unit.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>HF</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>9.769</td>
<td>7.692</td>
<td>5.658</td>
<td>7.52</td>
</tr>
<tr>
<td>B3</td>
<td>9.754</td>
<td>7.679</td>
<td>5.606</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>9.611</td>
<td>7.455</td>
<td>5.416</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>8.462</td>
<td>6.334</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Wurtzite band structure was investigated by Birman\textsuperscript{26} in 1959 and a spin-orbit splitting was reported for CdS. In 1960, D.G. Thomas\textsuperscript{27} studied wurtzite ZnO band structure at low temperature (4.2 K) and witnessed the spin-orbit splitting in the valence band via reflectance and absorption measurements. Rossler\textsuperscript{28} (among other researchers\textsuperscript{29,30}) confirmed Thomas’ results regarding the $\Gamma_7$ symmetry of the first and the third subbands (A and C) and the $\Gamma_9$ symmetry of the second subband (B), and adopted the empirical pseudopotential method (EPM) considering relativistic mass-velocity and Darwin corrections to calculate the energy band structure. Hopfield\textsuperscript{31} considered the hexagonal structure as a perturbation of a cubic structure and developed a “quasi-cubic” Hamiltonian for wurtzite ZnO and derived the energy states for the valence band maxima A, B and C. By setting the top valence band energy to zero ($E_A = 0$), he derived other eigenstates as

$$E_{B,C} = -\frac{\delta + \Delta}{2} \pm \sqrt{\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{2}{3}\delta\Delta}$$

The parameters $\delta$ and $\Delta$ represent contributions of spin-orbit and uniaxial field interactions, respectively, and can be obtained by measuring the level splitting $E_{AB}$ and $E_{BC}$. Reynolds et al.\textsuperscript{32} were able to observe free-exciton emission for the first time by investigating low temperature...
photoluminescence (PL) and reflection spectra of wurtzite ZnO single crystal, grown by a seeded physical vapor transport method, in the presence of an external magnetic field. The experiment confirmed the spin-orbit splitting. The authors, however, suggested the $\Gamma_9$ symmetry for the top valence band (A) and $\Gamma_7$ symmetry for the lower valence bands (B and C). They measured $\delta$ and $\Delta$ as 16 meV and 43 meV, respectively. Figure 2.3 represents the splitting of the ZnO VBM, via simulations based on the density functional theory. \cite{Lambrecht2002}

![ZnO band structure and valence band maximum splitting due to spin-orbit coupling](image)

Figure 2.3: ZnO band structure and valence band maximum splitting due to spin-orbit coupling. The open circles were obtained via atomic sphere approximation linearized muffin-tin orbital method (including spin-orbit coupling) and the black lines represent a fit to Rashba-Sheka-Pikus effective Hamiltonian. Reprinted figure with permission from Walter Lambrecht, Anna Rodina, Sukit Limpijumnong, B. Segall and Bruno Meyer, Valence-band ordering and magneto-optic exciton fine structure in ZnO, Physical review B, 65 (7), p.075207 (2002). Copyright (2002) by the American Physical Society.
Among various theoretical approaches toward calculating ZnO band structure, standard pseudopotential local density approximation (PP-LDA) is implemented by most researchers. In this approximation, the cationic $d$ electrons are not simply considered as core electrons in the valance band. Despite its infamous band gap underestimation and overestimation of occupied cationic $d$ bands, lattice constants provided by LDA comply with experimental values.\textsuperscript{34} Self-interaction corrected pseudopotential LDA (SIC-PP-LDA) mitigates these misestimations via the down-shifting of the $d$ bands, drastic alteration of the bandwidth of oxygen anion 2$p$ valence bands, and the reduction of $p$-$d$ interactions between oxygen and zinc valence bands. Vogel \textit{et al.} obtained a close estimate ($E_g = 3.77$ eV) using SIC-PP-LDA.\textsuperscript{35} Shih \textit{et al.}\textsuperscript{36} implemented the GW method combined with LDA to simulate ZnO band structure while addressing the band convergence issues caused by the perturbative nature of the method. GW method formulates a one-particle Green’s function for the electron-gas problem\textsuperscript{37}; and by obtaining the Green’s function $G$, the dynamical screened interaction $W$ and approximating the self-energy operator, quasiparticle energies and wave functions can be calculated by solving the pseudopotential equation.\textsuperscript{38} Figure 2.4 indicates band structure simulation by Ochi \textit{et al.}\textsuperscript{39} using various methods such as LDA, HF method, biorthogonal transcorrelated Hamiltonian method (BITC) and comparing these approximations with other studies such as the standard GW method ($G^0W^0$),\textsuperscript{40} variational quantum Monte Carlo (VMC)\textsuperscript{41} and experimental data by Zwicker and Jacobi\textsuperscript{42}. Band structure computational results indicate that in crystal momentum space (k-space), all energy states forming the valence band maximum (VBM) are directly below the energy states forming the conductance band maximum. This entails the fact that electrons in the VBM may have transitions to the CBM without momentum change and hence, the direct band gap of ZnO.
Introducing impurities into the lattice structure can change the properties of the host (e.g. by introducing new energy states into the band gap). Donor or acceptor impurities may substitute zinc or oxygen, resulting in a higher or lower carrier concentration. Since ZnO indicates strong n-type conductivity, it’s straightforward to dope the semiconductor with donor impurities for an increase in the free carrier concentration. Group III elements act as shallow donors by substituting Zn, having a dangling bond. Minami et al.\textsuperscript{45} reported preparing highly conductive transparent Al-doped ZnO (AZO) thin films for use in transparent displays. The group later reported doping of ZnO with boron, aluminum, gallium, indium \textit{via} rf magnetron sputtering and group III oxide powders (B$_2$O$_3$, Al$_2$O$_3$, Ga$_2$O$_3$ and In$_2$O$_3$). A general trend of decreased resistivity was observed.
and the lowest resistivity was observed when the doping concentration reached 2~3 atomic% for impurities Al, Ga and In, and 10 atomic% for boron. Fluorine can substitute for oxygen and act as a shallow donor due to its 2p orbital being half-filled. Hu and Gordon deposited F-doped ZnO films, via chemical vapor deposition (CVD). With deposition temperature of 450 °C and 0.25 at.% fluorine concentration, the highest doping efficiency of 96%, largest grain size of 250 nm, and highest electron mobility of 36 cm².V⁻¹.s⁻¹ was achieved. Hydrogen doping of ZnO was first conducted by Mollwo and later further studied by Thomas and Lander who observed smooth diffusion of hydrogen into the crystal structure and measured diffusion coefficients. They proposed hydrogen atoms remaining as interstitial protons, forming shallow donors. Van de Walle studied interstitial hydrogen sites in ZnO by using density functional theory (DFT) within the plane-wave pseudopotential local density approximation (PP-LDA) and proposed the non-amphoteric behavior of this element in ZnO as the host, in contrast to its behavior in other hosts where it counteracts prevalent conductivity.

Park et al. applied alkali metal dopants (such as lithium, sodium, potassium and rubidium) via solution process and achieved higher mobility n-type ZnO thin film transistors (TFTs) compared to undoped samples. Interstitial sites for alkali metals are preferable for their lower formation energies where they will act as shallow donors; in contrast with substitutional sites where the impurities behave as acceptors.

Whereas n-type doping of ZnO is relatively straightforward and the doped ZnO remains stable, albeit with limited dopant solubility, achieving the p-type ZnO has been controversial due to reproducibility and degradation issues. The II-VI semiconductors’ resistance towards doping has been long established. Aven considered acceptor doping difficulties to originate from (i) small solubility of the impurities compared to donor dopants, (ii) acceptor dopants acting as donors...
when occupying other sites such as interstitials, (iii) the tendency of acceptor dopants to pair with other defects to form electrically inactive complexes. Yet, p-type ZnO opens the door to various device opportunities via proper p-n junction (homojunction) being fulfilled and therefore, has been of great interest for the past two decades. Numerous experimental attempts have been made and theoretical calculations have been conducted to investigate the possibility of the achievement. Ryu et al.\textsuperscript{54} reported fabrication of homostructural p-n junction for ZnO for the first time, using Al-doped ZnO (n-type) and As-doped ZnO (p-type). A brief review of attempts at different dopants to realize p-type ZnO is presented as follows.

As mentioned, alkali metals may introduce acceptor levels if they are situated at substitutional sites. Lander\textsuperscript{55} discussed the behavior of lithium dopant both as a donor and as an acceptor. As an interstitial impurity (Li\textsc{i}), Li contributes to the free carrier concentration whereas when it substitutes Zn (Li\textsc{zn}), it pushes the Fermi level down to the center of the band gap. Wardle et al.\textsuperscript{56} theoretically investigated the formation energies of Li\textsc{i}, Li\textsc{zn} and their complexes with each other, with diffused hydrogen atoms in different sites, and with oxygen and zinc vacancies (VO and V\textsc{zn}, respectively). They concluded that the deep levels cannot merely originate from isolated Li\textsc{zn}. Lithium usually compensates the n-type conductivity in ZnO. However, claims of p-type Li-doped ZnO with hole concentration of \( p = 1.44 \times 10^{17} \) cm\(^{-3}\) was reported by Zeng et al.\textsuperscript{57} and Lee et al.\textsuperscript{58} reported the fabrication of homojunction diodes and back-gate field effect transistors (FETs) based on p-type Li-doped ZnO nanowires (NWs) and n-type ZnO thin films. Shin et al.\textsuperscript{59} employed Li-doped ZnO NWs to fabricate flexible piezoelectric nanogenerators.

Lin et al.\textsuperscript{60} estimated an acceptor level of 164 meV in sodium-doped ZnO films obtained by pulsed laser deposition (PLD). Lin et al. claimed realization of stable homojunction light
emitting diodes (LEDs) by applying n-type Al-doped ZnO and p-type Na-doped films and reported the electroluminescence (EL) and photoluminescence (PL) of the LEDs at low temperatures of 110 K and 10 K, respectively.

Copper-doped ZnO was studied by Dietz et al.\textsuperscript{61} for its electronic structure and it was observed that a hole can be formed in the 3d shell of Cu. Dingle\textsuperscript{62} observed the green luminescence of the impurity and proposed a binding energy for the deep acceptor level (~3.3 eV). To study the compensating behavior of copper, Muller\textsuperscript{63} doped ZnO with hydrogen and indium to increase the carrier concentration and by using Cu as a co-dopant, he observed a reduction in carrier concentration and assigned it to the acceptor behavior of Cu. Many groups, however, have reported acquiring n-type ferromagnetic Cu-doped ZnO samples instead.\textsuperscript{64,65,66,67}

Group V elements introduce acceptor levels into the band gap of ZnO due to their oxidation number. Kobayashi et al.\textsuperscript{68} [cross ref.] theoretically predicted the shallow acceptor behavior of nitrogen but deemed other group V elements (P, As, Sb and Bi) as border line deep acceptors. Whereas nitrogen is the most suitable candidate to replace oxygen, other elements (P, As, Sb) result in deep acceptor states if they occupy oxygen sites (substitution). [cross ref.]\textsuperscript{69}

Aoki et al.\textsuperscript{70} fabricated a ZnO diode by achieving phosphorus-doped ZnO, using excimer-laser pulses to deposit zinc phosphide (Zn\textsubscript{3}P\textsubscript{2}) on n-type ZnO substrate as dopant material, and observed white-violet electroluminescence at 110 K. Kim et al.\textsuperscript{71} used phosphorus oxide (P\textsubscript{2}O\textsubscript{5}) as the dopant and claimed obtaining p-type ZnO implementing low-temperature photoluminescence (acceptor-bound exciton peak near 3.35 eV at 10 K) and Hall measurements. They suggested thermal activation using rapid thermal annealing (RTA) to overcome reproducibility and degradation issues.
Ryu et al.\textsuperscript{72} reported synthesizing arsenic-doped ZnO for the first time \textit{via} pulsed laser ablation in an ultra-pure oxygen ambient, characterized by low-temperature PL and Hall measurements. Ryu \textit{et al.} later conducted more characterizations to present two acceptor levels of 115 and 164 meV above the valence band maximum (VBM), exciton binding energy of 12 meV and carrier concentration up to $10^{17}$ cm$^{-3}$ for As-doped ZnO samples with different doping concentrations.\textsuperscript{73}

Xiu \textit{et al.}\textsuperscript{74} grew antimony-doped ZnO \textit{via} electron cyclotron resonance assisted molecular beam epitaxy (ECR-MBE) and claimed achieving a p-type conductivity with a high hole concentration of $10^{18}$ cm$^{-3}$ and Hall mobility of 20 cm$^2$.V$^{-1}$.s$^{-1}$. Homojunction light emitting diodes were fabricated by Chu \textit{et al.}\textsuperscript{75} with Sb-doped ZnO (p-type) and Ga-doped ZnO (n-type) where low temperature electroluminescence (EL) exhibited strong UV emission. The group was able to obtain the constants for Varshni’s temperature-dependent band gap equation ($\alpha = 5.8 \times 10^{-4}$ eV/K and $\beta = 520$ K) from near band edge (NBE) peak position of the EL spectra measured at various temperatures.

Considering the deep level of oxygen-substituting group V dopants, Limpijumnong \textit{et al.}\textsuperscript{76} presented a model to describe the possibility of shallow level behavior of the dopants in the “mysterious key experimental observations” of p-type ZnO. They suggested the dopants to substitute for zinc instead and form a complex with two zinc vacancies (\textit{e.g.} As$_{Zn}$-2V$_{Zn}$). These complexes, however, have high formation energies and therefore, are scarce.

Following the predictions of Kobayashi \textit{et al.} on shallow acceptor behavior of nitrogen in ZnO, Sato \textit{et al.}\textsuperscript{77} tried growing N-doped ZnO films on $\alpha$-Al$_2$O$_3$ substrates by zinc evaporation in O$_2$-N$_2$ mixed radio-frequency plasmas. The investigations on films annealed at different temperatures indicated n-type conductivity in all samples. Minegishi \textit{et al.}\textsuperscript{78}, however, reported
achieving p-type N-doped ZnO by adding NH$_3$ and excess Zn into carrier gas and source during chemical vapor deposition (CVD). They claimed extreme difficulty in controlling the growth temperature. Joseph et al.$^{79}$ co-coped ZnO with Ga and N and claimed achieving high carrier concentration p-type ZnO thin films, but reported how subtle experimental parameter alterations may easily “flip” the carrier type. Look et al.$^{80}$ produced N-doped ZnO using MBE and compared their obtained hole concentrations ($p$) and hole mobility ($\mu_p$) to previous p-type ZnO reports. The group criticized the fact that the acceptor levels in the 150 meV range, reported by various groups achieving p-type ZnO via doping, cannot result in such high hole concentrations claimed by these groups and further cautioned how deceitfully high values for $p$ and low values for $\mu_p$ can be caused by artificially low Hall voltage differences. Tsukazaki et al.$^{81}$ observed violet to green regions in EL spectrum at room temperature from their fabricated ZnO LED with p-i-n junctions, using N-doped ZnO as p-type. The LED was structured with stacked ZnO films, with undoped ZnO film (i-ZnO) sandwiched between Ga-doped ZnO (n-type) and N-doped ZnO (p-type) films. In order to obtain high nitrogen concentration, repeated temperature modulation (RTM) was applied to the film, due to the fact that N concentration decreases at steadily high temperature annealing. This work was followed by other groups reporting the fabrication of LEDs using nitrogen as p-type dopant.$^{82,83}$ The p-type conductance of nitrogen in ZnO was challenged by Lyons et al.$^{84}$ using density functional calculation and concluding that the calculated ionization energy of 1.3 eV will denote nitrogen as a deep acceptor, preventing it from contributing to free carrier concentration. To resolve this issue, Liu et al.$^{85}$ suggested defect complexes which could be considered as shallow donors. Liu et al. considered nitrogen substituting oxygen paired with zinc vacancy (No–VZn) and nitrogen substituting zinc paired with oxygen vacancy (NZn–VO) as candidates for shallow acceptors, but refuted the NZn–VO complex since the complex may easily evolve into No–VZn
complex due to the lower energy of the latter. Yong et al.\textsuperscript{86} proposed the possibility of hydrogen stabilizing the No–V\textsubscript{Zn} complex, forming N\textsubscript{Zn}–mH–Vo where \( m = 1–4 \) is the number of hydrogen atoms bonding with the No–V\textsubscript{Zn} complex, and estimated an ionization energy of 138 meV for the N\textsubscript{Zn}–H–Vo complex. Reynolds et al.\textsuperscript{87} incorporated nitrogen in ZnO film growth via organometallic vapor phase epitaxy (OMVPE) and claimed the existence of V\textsubscript{Zn}–No–H\textsuperscript{+} complex with approximated ionization energy of 134 meV. In order to achieve stabilized No–V\textsubscript{Zn} complexes, Tang et al.\textsuperscript{88} implemented tellurium as a co-dopant.

Despite the fact that one of the main carrier-type identification methods used by most researchers is the Hall measurements, it should be noted that this identification method might lead to erroneous results. Ohgaki et al.\textsuperscript{89} discussed how Hall measurements with a Van der Puaw configuration of non-homogenous n-type ZnO films may lead to an improper carrier-type identification and indicate a “false hole concentration” in the films. The possibility of this improper identification in inhomogeneous samples was later confirmed by theoretical studies of Bierwagen et al.\textsuperscript{90}

Doping may as well be used to alter the band gap of the host; and band gap engineering has been of interest for various optical and electronic device applications. Magnesium and cadmium have been used to alter the band gap of ZnO, since magnesium oxide (MgO) and cadmium oxide (CdO) are II-VI compound WBGS with 7.8 eV\textsuperscript{91} and 2.2 eV\textsuperscript{92} band gaps, respectively. Note that the electronegativities of Mg, Zn and Cd on the Pauling scale are 1.31, 1.65 and 1.69, respectively. Makino et al.\textsuperscript{93} were able to tune ZnO band gap from 3.19 eV to 3.87 eV by achieving Cd\textsubscript{0.07}Zn\textsubscript{0.93}O and Mg\textsubscript{0.35}Zn\textsubscript{0.65}O alloys, respectively. They reported an issue with the limited solubility of magnesium and cadmium in ZnO. Das et al.\textsuperscript{94} used the spray pyrolysis method to fabricate nickel-doped wurtzite ZnO nanofibrous structured thin films. They observed
Ni substituting Zn for concentrations less than 4% and NiO phase was observed in XRD analysis for higher concentrations. They reported obtained data from two methods (optical transmittance and X-ray emission spectroscopy) indicated a decrease in the band gap (up to \( \sim 2.9 \) eV for 15% Ni concentration). The result is compelling since the decrease is not due to the ZnO band gap shifting toward the band gap of NiO. This cubic direct WBGS has a p-type semiconductivity with a band gap in the range of 3.6 to 4 eV\(^{95,96}\) and the reduction of the Ni-doped ZnO band gap may be attributed to Ni states appearing at the top of the valence band maximum. Ahn \textit{et al.}\(^{97}\) observed significant optical band gap reduction by doping ZnO with copper \textit{via} reactive rf magnetron sputtering and claimed achieving p-type ZnO. The reduction was in agreement with computational studies of Ferhat \textit{et al.}\(^{98}\) using density functional theory (DFT) and generalized gradient approximation (GGA). Chen \textit{et al.}\(^{99}\) also observed the optical band gap reduction in Cu-doped ZnO films, but an increase in the silver-doped ZnO sample was observed. Sernelius \textit{et al.}\(^{100}\) were able to synthesize heavily n-type aluminum-doped ZnO films (with electron concentration \( n = 4.5 \times 10^{20} \text{ cm}^{-3} \) for 2.14 at. % Al concentration) and observe a rise in the optical band gap. They reported band gaps of 3.40, 3.55, 3.79 and 3.90 eV for aluminum atomic percent of 0%, 0.95%, 1.40% and 2.14%, respectively). Similarly, an optical band gap increase of \( \sim 0.4 \) eV was observed in gallium-doped ZnO, deposited by laser molecular beam epitaxy (MBE), as the carrier concentration increased by the group III dopant.\(^{101}\) Selenium can also be implemented as a group VI dopant, incorporating oxygen vacancies, to tune ZnO band gap. Nenavathu \textit{et al.}\(^{102}\) measured an increase of 0.2 eV and 0.33 eV for 2 wt% and 5 wt% Se in the band gap of Se-doped ZnO nanoparticles (NPs) synthesized by thermos-mechanical method. As the Se doping concentration increased, a decline in crystal size was observed.
Another use of dopants, altering the band gap, is in high electron mobility field effect transistors (HEMTs), where heterostructures are the fundamental blocks of these types of devices. Heterostructures are formed when two different semiconductors with the same majority carrier type (e.g. n-type) with similar crystal structures but dissimilar band gaps, are in contact, and the difference in the band gaps will cause a band edge offset. Before contact, if the CBM (and the VBM) of one of the semiconductors is lower than (and higher than) the CBM (and the VBM) of the other semiconductor, this “normal” offset causes a band bending at the interface after contact (heterojunction). By engineering the Fermi level on both semiconductors before contact, one can coordinate the lower CBM to bend down toward the global Fermi level after contact in such a way that the Fermi level would be adjacent to the CBM at the interface. In case the Fermi level is increased slightly, it would overcome the CBM at the interface and the electrons would be trapped on the surface forming a 2-dimensional electron gas (2DEG). This surface Tampo et al.\textsuperscript{103} and Tsukazaki et al.\textsuperscript{104} separately reported the construction of ZnO/MgZnO heterostructures with MBE. Tampo et al. achieved heterostructures with room temperature mobility of 250 cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1} and 2750 cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1} at 4K with a sheet electron concentration of 10\textsuperscript{13} cm\textsuperscript{-2}. Tsukazaki et al. accomplished a highly confined 2DEG and measured mobilities as high as 14,000 cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1} at 0.5K. Recently, Falson et al.\textsuperscript{105} used ozone as an assistant in their MBE-grown ZnO/MgZnO heterostructure to reduce the residual impurity contents of the film in order to achieve exceedingly high electron mobilities (as high as 1,200,000 cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1}) at extremely low temperatures (T < 20 mK). Wang et al.\textsuperscript{106} investigated the previous claims via Monte Carlo method and confirmed the values reported by other researchers.

In a single crystal lattice, the crystal indicates a periodic structure. A hypothetical perfect periodicity occurs only in an ideal situation, however, and this periodicity is perturbed by
irregularities due to inevitable thermal excitations. The dimension of these irregularities may differ. Zero dimensional defects or “point defects” are defects which occur in matters of one or a few atoms. If a certain atom is missing from its location inside the lattice, it creates a “vacancy”. If an atom fills the vacancy by migrating to the vacant site, the vacancy simply switches places with the migrating atom. This type of defect is also known as the Schottky defect. In an ideal single crystal, the atoms are located in places which can be reached by lattice point position vectors. If an atom is misplaced in a position which cannot be reached by a position vector (namely, between the lattice points) it is called an “interstitial” atom. A “Frenkel Pair” or a “Frenkel Defect” occurs when an interstitial atom is placed in the neighborhood of its vacancy. In compound crystals where the lattice is composed of two or more atoms, an “antisite” atom is an atom which is mispositioned at another constituent atom’s position (e.g. a carbon atom replacing the silicon atom in a silicon carbide crystal). Whereas the concept of a pure and perfectly periodic crystal is ideal for basic theoretical and computational solid state physics, pure crystal structures are impractical and impurities are type of point defects which may intentionally or unintentionally be introduced into the lattice structure. When impurities are intentionally introduced into a lattice, the process is called “doping”. The “dopant” atom usually replaces a constituent atom and is considered as a “substitutional” defect. If the impurity’s oxidation number matches the oxidation number of the original atom which was expected at that position, the substitution is known as an “isovalent” substitution. On the contrary, if the oxidation number of the original atom differs from the impurity’s oxidation number, an “aliovalent” substitution has occurred. In the latter case, an imbalance may occur and the impurity may be ionized, contributing to the free carrier density of the crystal.
The formation energy of a type of point defect (e.g. a vacancy) may differ from another. This is due to the possible charge of the defect. In ZnO, an oxygen vacancy may be neutral in charge or it might be singly or doubly charged. The Fermi level comes into play when the formation energy of a charged defect as \( q \varepsilon_f \) where \( q \) is the charge of the defect and \( \varepsilon_f \) is the Fermi level. Higher dimensional defects may also occur during crystal growth or by physical impacts. This section focuses on point defects in ZnO and the methods used to identify and characterize these defects. Stoichiometric ZnO should be nonconductive as a pure semiconductor. But due to its overt n-type conductivity, it has been long assumed that ZnO conductivity relies on it being either ordinarily nonstoichiometric or containing unintentional impurities during growth. Oxygen deficiency is always a factor in the formation of ZnO single crystals. Although Zn-rich environments result in a more conductive film, insufficient oxygen during film growth may result in mixed phases of metallic Zn and ZnO. Oxygen paucity may result in Zn interstitials (Zn\(_i\)) as well as oxygen vacancies (V\(_{O}\)). In earlier studies, researchers considered the oxygen vacancies (V\(_{O}\)) as the intrinsic donors whereas some other researchers believed that the formation of zinc interstitials (Zn\(_i\)) and zinc antisites (Zn\(_{O}\)) are the primary sources of the shallow donors in ZnO.

Kobayashi et al. computed the band structure energy levels by using the empirical tight-binding approximation. The approximation considers the four nearest-neighbor atoms to be equivalent, despite the crystal structure not being cubic. Bloch-type orbitals and a 4 x 4 Hamiltonian matrix were constructed, where each element of the matrix was a 4 x 4 matrix and the crystal eigenstates were a linear combination of the Bloch-type basis states. In Bloch’s theorem, the eigenstates for electrons in a lattice can be expanded in terms of Bloch’s waves (a Bloch’s wave is a wave which is constructed by the product of a plane wave \( e^{-i\mathbf{k} \cdot \mathbf{r}} \) and a periodic function \( u(\mathbf{r}) \)). These matrix elements were calculated by fitting the band structure at certain wave
vectors such as the \( \Gamma \) point. Kobayashi et al. stated that the oxygen vacancies as well as zinc antisites may produce shallow donors.

Oba et al. used plane-wave pseudopotential method within the generalized gradient approximation (GGA) to calculate the formation energies of different defect types in two extreme conditions: the oxygen-rich limit and the zinc-rich limit. In general, the concentration of a certain defect \( (C_d) \) is obtained from Boltzmann’s distribution:

\[
C_d = N_d \exp(\frac{-\Delta G_f}{k_B T})
\]

with \( N_d \) being the number density of possible defect sites, \( k_B \) being the Boltzmann constant and \( T \) being the absolute temperature. \( \Delta G_f \) is the Gibbs free energy of formation, defined by:

\[
\Delta G_f = P \Delta V_f - T \Delta S_f + \Delta E_f
\]

where \( \Delta V_f \) is the change in the system volume after the formation of the defect, \( P \) is the absolute pressure and \( \Delta S_f \) is the change in entropy. \( \Delta E_f \) is the change in total energy of the system (e.g. a supercell for theoretical calculations), containing the chemical potential terms. Considering that the change in the total energy \( (\Delta E_f) \) corresponds to the defect formation energy \( (\Delta E_{formation}) \), the formation energy of a defect in a charge state \( q \) may be obtained from:

\[
\Delta E_{formation}(q) = E_{tot}(q) - n_{Zn}\mu_{Zn} - n_{O}\mu_{O} + q\epsilon_f
\]

where \( n_i \) is the number of atom specie \( i \) in the supercell, \( \mu_i \) is the atomic chemical potential, \( \epsilon_f \) is the Fermi level and \( E_{tot} \) is the total energy of the supercell. The variables \( \mu_O \) and \( \mu_{Zn} \) are correlated as:

\[
\mu_O + \mu_{Zn} = \mu_{ZnO(bulk)}
\]
In case of a zinc-rich environment $\mu_{Zn} = \mu_{Zn(bulk)}$ and $\mu_{O} = \mu_{ZnO(bulk)} - \mu_{Zn(bulk)}$; whereas in an oxygen-rich environment $\mu_{Zn} = \mu_{ZnO(bulk)} - \mu_{O(bulk)}$ and $\mu_{O} = \mu_{O(bulk)}$. Oba et al. deduced that zinc antisites and zinc interstitials (tetrahedral site) are the only intrinsic defect types which can explain the n-type conductivity of ZnO, based on the electronic structure, despite the fact that oxygen vacancies, according to their calculations, are the dominant species by having the least formation energy.\textsuperscript{111}

Similar to Oba et al.’s theoretical approach, Kohan et al. applied the plane-wave soft-pseudopotential method and used the density functional theory (DFT) in the local density approximation (LDA) to simplify the many-body electronic system to be able to find the total energies from solving the Schrodinger equation; and concluded that native $V_O$ and $V_{Zn}$ (zinc vacancies) are the dominant crystal defects in a ZnO single crystal in a zinc-rich and an oxygen-rich environment, respectively. Whereas Liu et al.\textsuperscript{112} had considered $Zn_i$ to be responsible for the green luminescence previously, Kohan et al. attributed it to transitions between conduction band minimum (CBM) and the $V_{Zn}$ acceptor levels (2.6 eV) and deducted that the transitions between charged $V_O$ levels may result in visible luminescence as well.\textsuperscript{113} It’s indispensable to note that the above approximations are notorious for underestimating the band gap and making corrections is inevitable.

Contrastively, Lin et al. used full-potential linear muffin-tin approximation to claim the origin of the green luminescence to be from CBM transitions to oxygen antisites ($O_{Zn}$) rather than transitions to $V_{Zn}$ or $V_O$.\textsuperscript{114} Xu et al. suggested transitions from the deep donor complex $V_O-Zn_i$ defects to the valence band maximum (VBM) as a possible candidate.\textsuperscript{115}
Figure 2.5: Native point-defect formation energies as a function of Fermi level position in zinc-rich (left) and oxygen-rich (right) environments. The lowest-energy charge states are represented on the graph. Reprinted figure with permission from Anderson Janotti and Chris Van de Walle, Native point defects in ZnO, Physical Review B, 76 (16), p.165202 (2007). Copyright (2007) by the American Physical Society.

As mentioned before, Van de Walle discussed why native defects cannot primarily contribute to the n-type conductivity and how hydrogen impurities play a significant role as a shallow donor in ZnO, increasing the conductivity in contrast with H\textsubscript{2} passivation of other semiconductors. Hydrogen presence is inevitable in most ZnO growth techniques even in ultra-high vacuum methods. Furthermore, in contrast with claims of Zhang et al.\textsuperscript{116} regarding the low formation enthalpy of Zn\textsubscript{i} in Zn-rich and O-rich conditions and the n-type conductivity of ZnO based on the abundance of Zn\textsubscript{i}, Janotti and Van de Walle\textsuperscript{117} discussed the unlikeliness of the native point defects being the origin of the n-type characteristic of most ZnO crystals by arguing V\textsubscript{O} being a rather deep donor and Zn\textsubscript{i} having a high formation energy. Despite Zn\textsubscript{i} being a shallow donor, according to Janotti and Van de Walle, the formation of Zn\textsubscript{i} is high compared to diffusion migration
barriers as low as 0.57 eV; making Zn$_i$ an unstable defect. They provided the formation energy of the point defects as a function of the Fermi level (Figure 2.5). Look et al. challenged the claim of Zn$_i$ not being a prominent shallow donor contributor (due to its high formation energy) by presenting the possibility of the formation of complex Zn$_i$ defects according to low temperature photoluminescence and Hall-effect measurements of electron irradiated ZnO. Zn$_i$ is mobile and a potential complex partner is required to stabilize the defect. Nitrogen may substitute for oxygen in case of V$_O$ and form a Zn$_i$-NO complex. Look et al. also confirmed traces of Al and Ga impurities, contributing to conductivity as background shallow donors, in all of the ZnO samples grown via seeded chemical vapor transport (SCVT) method by low temperature photoluminescence. Controversially, Selim et al. reported an overall absence of Zn$_i$ in their experiments, even for the Zn-vapor annealed samples, and considered hydrogen atoms situated in oxygen vacancies to be the primary shallow donors. McCluskey and Jokela discussed the possible primary sources of conductivity in an industrially manufactured single crystal ZnO samples by performing secondary ion mass spectrometry (SIMS) and claimed H and group III impurities such as Al, Ga, and B as the primary sources of n-type conductivity in the samples.

Creating p-type ZnO via either introducing impurities or creating point defects such as V$_{Zn}$ or O$_i$ is theoretically possible. But due to the low formation enthalpies of “hole killers” as well as the high formation energy of O$_i$, ZnO cannot become p-type solely depending on native defects (Cross Ref. Zhang). Nitrogen may substitute for oxygen easily in V$_O$ and form a deep acceptor No defect. But even then, the p-type behavior may be easily neutralized by inevitable associate hydrogens. A single-hydrogen- defect and two double-hydrogen-defect lines were detected by vibrational spectroscopy on ZnO samples. The former was associated to either interstitial hydrogen (H$_i$) or H associated with another impurity. The latter were associated with two O-H bonds (one
in parallel with the c-axis and the other one 100° away from the c-axis). The double-hydrogen-defect lines are in theoretical agreement with the hydrogenized zinc vacancy ($V_{ZnH_2}$) energy levels.\textsuperscript{125}

Interstitial defects such as O\textsubscript{i} and Zn\textsubscript{i} can be situated in the tetrahedral sites (tet) or the octahedral sites (oct). Denoting $d_0$ as the Zn-O bond length along the c-axis, a tetrahedral interstitial atom forms bonds with four nearest neighbors (center of a tetrahedron), has a Zn and an O atom as nearest-neighbor with a distance of $\sim 0.833 \ d_0$; whereas an octahedral interstitial atom forms bonds with six equidistant neighbors (three Zn and three O atoms) of length 1.07 $d_0$.

Hydrogen impurities caused by moisture presence is inevitable in ZnO sol gel fabrication processes. It’s crucial to consider the widespread existence of the aforementioned impurities when the characterization of the ZnO layers is concerned. At ambient temperature, water molecules are adsorbed and cannot be fully depleted from ZnO layer surface even with desorption processes. This is due to the positive Gibbs free energy difference of the water molecules adsorbed to the surface.\textsuperscript{126} During the sol gel process, moisture may appear on the substrate as well as the semiconductor/semiconductor interface during deposition. The subthreshold swing (SS) measurements suggest defect level creation inside the band gap as a result of oxygen and moisture adsorption.\textsuperscript{127}

The oxygen (partial) pressure during growth plays a major role in the defect density near the interface. Lower oxygen pressure increases defects such as dislocations and low-angle grain boundaries.\textsuperscript{128} Oxygen vacancy formation is augmented on the surfaces of polar planes (i.e. (0001) and (000\overline{1})) of ZnO.\textsuperscript{129}

Fu \textit{et al.} reported an intensification of the UV photoluminescence (PL) emission of ZnO-SiO\textsubscript{2} nanocomposites grown via sol gel process compared to ZnO. They deduced the formation of
Zn-O-Si bonds at the ZnO-SiO$_2$ interface from the X-ray photoelectron spectroscopy (XPS) and PL spectra and attributed the intensification to both ZnO and ZnO-SiO$_2$.\textsuperscript{130}

In comparison to other WBGS, ZnO growth methods are more assorted. A diversity of methods, such as laser induced deposition\textsuperscript{131}, metalorganic chemical vapor deposition (MOCVD)\textsuperscript{132}, plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD)\textsuperscript{133}, vapor phase epitaxy (VPE)\textsuperscript{134}, atomic layer deposition (ALD)\textsuperscript{135}, plasma-enhanced atomic layer deposition (PEALD)\textsuperscript{136}, have been utilized in order to grow ZnO on various substrates. Whereas relatively large single crystal ZnO substrates are attainable\textsuperscript{137}, polycrystalline and amorphous films and nanostructures are frequent and affordable. The following section aims to provide a brief insight on the synthesis methods of ZnO structures.

Hydrothermal synthesis was one the early methods to be used to grow ZnO crystals. In this method, a supersaturated solution along with its nutrient is placed inside an autoclave, a vessel which can contain high temperature and pressure. By tuning the temperature, crystallization occurs. Laudise et al. achieved single crystal ZnO via hydrothermal growth process.\textsuperscript{138}

Molecular beam epitaxy (MBE) is another growth method for single crystal ZnO. During epitaxial growth, reflected high energy electron diffraction (RHEED) analysis is implemented simultaneously to monitor the growth process. Johnson et al. claimed the fabrication of ZnO heterointerfaces via MBE with an electron mobility of 260 cm$^2$.V$^{-1}$.s$^{-1}$. The ZnO layer indicated an n-type carrier concentration of $9 \times 10^{18}$ cm$^{-3}$, and ohmic behavior was observed across the ZnO/GaN and SiC/ZnO heterointerfaces.\textsuperscript{139} Later, Ogata et al. used metalorganic vapor-phase epitaxy (MOVPE) to deposit high quality ZnO layers on ZnO/Si and ZnO/Sapphire substrates grown by MBE.\textsuperscript{140}
In the spray pyrolysis method, thin films will be formed when a solution is sprayed upon a heated surface. Upon contact, chemical reactions may occur and other constituents may evaporate. Aranovich et al.\textsuperscript{141} investigated the electrical, optical and thermoelectrical properties of ZnO thin films deposited \textit{via} spray pyrolysis. The group used aqueous solutions of zinc dichloride plus hydrogen peroxide and zinc acetate.

Li \textit{et al.}\textsuperscript{142} synthesized ZnO nanowires on copper coated silicon (100) substrate \textit{via} vapor-liquid-solid process. The nanowires were mainly (0002) oriented but a tinge of (1000) orientation was also observed. Matsumoto \textit{et al.}\textsuperscript{143} reported the growth of single crystals of ZnO \textit{via} vapor transport deposition (VTD) when Zn or ZnCl\textsubscript{2} were used as transport agents whereas Huang \textit{et al.}\textsuperscript{144} reported the formation of crystalline nanowires using gold as a catalyst.

Pulsed laser deposition (PLD) was utilized to study the piezoelectric properties of textured ZnO coated nanofibers.\textsuperscript{145} Izaki \textit{et al.} deposited micrometer-thick ZnO films cathodically from aqueous zinc nitrate electrolyte. The electrochemical grown film indicated an optical band gap of 3.3 eV.\textsuperscript{146} Quantum sized ZnO particles were synthesized \textit{via} electrophoretic deposition from colloidal suspension of ZnO. The particles were several nanometers wide in diameter and the particle size could be tuned by the change in aging time or growth temperature. Due to quantum confinement, blue shift was observed in photoluminescence and the shift could be controlled by the particle size.\textsuperscript{147} Milimeter-long nanobelts (nanoribbons) were synthesized \textit{via} thermal evaporation of the metal oxide by Pan \textit{et al.} The nanostructures were single crystalline and the diameter of the belts ranged from 30 to 300nm.\textsuperscript{148}

Chemical vapor deposition (CVD) process and its derivatives, such as MOCVD and PEMOCVD, are often utilized to fabricate ZnO films. Tiku \textit{et al.}\textsuperscript{149} achieved (11\overline{2}0) ZnO films on (01\overline{1}2) sapphire at a substrate temperature of 700C using the reaction of Zn vapor and CO\textsubscript{2} and
later, Minegishi et al.\textsuperscript{150} claimed to have synthesized p-type ZnO for the very first time via CVD. Claims over fabrication of p-type ZnO have been challenged regularly by peer researchers and the issue is still controversial. Kim et al. investigated the trapped oxygen in the grain boundaries of plasma-enhanced chemical vapor deposition (PECVD) grown polycrystalline ZnO. They observed a deviation of stoichiometry of the crystalline thin films, with a higher oxygen quantity.\textsuperscript{151}

Sputtering is a common and straightforward method to deposit films. Direct-current reactive magnetron sputtering (dc-RMS) has been used by various groups, with different Ar:O\textsubscript{2} ratios. Singh et al. observed an increase in the grain size when the oxygen total or partial pressure was increased. The paucity of total oxygen in the lowest overall pressure and the lowest oxygen ratio resulted in a mixed phase of Zn and randomly oriented grains of nanocrystalline (NC) ZnO. Otherwise, single-phase highly c-axis oriented ZnO films were observed.\textsuperscript{152} Kannan et al. used dc-RMS to fabricate stable humidity sensors. The resistivity of the NC-ZnO changed 4 orders of magnitude from 6.3\% to 84\% with change in relative humidity (RH). The grains of NC-ZnO were distorted and randomly oriented.\textsuperscript{153} Suchea et al. used dc-RMS (with Zn target) and dc-MS (with ZnO target) to realize NC-ZnO at room temperature. Decrease of oxygen concentration resulted in a significant compressive stress in the film synthesized using the metallic target.\textsuperscript{154} Fortunato et al. obtained highly stoichiometric, hence resistive ZnO films containing small and dense NC-ZnO with sputtering power density manipulation in radio-frequency magnetron sputtering (rf-MS).\textsuperscript{155} Kumar et al. have observed an increase in crystallinity in c-axis orientation of the film with increasing substrate’s temperature while sputtering.\textsuperscript{156} This is in agreement with Mandal et al.’s work. Both groups have observed a red shift of the band gap of the samples, and the relaxation of the NC-ZnO at higher substrate temperatures.\textsuperscript{157} The dc magnetron sputtering (dc-MS) was used by Fang et al. for the deposition of conductive Al-doped ZnO thin films. Annealing the film in
vacuum resulted in the reduction of oxygen atomic ratio and a higher carrier concentration, whereas re-annealing the sample in an ambient air restored the stoichiometry, equalized the surface and decreased the mean grain size.\textsuperscript{158} Yang \textit{et al.} deposited Al-doped NC-ZnO \textit{via} rf-MS and reported an increase in grain size when the deposition power was raised.\textsuperscript{159} Li \textit{et al.} used dc-RMS (with Zn target) and dc-MS (with ZnO:3wt\%Al\textsubscript{2}O\textsubscript{3} target) to grow ZnO and Al-doped ZnO thin films. No metallic Zn or Al\textsubscript{2}O\textsubscript{3} peaks were observed in XRD patterns while the intensities of the peaks for ZAO were an order of magnitude larger than ZnO peaks. However, the ZAO films indicated more strain and more roughness compared to the ZnO samples. Strain decreased with the substrate temperature being increased during deposition. However, the grain size of NC-ZnO did not change significantly.\textsuperscript{160} Lee \textit{et al.} have made a comprehensive comparative study for deposition of NC-ZnO using dc and rf magnetron sputtering with argon or argon/oxygen mixture. They found that the films deposited by rf magnetron sputtering exhibit lower resistivity than the one by dc magnetron sputtering. It was conjectured that grain boundary scattering is the major mechanism for reducing carrier mobility, thus the electrical conductivity.\textsuperscript{161}

Solution process is a cost effective synthesis method which can be executed in the ambient temperature. Contrary to many methods which require low pressure, solution process can be realized in the atmospheric pressure. Bahnemann \textit{et al.} synthesized colloidal ZnO suspensions in water, acetonitrile and 2-propanol. The ZnO sol contained transparent colloidal spherically – shaped particles with diameters in the range of 50Å. During particle growth, quantum confinement was observed due to the size of the particles being in the Angstrom range. After the final stage, particles contained 2000–3000 ZnO molecules and indicated many photophysical properties of bulk ZnO.\textsuperscript{162}
Delving briefly into the history of semiconductor devices and field effect transistors, Howard\textsuperscript{163} argues that patents of Lilienfeld (1934) and Heil (1935) indicate the first relevant structures of a field effect device, but lack a comprehensive understanding of the key aspects and the operation of semiconductors in these then-advanced devices. Shockley (1939) on the other hand, Howard conveys, discusses the depletion of the metal-semiconductor contact region from charge carriers and presents an appreciation of the switching capability of his structure (representing the first metal-semiconductor field effect transistor or MESFET) and should be considered as the first researcher who has invented the concept of field effect devices. Shockley, Bardeen and Brattain, at Bell Telephone Laboratories, collaborated on invention, enhancement and exploration of the first functioning transistor in early 1946.\textsuperscript{164} Bipolar junction transistors (BJTs) were first developed by Teal \textit{et al.}\textsuperscript{165} in 1951 and were one of the most successful electronic devices in terms of efficiency and fabrication cost for decades to come. Nonetheless, the necessity of size reduction and power consumption in transistors limits the use of BJTs in processing applications and electronic displays. As researchers strived to remain allegiant to Gordon Moore’s prediction of larger integrated circuits being crammed on a chip in years to come (also known as the Moore’s Law)\textsuperscript{166}, the semiconductor-related characteristics such as device size, fabrication expenses, industry revenue, and processing speed remained semi-linear when plotted on a semi-log scale vs. each technology generation (which spans two to three years).\textsuperscript{167,168,169} Field effect transistors (FETs), specially metal-oxide-semiconductor field effect transistors (MOSFETs) alleviated the plight of BJTs’ limitations, \textit{e.g.} their low-power operation restriction was attenuated by introducing insulating dielectrics into the structure. As a result, MOSFETs are widely employed in modern electronics and state-of-the-art devices embody FETs for different applications. Nontoxicity and direct wide band gap of ZnO has further enhanced the use of field effect devices in
broad organic/inorganic applications and contemporary interdisciplinary studies on topics such as nanogenerators\textsuperscript{170}, nanopiezotronics\textsuperscript{171} and nanosized gas-sensors\textsuperscript{172}, bio-sensors\textsuperscript{173} and ion-sensors\textsuperscript{174} indicate the significance of this semiconductor. Thin film transistors (TFTs) are field effect devices which have extensive applications in large area display electronics such as organic light emitting diodes (OLEDs) and liquid crystal displays (LCD), flexible electronics, switching devices, and logic circuits. Worldwide revenue of TFT LCD industry has increased from $1B in 1989 to $110B in 2012.\textsuperscript{175}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/MOSFET_TFT.pdf}
\caption{Cross-section schematics of typical MOSFETs and TFTs.}
\end{figure}

Despite fundamental similarities between TFTs and MOSFETs, such as the number of terminals and modulation of conductivity by gate and body voltage biases, several differences exist. One of the main differences between TFTs and MOSFETs is their device structures (Figure 2.6). In basic MOSFETs, oppositely doped semiconductors are applied in order to fabricate a device with controlled functionality \textit{via} a gate contact voltage bias. Since the semiconductor body is not conductive without a gate bias (normally off), the device is referred to as an enhancement-mode device (non-zero gate bias required for conduction). Whereas the active semiconductor body is doped with either donors (n-type) or acceptors (p-type), source and drain contact regions are heavily doped with opposite type dopants. For an accessible comparison, a MOSFET with p-type semiconductor body and n-type source and drain contacts is considered, namely an n-MOSFET.
The contrast of the carrier types prevents conduction from source to drain (n-type) through the semiconductor body (p-type). When a positive gate-source voltage bias ($V_{GS}$) is applied, the positively charged carriers in the p-type semiconductor body are repelled and a depletion region is formed under the gate oxide of the MOSFET. As $V_{GS}$ increases, the minority charge carriers (negatively charged carriers) are drawn towards the gate. When $V_{GS}$ reaches a certain limit (threshold voltage), a layer filled with minority carriers is formed (inversion layer) under the gate oxide region and source-to-drain conduction is achieved through the inversion layer carriers. As a result, the n-MOSFET can be turned on if $V_{GS}$ higher than the threshold voltage ($V_{TH}$) is applied. In basic TFTs, however, the same semiconductor body with a certain carrier type covers the regions under the source and drain metallic contacts and the gate oxide. In case of a heavily n-type doped TFT, the semiconductor body is conductive when $V_{GS} = 0$ (normally on) and the device it is referred to as a depletion-mode device (non-zero gate bias required for charge carrier depletion). If negative $V_{GS}$ is applied, the carriers are repelled from the gate oxide and with $V_{GS}$ below the $V_{TH}$, they will be depleted from the semiconductor body. Consequently, the TFT will be turned off if a $V_{GS}$ lower than $V_{TH}$ is applied.

The aforementioned basic ideal enhancement-mode n-MOSFET contains three conditions, referred to as accumulation ($V_{GS} < 0$), depletion ($0 < V_{GS} < V_{TH}$) and inversion ($V_{TH} < V_{GS}$) conditions; whereas the basic ideal heavily n-type depletion-mode TFT has two conditions: depletion ($V_{GS} < V_{TH}$) and accumulation ($V_{TH} < V_{GS}$). And since ZnO is intrinsically heavily n-type, ZnO TFTs are mainly of the depletion-mode type transistors.

Another distinction between TFTs and MOSFETs is the crystal size and quality of the semiconductors employed in fabrication processes. Conventionally, MOSFETs contain doped single crystal semiconductors and are fabricated on high quality substrates; TFTs predominantly
embody amorphous or polycrystalline semiconductors and they can be fabricated on various substrates since amorphous or polycrystalline structures are usually substrate-insensitive, causing TFTs perfect for large area electronics. ZnO TFT fabrications have been reported on numerous gate dielectrics substrates such as silicon dioxide (SiO₂), silicon nitride (SiNₓ), hafnium dioxide (HfO₂), hafnium silicon oxide (HfSiOₓ), aluminum oxide (Al₂O₃), Al₂O₃ and TiO₂ superlattice (ATO), some reported achieving transparent devices. This exhibits the exceptional versatility of ZnO in comparison to other competitive direct wide bang gap semiconductors such as GaN and SiC which require fine lattice matching, sometimes via buffer layers, during growth. The downside to ZnO TFTs is the mediocre channel mobility in these devices. Reports indicate the channel mobility dependence on substrate quality and since crystal orientation greatly influences channel mobility, annealing temperature plays a major role in device enhancement.

Table 2.4 lists the characteristics of ZnO TFTs reported by various groups and compares them with the values obtained from the fabricated ZnO TFT in this dissertation, the 8L sample. In the preparation of the 8L sample, the spin-coating process was performed 8 times, resulting in a thin film containing 8 layers of ZnO with total thickness of approximately 190 microns.

Table 2.4 Comparison of ZnO TFT characteristics, deposited via different methods.

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Temperature (°C)</th>
<th>Channel mobility (cm² V⁻¹ s⁻¹)</th>
<th>On/off ratio</th>
<th>V_TH (V)</th>
<th>I Sat (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion beam 185</td>
<td>600–800</td>
<td>0.3–2.5</td>
<td>10⁶</td>
<td>10 to 20</td>
<td>70</td>
</tr>
<tr>
<td>Sol gel 186</td>
<td>700</td>
<td>0.2</td>
<td>10⁷</td>
<td>N/A</td>
<td>14</td>
</tr>
<tr>
<td>Pulsed laser 187</td>
<td>450</td>
<td>0.031–0.97</td>
<td>10⁶</td>
<td>1.0 to 2.5</td>
<td>80</td>
</tr>
<tr>
<td>rf magnetron sputtering 188</td>
<td>room temperature</td>
<td>20–70</td>
<td>5x10⁵</td>
<td>1.8</td>
<td>1000</td>
</tr>
<tr>
<td>This work (8L)</td>
<td>800</td>
<td>0.58</td>
<td>10⁷</td>
<td>-34.5</td>
<td>86</td>
</tr>
</tbody>
</table>
In order to prepare ZnO TFTs, ZnO layers are first deposited via the sol-gel spin-coating method. A precursor is prepared, spin coated on a substrate and spin coated at 3000 rpm for 30 s. Then the substrate is calcined on a hotplate, at approximately 300 °C for 5 minutes, to evaporate the solvents in the precursor. The process is repeated until the desired thickness is achieved. Eventually, the deposited film is annealed in an oven in ambient for an hour, to achieve a nanocrystalline ZnO thin film. Figure 2.7 shows the flow diagram for this process.

![Flow diagram of the sol-gel deposition process](image)

Figure 2.7: Flow diagram of the sol-gel deposition process.

Afterwards, the metallic contact is deposited on the film to form the transistor terminals. To do so, photolithography is realized by spin-coating photoresist on the film, followed by soft baking at 100 °C for 30 seconds. Then, the sample is exposed to the UV light through a mask blocking parts of the UV light. The photoresist exposed to the UV becomes solvable in the developer solution. However, if the inverse of the mask is intended for the pattern, reverse photolithography is achieved by the supplementary steps of baking the substrate again and exposing the whole sample to the UV light (flood UV exposure). The sample is then developed, and the solvable photoresist is removed, leaving the desired pattern. The metallic contacts can then be deposited. In this experiment, metal deposition was realized by a homemade DC magnetron.
sputtering system in which the sample is put inside a closed chamber and the air is pumped out via a high vacuum pump. The chamber is then filled with the noble gas argon. For the sputtering process to occur, the argon atoms are ionized, and voltage bias is applied to the metal “targets” desired to be sputtered on the sample. The argon ions obtain energy by accelerating towards the metallic target. The collision of argon ions with the target causes the atoms to be sputtering off of the target and be deposited on the sample above the target. After metal deposition, the sample is put in acetone for the lift-off process in which the patterned photoresist is solved and etched away from the sample. As a result, the inverse of the photoresist pattern, containing no photoresist, retains the metal due to metal adhesion to substrate’s surface. Figure 2.8 shows the flow diagram for the reverse photolithography process.
Figure 2.8 Flow diagram for the reverse photolithography process.
References


Chapter 3

Growth and Characterization of ZnO Channel Layers

3.1 Sol-gel Spin-Coating Growth Method

This chapter focuses on the growth method applied to deposit and the methods implemented to characterize the ZnO channel layers used to fabricate ZnO TFTs. ZnO was grown using the sol-gel spin-coating method by dropping the solution on the substrate followed by calcining the wafer. In order to prepare the sol-gel precursor, first, monoethanolamine (stabilizer) was diluted by isopropanol (solvent) and zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}]\) was dissolved in the mixture. The molar ratio of Zn ions to monoethanolamine was kept at 1:1 and the Zn concentration was kept at 0.3 mol / L. The solution was stirred (600 rpm) at 80 °C and for 2 h and then aged for 24 h in ambient temperature to yield a clear, homogenous and stable precursor. As the conductive substrate, two heavily-boron-doped silicon wafers (0.01 – 0.02 ohm.cm) were cleaned by acetone, methanol and deionized (DI) water, followed by hydrofluoric (HF) acid to remove possible redundant surface oxide. The wafers were then dry oxidized in order to achieve the bottom gate oxide layers. The precursor was then dropped on the oxidized wafers and rotated at 3000 rpm for 30 s. The coated wafers were then calcined at 285 °C for 5 minutes in order to remove the organic residuals through evaporation. In order to study films with different thicknesses, as well as the effect of number of layers on film characteristics, the spin-coating and
calcination processes were repeated several times to achieve desired thicknesses. 5 sample wafers were prepared with different number of layers: 1 layer (1L), 2 layers (2L), 3 layers (3L), 4 layers (4L), 8 layers (8L). The wafers were diced into 4 quadrants to be annealed in 4 different temperatures: 600 °C, 700 °C, 800 °C and 900 °C. The wafers were annealed in ambient air for 1 h to accommodate the formation of ZnO nanocrystallines through coalescence. The film thicknesses were measured with a profiler. Table 3.1 lists the range of the films’ thicknesses. 1 cm by 1 cm pieces from each quadrant, close to the center of the original wafer, were chosen for Raman spectroscopy and photoluminescence measurements.

Table 3.1 Thickness range for ZnO samples with different number of layers annealed at different temperatures.

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>1L</th>
<th>2L</th>
<th>3L</th>
<th>4L</th>
<th>8L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anneal. Temper.</td>
<td>33~40</td>
<td>60~65</td>
<td>76~79</td>
<td>105~115</td>
<td>180~185</td>
</tr>
<tr>
<td>600 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700 °C</td>
<td>25~30</td>
<td>50~55</td>
<td>75~79</td>
<td>90~115</td>
<td>155~175</td>
</tr>
<tr>
<td>800 °C</td>
<td>30~50</td>
<td>50~63</td>
<td>75~85</td>
<td>90~105</td>
<td>183~196</td>
</tr>
<tr>
<td>900 °C</td>
<td>40~49</td>
<td>60~70</td>
<td>75~85</td>
<td>100~115</td>
<td>200~225</td>
</tr>
</tbody>
</table>

Raman spectroscopy and photoluminescence were conducted by a homemade system with a blue laser (442 nm) for Raman scattering and a UV laser (325 nm) as an excitation source. A thermoelectrically cooled charge-coupled device (CCD) was used to collect the outgoing signals.
3.2 Raman Spectroscopy

Raman spectroscopy is a characterization method used to identify the crystal vibrational modes in a material. In this method, a monochromatic light source is used to excite a molecule from a vibrational state into a virtual excited state located between electronic states. The molecule then de-excites to a different vibrational state close to the initial state by emitting a photon, containing the energy difference between the initial and final vibrational states. Since these vibrational modes in the crystal structure interact with particles and quasiparticles, and can be created or annihilated, it’s plausible to view these modes as quasiparticles. Photons of a specific wavelength interact with these quasiparticles, named as phonons, and are scattered either elastically or inelastically. In case of an elastic scattering in this photon-phonon interaction, namely Rayleigh scattering (named after Lord Rayleigh), the wavelength of the outgoing photon will be unaltered. In case of an inelastic scattering, namely Raman scattering (named after the discoverer of the phenomenon, Chandrasekhara Venkata Raman), the energy of the outgoing photon may be larger or smaller than the energy of the incoming photon. If the incoming photon interacts inelastically with a phonon at the ground state (near the Γ point in the Brillouin zone with the wave vector $\mathbf{k} = 0$), the collision will definitely result in a reduction in the outgoing photon’s energy (Stokes scattering) resulting in the outgoing phonon jumping to an excited state. The inelastic collision of a photon with a phonon in an excited state however, may result in an energy loss of the photon similar to the previous case, or an energy loss of the excited phonon, lowering the state of the outgoing phonon and increasing the energy of the outgoing photon (anti-Stokes scattering). In the low temperature range, the probability of the incoming photon interacting with an excited phonon is several orders of magnitude smaller than the probability of its interaction with a ground state phonon. At relatively high temperatures, the population of thermodynamically excited states
is higher compared to the population of the same states at a lower temperature due to Maxwell-Boltzmann’s distribution law

\[
\frac{N_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}.
\]

\(N_i\) is the number of the phonons in state \(i\), \(\beta\) is defined as \(\beta \equiv (k_B T)^{-1}\) where \(k_B\) is Boltzmann’s constant and \(T\) is the absolute temperature and \(N\) is the total number of phonons. The sum in the denominator is over all vibrational mode energies. The population of the first excited state phonons \((N_1)\) to the population of the ground state phonons \((N_0)\) can be derived by

\[
\frac{N_1}{N_0} = \frac{e^{-\beta E_1}}{e^{-\beta E_0}} = e^{-\beta \Delta E}
\]

where \(\Delta E = E_1 - E_0 > 0\). The energy difference (Raman shift) of the incoming and outgoing photons may be contributed to the creation or annihilation of phonons. As the temperature increases, \(\beta\) decreases, the population ratio gets closer to unity and therefore, an amplification is observed in anti-Stokes scattering. Since the energy differences between the vibrational modes of a material are unique, they may be considered as the fingerprints of that substance. The characterized material can be in gas, liquid or solid phases. In solid phases of the matter, the appearance of different modes may depend on the polarization of the incoming light and the orientation of the crystal structure.

In contrast with Raman scattering, in infra-red spectroscopy (IR), incident photons with frequencies equal to vibrational frequencies of different modes are absorbed. Whereas in Raman spectroscopy Raman shifts are analyzed, in IR spectroscopy the vibrational energies are directly obtained via absorption/transmittance (Figure 3.1).
Figure 3.1: Infra-red transition (a), Rayleigh scattering (b), Stokes (c) and anti-Stokes (d) Raman scattering, and fluorescence (e) among electronic and vibrational energy levels.

The propagation direction of a plain electromagnetic wave is obtained by the direction of the Poynting vector $\hat{S}$ from $\hat{S} = \frac{1}{\mu_0} \overrightarrow{E} \times \overrightarrow{B}$ where $\mu_0$ is the permeability of vacuum. The direction of importance, however, is the direction of the electric field $\overrightarrow{E}$. In Raman spectroscopy, in order to be consistent in calculating the energy shifts (vibrational mode transitions), a single wavelength is utilized for the incoming wave. To achieve this, monochromatic lasers are used as the incoming light source where the laser goes through a filter. The filter blocks unwanted wavelengths, as well as linearly polarizing the electric field in a certain direction. The dependence of the magnitude of the electric field as a function of time can be considered as a simple harmonic oscillator (SHO) and expressed as $E = E_0 \cos 2\pi ft$. 
To achieve a basic understanding of Raman and Rayleigh scattering, the photon-phonon interaction and vibrational excitation can be approached with a combination of classical and quantum mechanical perspective.

In a classical approach, let us consider a diatomic molecule where the atoms can be considered as point masses (nucleus radii of the atoms become negligible compared to the molecule diameter) with a dipole moment $P$. The dipole moment is a function of the instantaneous interacting photons’ electric field and the polarizability of the molecule ($\alpha$). In general, polarizability is an intrinsic property of the material. Considering the oscillations of the magnitude of the electric field of the incoming wave, the dipole moment of the molecule can be written as

$$P = \alpha E = \alpha E_0 \cos 2\pi ft.$$ 

If the molecule has an initial vibrational frequency $f_m$ the “small” nuclear displacement can be expressed as $x = x_0 \cos 2\pi f_m t$ with $x_0$ being the amplitude of this displacement. The condition for the existence of Raman scattering is whether the polarizability of the molecule alters with displacement. If the dependence is non-zero, polarizability can be approximated by Taylor expansion

$$\alpha = \alpha_0 + x \left( \frac{\partial \alpha}{\partial x} \right)_0 + \frac{1}{2} x^2 \left( \frac{\partial^2 \alpha}{\partial x^2} \right)_0 + \cdots$$

where $\alpha_0$ is the initial polarizability of the molecule in the absence of an interaction (and hence, the equilibrium position $x_0$), and $\left( \frac{\partial \alpha}{\partial x} \right)_0$ is the change of the polarizability with respect to displacement at $x_0$. The dipole moment can then be rewritten as

$$P = \alpha \left( E_0 \cos 2\pi ft \right) = \left( E_0 \cos 2\pi ft \right) \left( \alpha_0 + x \left( \frac{\partial \alpha}{\partial x} \right)_0 + \frac{1}{2} x^2 \left( \frac{\partial^2 \alpha}{\partial x^2} \right)_0 + \cdots \right).$$

By replacing displacement $x$ with its oscillatory form and only keeping the first order correction term, the dipole moment can be written as
\[ P = \alpha_0 \left( E_0 \cos 2\pi ft \right) + \left( \frac{\partial \alpha}{\partial x} \right)_0 \left( x_0 \cos 2\pi ft \right) \left( E_0 \cos 2\pi ft \right) + \cdots \]

Evidently, the “correction terms” to the initial value do not exist if the polarizability of the material stays unaltered with nucleus displacements, i.e. \( \left( \frac{\partial \alpha}{\partial x} \right)_0 = 0 \). In other words, in case of a zero change in polarizability with small displacements, the material is Raman- inactive. Using the trigonometric identities, in the second term, the multiplication of the two oscillatory functions can be expressed as two separate single oscillatory functions with distinct frequencies

\[ \cos 2\pi f_m t \cos 2\pi f t \cos 2\pi \theta \cos 2\pi \phi \cos 2\pi s \cos 2\pi t = \frac{1}{2} [\cos 2\pi t (f + f_m) + \cos 2\pi t (f - f_m)] \]

and hence,

\[ P = E_0 \alpha_0 \cos 2\pi ft + \frac{1}{2} E_0 x_0 \left( \frac{\partial \alpha}{\partial x} \right)_0 [\cos 2\pi t (f + f_m) + \cos 2\pi t (f - f_m)] . \]

Therefore, we can consider the first term to be the inelastic interaction representing the Rayleigh scattering where the outgoing photon frequency is unaltered. The second term contains two oscillatory functions, representing two waves, one with higher frequency and one with lower frequency compared to the initial value. The higher frequency represents higher energy of the outgoing wave (noting that a photon’s energy is linearly dependent on its frequency \( E = hf \) where \( h \) is the Planck’s constant) and was referred to as the anti-Stokes mode. The second oscillatory function with lower frequency represents the Stokes Raman scattering. The signal for Stokes Raman scattering is more intense compared to the anti-Stokes Raman scattering and easier to observe. In fact, Chandrasekhar Raman was able to observe the Stokes mode with his eyes by using the sun as his light source, a telescope as the collecting lens.\(^1\) Thereby, Stokes mode is commonly used among researchers for Raman spectroscopy.

The quantum mechanical aspect of the Raman scattering comes into play when vibrational mode transitions are deliberated. The vibration frequencies of a certain material are unique because
quantum mechanics (QM) dictates certain frequencies to be allowed due to the quantization of the vibrational energies of the material. In diatomic molecule previously mentioned, for instance, if the masses are $m_1$ and $m_2$ for each atom, and the distances of the nuclei from the center of mass (CM) are $r_1$ and $r_2$ respectively, in order to simulate the molecular vibrations into a simple physical problem, we can consider the chemical bond to be analogous to a spring with a constant $K$. If we consider the classical approach, the classical Lagrangian $L = T - V$ for the system ($T$ representing the kinetic energy and $V$ representing the potential energy) can then be derived and it can be observed that there are no limitations on the vibrational frequencies. In one-dimensional diatomic molecule Lagrangian, one can turn the two-body problem into a single body with a “reduced mass” defined as $\mu \equiv \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^{-1}$ with displacement $X$ from the CM and obtain

$$L = \frac{\mu \dot{X}^2}{2} - \frac{KX^2}{2}$$

where $\dot{X}$ is defined as the time derivative of the displacement. By inserting the Lagrangian into the Euler-Lagrange equation

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{X}} - \frac{\partial L}{\partial X} = 0$$

the simple harmonic oscillator (SHO) equation can be obtained

$$\mu \ddot{X} + KX = 0.$$  

The solutions for this differential equation are a sum of imaginary exponential functions of time. The solution for displacement $X(t)$ can be expressed as a sum of real oscillatory functions. Eventually, we can express $X(t)$ as a single oscillatory function $X(t) = X_0 \cos(2\pi ft + \theta_0)$ where $\theta_0$ and $X_0$ are the phase constant and the oscillation amplitude, respectively, defined by the initial
boundary conditions; and $f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ is the oscillation frequency. No limitations were forced in this derivation. Namely, the vibrational frequencies can be continuous.

If we consider the QM approach, however, the Hamiltonian of the system (the Schrödinger equation), which should be considered for a two-body wave-particle system, can be rewritten into a single wave-function since the wave-particles overlap each other and can be treated as a single wave-function $\psi$. The Hamiltonian operator for a single wave-particle with a reduced mass $\mu$ and total momentum $P$ oscillating with angular frequency $\omega$, which resembles the simple quantum harmonic oscillator (QHO) system, can then be expressed as

$$\hat{H} = \left( \frac{\hat{P}^2}{2\mu} + \frac{\mu \omega^2 \hat{R}^2}{2} \right).$$

By expressing all the operators in position-space, i.e. $\hat{P} \equiv -i\hbar \frac{\partial}{\partial x}$ and $\hat{R} \equiv x$, and considering the isolated oscillator as a closed system, i.e. $\psi(\vec{r}, t) \equiv e^{-\frac{iEt}{\hbar}} \psi(\vec{r})$, the Hamiltonian ($\hat{H} \equiv i\hbar \frac{\partial}{\partial t}$) can be expressed as

$$\hat{H} |\psi> = \left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{\mu \omega^2 x^2}{2} \right) |\psi> = E |\psi>.$$

Note the dissimilarity between the above equation (the general differential equation governing the one-dimensional QHO) and the general differential equation governing the SHO in one dimension

$$\left( \frac{d^2}{dt^2} + \omega^2 \right) x = 0$$

(where the angular frequency $\omega$ is a real number).

For a simpler representation, by defining the dimensionless variables $y \equiv x \sqrt{\frac{\mu \omega}{\hbar}}$ and $\epsilon \equiv \frac{E}{\hbar \omega}$, the Schrödinger equation becomes

$$\left( \frac{\partial^2}{\partial y^2} - y^2 + 2\epsilon \right) \psi = 0.$$ This QHO Schrödinger equation can be solved by spectral method (considering the solution as a sum of basis functions in series form). The solution for a bound eigenstate $\psi$ in position-space is a product of a compressed...
exponential decay function \( e^{-\frac{ax^2}{2}} \) where \( \alpha \equiv \frac{\mu \omega}{\hbar} \), discrete normalization coefficients \((\alpha/\pi)^{1/4} (2^n n!)^{-1/2}\) and a discrete set of polynomials called Hermite polynomials which the \( n^{th} \) order can be derived from \( H_n(y) = (-1)^n e^{y^2} \frac{\partial^n}{\partial y^n} (e^{-y^2}) \) where \( y \equiv x\sqrt{\alpha} \). Therefore, the “eigenstate” wave-function for the \( n^{th} \) order QHO is

\[
\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} (2^n n!)^{-1/2} e^{-\frac{ax^2}{2}} \cdot H_n(x\sqrt{\alpha}).
\]

By setting \( n = 0 \) and \( H_0(y) = 1 \), we can obtain the ground state as \( \psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{ax^2}{2}} \)
and its corresponding energy as \( E_0 = \frac{1}{2} \hbar \omega \), since \( \epsilon = \frac{1}{2} \).

Several differences are discernible between the classical method and the quantum mechanical approach. The ground state \( \psi_0(x) \) is simply a Gaussian distribution and unlike the classical approach, the position probability density \( |\psi_0(x)|^2 \) does not cease to exist beyond the oscillation amplitude or any finite point in position space. This implies that a negative kinetic energy in QHO is not inconceivable. The nodes in the standing waves of SHO are the nodes of the oscillatory functions and the oscillator’s position is terminated at the boundaries, whereas the origin of the nodes for the stationary states of QHO, is the roots of the Hermite polynomials \( H_n(y) \).

Outside the classical boundary (mandated by the total energy of the oscillator), \( e^{-\frac{ax^2}{2}} H_n(y) \) is only terminated at infinity and therefore, the quantum oscillator has a non-zero probability of being outside the classical boundary. The ground state energy \( E_0 \) is in disagreement with the classical approach as well, in the sense that the minimum energy is non-zero and a minimum value is enforced. But the main difference, which is of concern when considering a Raman shift, is the discreteness of the energy states in QHO which originates from the form of the differential equation. Along solving the differential equations, the solutions for the SHO are continuous.
exponential (however imaginary) functions, whereas the solution for the QHO is in series form (dictating discreteness). Accordingly, the energy states can be denoted as $E_n = \left(n + \frac{1}{2}\right) \hbar \omega$, representing $n$ as the order of oscillation and the minimum energy interval $\Delta E = \hbar \omega$ between energy states. The former equation is obtained during solving the QHO Schrödinger equation via the spectral method, by setting the recursive coefficients to zero after $n$ terms (in order to avert the divergence catastrophe) and combining the results of the even and odd parities of possible bound eigenstates. Hence, a requirement for legitimate transitions from first state $\nu'$ to the final state $\nu''$ is the transition energy difference of an integer factor $N$ of $\hbar \omega$ (i.e. $\Delta E / \hbar \omega = \Delta \nu = \pm N$). In QM, another requirement for a possible transition in general, is that the value of the transition moment integral

$$\overline{M}_{\nu',\nu''} \equiv \int_{-\infty}^{+\infty} \psi^\ast \mu \psi'' dV,$$

must be non-zero; where $\psi'$ and $\psi''$ are the initial and final transition states, $\mu$ is the transition moment operator and $\overline{M}_{\nu',\nu''}$ is the transition dipole moment. For instance, in infra-red (IR) spectroscopy, $\mu$ translates to the electric dipole moment of the molecule $\mu = \sum_n q_n \vec{x}_n$ (with point charge $q_m$ being at position vector $\vec{x}_m$) and in Raman spectroscopy, it translates to the polarizability tensor $\alpha_{\nu',\nu''}$. The symmetry of the integrand changes with the symmetry of $\mu$; and since $\psi'$ and $\psi''$ are orthonormal eigenstates, the symmetry of the integrand defines whether the value of the transition dipole moments is non-zero. The polarizability tensor $\alpha_{\nu',\nu''} = \alpha_{\nu',\nu''} - i\alpha'_{\nu',\nu''}$ is comprised of a symmetric component $\alpha$ and an antisymmetric component $\alpha'$. In case of complex wavefunctions and systems which are not symmetric under time reversal, such as magnetic phenomena, there will be non-zero antisymmetric components in the polarizability tensor. In normal Raman scattering, however, the polarizability tensor is symmetric.
\[
\left[ \alpha_{x_i x_j} \right]_{\nu', \nu''} = \left[ \alpha_{x_j x_i} \right]_{\nu', \nu''}
\]. Therefore, if one of the six transition moment integrals is non-zero, namely

\[
[\alpha_{xx}]_{\nu', \nu''} = \int_{-\infty}^{\infty} \psi'_* \alpha_{xx} \psi'' dV \neq 0
\]

\[
[\alpha_{xy}]_{\nu', \nu''} = \int_{-\infty}^{\infty} \psi'_* \alpha_{xy} \psi'' dV \neq 0
\]

\[
\vdots
\]

the vibration transition is Raman-active. In the aforementioned integrals (Raman spectrum selection rules), the integrand’s symmetry is dependent on the symmetry of the product of electric dipole moments \( \mu_{x_i} \) where \( x_i \) represents space coordinates \( x, y \) and \( z \). For example, the symmetry of \( \alpha_{xy} \) is related to the symmetry of \( \mu_x \mu_y \). The symmetric and antisymmetric terms can be obtained from

\[
\alpha_{x_i x_j} = \frac{2}{\hbar} \sum_{i \neq j} \frac{\omega_{ji}}{\omega_{ji}^2 - \omega^2} \Re \left( \langle i | \mu_{x_i} | j \rangle \langle j | \mu_{x_j} | i \rangle \right) = \alpha_{x_j x_i}
\]

\[
\alpha'_{x_i x_j} = -\frac{2}{\hbar} \sum_{i \neq j} \frac{\omega}{\omega_{ji}^2 - \omega^2} \Im \left( \langle i | \mu_{x_i} | j \rangle \langle j | \mu_{x_j} | i \rangle \right) = -\alpha'_{x_j x_i}
\]

where \( x_i \) and \( x_j \) are permutations of space coordinates \( x, y \) and \( z \); \( |i\rangle \) and \( |i\rangle \) represent the ground and \( j^{th} \) excited state of the molecule; \( \omega \) is the angular frequency of the incident plane wave and the angular frequency shift is \( \omega_{ji} = \omega_j - \omega_i \). If the polarizability ellipsoid (a surface obtained from plotting \( \frac{1}{\sqrt{\alpha_{x_i x_j}}} \) in three dimensions) is visualized, the Raman-active vibrational modes are the ones in which at least one of the ellipsoid properties (orientation, shape or size) of changes from one extreme displacement to the other. Figure 3.2 indicates how the polarizability ellipsoid evolves as the atoms are displaced in different vibrational modes of a linear (CO\(_2\)) and a non-linear
(H₂O) triatomic molecule. For a CO₂ molecule, the second and third modes’ ellipsoids (ν₂ and ν₃) have the same variations at the extremums (+δx and −δx), resulting in these modes to be Raman-inactive; whereas in an H₂O molecule at least one ellipsoid property at +δx contrasts with the one at−δx, resulting in all modes to be Raman-active in H₂O.

Since most of the population of phonons reside in the ground state (n = 0) and the next most populous state is the first excited state (n = 1), the probability of transitions occurring between these two states, and consequently the signal intensity of this shift, is notably higher than transitions between other states.

Since the wurtzite ZnO crystal has a unit cell with N = 4 atoms, the 3N = 12 vibrational modes are divided into 3 acoustic modes (1 longitudinal and 2 transverse) and 3N − 3 = 9 optical modes (3 longitudinal and 6 transverse). These modes may be written as the irreducible normal modes Γ_{opt} = A₁ + 2B₁ + E₁ + 2E₂ for the wurtzite structure (C₆ᵥ symmetry). B₁ modes are both Raman and IR inactive (silent modes). A₁ and E₁ modes are polar and are both Raman and IR active, splitting into transverse optical (TO) and longitudinal optical (LO) modes; e.g. A₁ (TO), A₁ (LO), E₁ (TO) and E₁ (LO) modes. E₂ modes are non-polar, with a high (E₂^H) and a low (E₂^L) frequency; also referred to as E₂(high) and E₂(low). The E₂^L (E₂^H) mode has been attributed to the vibration of the zinc (oxygen) sublattice.⁴
Figure 3.2: Polarizability ellipsoids’ evolutions during displacements in different vibrational modes $\nu_1$, $\nu_2$ and $\nu_3$ in (a) CO$_2$ and (b) H$_2$O molecules.
The propagation/polarization orientations of the incident/scattered rays in Raman scattering are of great importance. In Porto’s notation \( A(B, C)D \) indicates the propagation orientation of the incident ray to be A, the propagation orientation of the scattered ray to be D, the polarization orientation of the incident ray to be B, and the polarization orientation of the scattered ray to be C.

Damen et al. studied the vibrational modes of wurtzite ZnO. Table 3.2 presents the experimental Raman shifts, and the required configurations to observe the vibrational modes, obtained by Damen et al. The Raman shift obtained from bulk single crystal ZnO sample, purchased from Eagle-Picher Technologies LLC, are in agreement with the presented values (Figure 3.3). Despite the fact that \( E_1(\text{TO}) \) is forbidden in the \( \overline{Z}(\overline{-, -}) \overline{Z} \) configuration, the presence of this mode is probably due to the breakdown of the selection rule. Damen et al. attributed the peaks around the 204, 330 and 538 cm\(^{-1}\) to multi-phonon processes.

Table 3.2 Experimental Raman shifts and configurations required to observe the phonon modes in bulk single-crystal wurtzite ZnO. The bar over a direction (e.g. \( \overline{X} \)) represents the opposite of that direction (e.g. \( X \)).

<table>
<thead>
<tr>
<th>Mode (Symmetry)</th>
<th>Raman shift (cm(^{-1}))</th>
<th>Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_2^I )</td>
<td>101</td>
<td>( X(Y,Y)\overline{X} ); ( X(Y,Y)Z ); ( Z(Y,Y)\overline{Z} ); ( Z(Y,X)\overline{Z} )</td>
</tr>
<tr>
<td>( E_2^{II} )</td>
<td>437</td>
<td>( X(Y,Y)\overline{X} ); ( X(Y,Y)Z ); ( Z(Y,Y)\overline{Z} ); ( Z(Y,X)\overline{Z} )</td>
</tr>
<tr>
<td>( E_1(\text{TO}) )</td>
<td>407</td>
<td>( X(Z,Y)\overline{X} ); ( X(Y,Z)Y )</td>
</tr>
<tr>
<td>( E_1(\text{LO}) )</td>
<td>583</td>
<td>( X(Y,Z)Y )</td>
</tr>
<tr>
<td>( A_1(\text{TO}) )</td>
<td>380</td>
<td>( X(Y,Y)\overline{X} ); ( X(Z,Z)\overline{X} )</td>
</tr>
<tr>
<td>( A_1(\text{LO}) )</td>
<td>574</td>
<td>( Z(Y,X)\overline{Z} )</td>
</tr>
</tbody>
</table>
Whereas the first order Raman scattering (one phonon process) deals with phonons near the $\Gamma$ point (where the wave vector $\vec{k} = 0$), the second (or higher) order Raman scattering (multi-phonon processes) can occur for phonons throughout the entire Brillouin zone.\textsuperscript{7}

Table 3.3 summarizes the values reported by various experimental groups, along with the $E_2^H$ mode Raman shift obtained from the sol-gel derived ZnO film fabricated in this work. The table contains the six optical normal modes of ZnO, as well as the commonly observed peaks, believed to be related to multi-phonon processes (higher order vibrational modes).

Calzolari and Nardelli\textsuperscript{8} used the Perdew-Burke- Ernzerhof\textsuperscript{9} (PBE) method with Hubbard-like corrections (PBE+U) to calculate the Raman shifts, where $U$ is a parameter describing the on-
site Coulomb interactions. Their calculated results for $E_2^L$, $A_1$(TO), $E_1$(TO) and $E_2^H$ modes (106, 384, 408 and 436 cm$^{-1}$, respectively) were in agreement with other reported experimental values.

The $E_2$ mode frequencies (101 and 437 cm$^{-1}$) are reported for a stress-free wurtzite ZnO lattice. These values will have a shift if the lattice is under stress. In case of a compressive stress, the $E_2$ frequencies will increase whereas under a tensile stress, a decrease in the $E_2$ frequencies will be observed. Stress may arise from the lattice mismatch and distortion, or the mismatch of thermal expansion coefficients of the substrate and the deposited film.

Raman spectroscopy was performed in order to investigate the dependence of the crystal quality of the ZnO films, grown by the sol-gel spin coating method, on the annealing temperature. $E_2^H$ peak was observed in all samples. Figure 3.4 depicts the dependence of the $E_2^H$ peak on the annealing temperature. For the sample with higher number of deposited layers (Figure 3.4(e)), the difference is more apparent with the magnitude of the peak becoming larger as the annealing temperature increases. For this set of data collection, the following settings were used: 2400 gratings per mm and 5000 ms exposure time.

The magnitude enhancement of the $E_2^H$ peak of the 8-layer sample, compared to other samples, can be attributed to the higher thickness of the film whereas in thinner samples, the background signal is comparable to the signal from $E_2^H$ mode. As the annealing temperature increases, the grain size becomes larger and the number of received signals from vibrational modes (i.e. oxygen sublattice vibration) rises. Due to the non-linearity across the charge-coupled device (CCD), the $E_2^H$ values were corrected.
Table 3.3 Raman shift values reported by experimental groups.

<table>
<thead>
<tr>
<th>Sample Dim. [Ref.]</th>
<th>E₂¹</th>
<th>A₁(TO)</th>
<th>E₁(TO)</th>
<th>E₂²¹</th>
<th>A₁(LO)</th>
<th>E₁(LO)</th>
<th>E₂²¹ – E₂¹</th>
<th>2×E₂¹</th>
<th>Misc. Multi-Phonon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder[14]</td>
<td>–</td>
<td>383</td>
<td>410</td>
<td>438</td>
<td>540</td>
<td>584</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bulk[16]</td>
<td>98</td>
<td>378</td>
<td>409.5</td>
<td>437.5</td>
<td>576</td>
<td>588</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>–</td>
<td>383</td>
<td>423</td>
<td>437</td>
<td>–</td>
<td>578</td>
<td>331</td>
<td>–</td>
<td>316, 534, 505, 549</td>
</tr>
<tr>
<td>Conventional sol-gel film (300nm)[24]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>437</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>This work</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>436.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 3.4: The dependence of Raman spectra of ZnO layers deposited via sol-gel spin-coating method on the annealing temperature for (a) 1 layer, (b) 2 layers, (c) 3 layer, (d) 4 layers and (e) 8 layers.
Figure 3.5 compares the position and the full width at half maximum (FWHM) of the $E_2^H$ peak of the 8-layer samples annealed at different temperatures. Although the positions and the FWHM of the peaks seem to differ, the range of the difference is within the experimental error limit. Therefore, although the increase of the magnitude of the $E_2^H$ peak is sometimes attributed to the enhancement of crystal quality, a strong conclusion about crystal quality difference between the samples cannot be stated solely based on this data set.

### 3.3 Photoluminescence

 Whereas Raman spectroscopy is used to identify chemical bonds through vibrational modes of a material, photoluminescence spectroscopy is a crude characterization method to outline its electronic structure properties. Photoluminescence is a type of luminescence generated by photo-excitation. The incident photons from a light source may alter the electronic state of a
molecule which then relaxes to a final state via one or several relaxation mechanisms. De-excitation of the molecule may occur via emitting phonons or photons, corresponding to vibrational or electronic de-excitations, respectively. In photoluminescence spectroscopy (referred to as PL hereafter), a material is exposed to a monochromatic light and the re-emitted photons with different wavelengths are collected by a spectrometer. In WBGSs, the incident wavelength is in the UV range to overcome the band gap and the re-emitted photons contain information about the formation of different donor-acceptor pairs (DAP) or the existence of electronic states inside the band gap due to crystal defects such as dopants, vacancies or interstitial atoms. Photoluminescence spectroscopy usually spans the wavelengths (or their corresponding energies) in the UV, visible and IR range. PL is a viable characterization method for direct band gap semiconductors.

Room temperature PL on ZnO exhibits a narrow UV luminescence which is dedicated to ZnO near band edge (NBE) excitonic emissions, followed by a presumable visible luminescence. Narrower and more intense excitonic emission indicates a higher crystal quality\(^{26}\) due to less non-radiative recombination and defect transition. Despite the visible luminescence from defects being undesirable in many applications, engineering these defects or associating ZnO luminescence with other materials may bring about visual applications and display devices.\(^{27}\)

Low temperature (~4K) PL from ZnO samples indicate UV emission spikes caused by recombination of DAP and their longitudinal optical phonon replicas.\(^{28}\) Room temperature PL, however, is not able to resolve the DAP related spikes. Investigation of the visible luminescence in ZnO is accompanied by the comparison of point defect energy levels in the gap. Various point defects exist in wurtzite ZnO structures, such as charged vacancies and interstitials, which contribute to the luminescence of ZnO from the violate to the IR spectral range. The visible luminescence of ZnO has been rather complicated and controversial. Red luminescence has been
attributed to positively charged oxygen vacancy \((V_{O^+})\), negatively charged oxygen interstitial \((O^-)\), zinc interstitial \((Zn_i)\), zinc vacancy \((V_{Zn})\) and lattice disorders along the c-axis \(^{29,30,31}\) whereas orange luminescence has been attributed to transitions from the conduction band minimum (CBM) to \(O_i\) or from \(Zn_i\) to \(O_i\). \(^{32}\) The yellow luminescence has been ascribed to related transitions from the C.B. to either native \((O_i)\) \(^{33,34}\) or extrinsic (lithium impurities) \(^{35,36}\) defects. The origin of the green luminescence has been the most controversial, complicated and discussed topic among researchers. Vanheusden \textit{et al.} \(^{37}\) attributed the green emission to transitions from the conduction band to \(V_{O^+}\). The green luminescence has been attributed to several other recombination mechanisms such as hydrogen outdiffusion in thin ZnO films \(^{38}\), deep \(V_{O}\) donor level transitions to the valence band \(^{39}\), \(V_{Zn}\) on non-polar nanostructure surfaces \(^{40}\), and transitions from \(V_{Zn} + V_{O}\) divacancies \((V_{ZnO})\) \(^{41}\) and \(V_{Zn}\) complexes. \(^{42}\) The green luminescence has also been ascribed to unintentional copper \((Cu)\) contamination in samples. \(^{43,44,45}\) Blue and violet luminescence may correspond to electron transitions from CBM to \(V_{Zn^-}\) \(^{46}\), \(Zn_i\) to the maximum of the valence band maximum (VBM) \(^{47}\), \(Zn_i\) to \(V_{Zn}\) \(^{48}\) and extended \(Zn_i\) to VBM. \(^{49}\) Fu \textit{et al.} \(^{50}\) observed the intensity of UV luminescence increase in ZnO-SiO\(_2\) nanocomposites. They ascribed the luminescence to the creation of levels due to the formation of Zn–O–Si bonds at the ZnO/SiO\(_2\) interfaces. Figure 3.6 illustrates \(^{51}\) some of the defect energy states in the band gap reported by different groups. The figure includes impurities such as lithium \((Li)\) and hydrogen interstitials \((H_i)\) as well as native defects such as oxygen antisites \((O_{Zn})\).

Figure 3.7 shows the photoluminescence (PL) of the bulk single crystal ZnO sample (refer to Figure 3.3 for Raman). The spectrum can be divided into the UV PL and the visible PL. The visible PL indicates a broad green luminescence centered at 510nm in addition to a blue
luminescence centered at 470 nm. In addition to the peak centered at 377 nm, the UV PL seems to contain another peak centered at 390 nm. Both peaks will be discussed shortly.

Figure 3.6: Energy states created by native point defects as reported by (a) Djurišić et al.\textsuperscript{52}, (b) Lima et al.\textsuperscript{53}, (c) Lin et al.\textsuperscript{54}, (d) Nikitenko et al.\textsuperscript{55}, (e) Van de Walle\textsuperscript{56}, (f) Janotti and Van de Walle\textsuperscript{57}, and (g) Zwingel.\textsuperscript{58} Reprinted figure under MDPI’s Open Access Policy. Figure by Magnus Willander, Omer Nur, Jamil Rana Sadaf, Muhammad Israr Qadir, Saima Zaman, Ahmed Zainelabdin, Nargis Bano, and Ijaz Hussain, Luminescence from zinc oxide nanostructures and polymers and their hybrid devices, Materials 3, No. 4, pp. 2643-2667 (2010). Copyright (2010) by the Molecular Diversity Preservation International.

Figure 3.7: PL spectrum of bulk ZnO.
Figure 3.8: PL spectra of ZnO films for different annealing temperatures: (a) 1 layer, (b) 2 layers, (c) 3 layer, (d) 4 layers and (e) 8 layers. The insets depict the visible region.
PL of ZnO channel layers deposited via spin-coating was obtained with the 2400 grating per mm setting. For the exposure time interval, 200 ms was chosen to avoid saturation in the UV region. For a higher data resolution, wavelength step-size was chosen to be 0.2 nm. Figure 3.8 shows the PL spectra in the visible and UV range and the insets represent the magnified visible portion of the films’ PL. The UV PL for the single layer ZnO (Figure 3.8 (a)) depicted 2 distinct peaks. These 2 peaks become less distinct as the number of layers increases. The peak around 380 nm (3.26 eV) is the near band edge (NBE) emission. The peak around 390 nm (3.18 eV) has been attributed to the exciton-exciton “P” emission where a photon, an electron and a hole are produced as the result of an exciton-exciton scattering.\textsuperscript{59,60,61} Figure 3.9 shows the peak position for the NBE emission (Xc1) and the exciton-exciton “P” emission (Xc2) as a function of annealing temperature and Figure 3.10 shows the peak positions as a function of the number of layers. The UV luminescence exhibits an increase in magnitude as the number of layers increases. Since the penetration depth of UV laser with a 325 nm wavelength is in the range of 40 nm\textsuperscript{62} to 60 nm\textsuperscript{63}, the magnitude of the UV emission of the 4-layer sample compares to the UV emission of the 8-layer sample.

![Figure 3.9](image-url)

Figure 3.9: Peak position center, Xc, for (a) the NBE emission, Xc1, and (b) the exciton-exciton “P” emission, Xc2, as a function of annealing temperature.
Figure 3.10: Peak position center, Xc, for (a) the NBE emission, Xc1, and (b) the exciton-exciton “P” emission, Xc2, as a function of the number of layers.

To further analyze the PL spectra, the ratio of the area under the curve for the UV emission over the visible emission (A(UV)/A(Vis)) was calculated to obtain a qualitative perspective over the crystal quality of the samples. Lower A(UV)/A(Vis) is assumed to be an indication of higher number of defects due to the visible emission of midgap states originating from point defects formerly discussed. Figure 3.10 shows A(UV)/A(Vis) evolution as a function of the annealing temperature and the number of ZnO layers.

Figure 3.11: Ratio of the integrated area under the UV PL over the visible PL as a function of (a) annealing temperature and (b) number of layers.
3.4 Scanning Electron Microscopy

To fabricate thin film transistors (TFTs), the annealing temperature of 800 °C was chosen based on the fact that for the higher annealing temperature (*i.e.* 900 °C), the increase in the grain size results in the formation of gaps between the grains according to Scanning Electron Microscopy (SEM) images. The ZnO film becomes non-continuous and hence, the reduction of carrier mobility. Figure 3.12 shows the SEM images (SEM, JSM-7000F, JEOL, JAPAN) from the samples with different annealing temperatures. As the annealing temperature increases, the grain size becomes larger and the grain boundaries become less significant. However, for the sample with 900 °C annealing temperature, the films continuity is drastically affected.

![Figure 3.12: SEM images of the 2-layer ZnO film annealed at 600 °C (top left), 700 °C (top right), 800 °C (bottom left), and 900 °C (bottom right).](image-url)
References


10 Available online: https://wiki.fysik.dtu.dk/gpaw/tutorials/hubbardu/hubbardu.html, April 2018.


Chapter 4

Formation of Depletion Layers at ZnO-ZnO Interlayer-Interfaces

4.1 Introduction

Multiple peaks were observed in transconductance of zinc oxide (ZnO) thin film transistors (TFTs), fabricated via sol-gel spin-coating technique, consisting multiple layers due to the deposition growth method. Sol-gel spin-coating growth method contains reiterations in the ambient. ZnO surfaces in contact with the ambient, which later evolve into ZnO-ZnO interfaces during the growth process, are discussed and depletion layers created by possible surface adsorption of ambient impurities (such as O₂) caused by surface defects are rationalized. Depletion layers may exist in other n-type metal-oxide high native point defect concentration wide band gap semiconductors deposited by sol-gel spin-coating method since the layer deposition is recurred and the chemical activity of the surface defects may cause chemisorption of O₂. The same effect may occur in other metal oxide wide band gap semiconductors fabricated via the same growth method.

After several decades of study, zinc oxide remains a prominent transparent wide band gap semiconductor (WBGS) for its robust structure as well as economic aspects of fabrication methods
compared to other WGBSs due to its substrate-agnostic behavior.\textsuperscript{1,2,3} The direct gap of ZnO, combined with its high excitonic binding recombination energy\textsuperscript{4}, keeps ZnO desirable for optoelectronic applications in the blue and UV spectral region. The increase in the transparent display revenue in the forthcoming decades\textsuperscript{5} emboldens the significance of defect and trap analysis of ZnO (and ZnO derivative) channel layers. Among the various defect types in ZnO, the omnipresence of oxygen vacancies (\textit{V}_O) has been noted the earliest, considered as a color center (\textit{F} center), and the origin of the yellow color of ZnO.\textsuperscript{6,7,8} The negative formation energy as well as high stability, makes oxygen vacancies (\textit{V}_O) the most frequent native defect type in ZnO.\textsuperscript{9} Solution-process derived zinc oxide (ZnO) thin film transistors (TFT) have been widely studied due to the cost-effectiveness, simplicity and agility of the related growth methods. Device characteristics are sometimes simply reported without deep analysis. Furuta \textit{et al.}\textsuperscript{10} deposited ZnO \textit{via} rf magnetron sputtering from a ZnO target at different O2 partial pressures. It was reported that in an oxygen-deficient growth-environment, a hump was observed, and the ON voltage was shifted to the left as a result of donor-like traps, at the vicinity of the conduction band, being ionized and contributing to free carriers. The hump-effect seem to be absent in ZnO and ZnO-derivative TFT reports with a single spin-coating process.\textsuperscript{11,12,13,14} The anomalies in the mobility and transfer characteristics of ZnO TFTs involving the spin-coating process repetition, however, have either been observed in some reports but scarcely discussed\textsuperscript{15,16}, or might have been overshadowed by high OFF drain current ($I_{D,OFF}$).\textsuperscript{17,18} In this study, the kink-effect present in the transconductance and the mobility of ZnO TFTs studied previously\textsuperscript{19}, fabricated \textit{via} sol gel spin-coating technique, has been scrutinized and the rationale behind the creation of ZnO-ZnO interlayer-interface depletion layers has been justified.
4.2 Experimental

Three samples (1L, 4L and 8L) with different number of layers (1, 4 and 8 layers, respectively) of ZnO were fabricated via the spin-coating technique, with final mean thicknesses of 30 nm, 100 nm and 190 nm, respectively, measured with a profilometer. The precursor was prepared by dissolving zinc acetate dehydrate in monoethanolamine (MEA) as stabilizer, diluted with isopropanol. The weight ratio of 1:1 (zinc to MEA) was attained and the precursor was stirred at 80 °C for 2 hours at 600 rpm. The precursor aged in ambient pressure and temperature in a container for 2 days. For part of the experiment, however, to achieve a functional 1-layer TFT, multiple precursors with different aging-times were tried; and for the 1 layer ZnO sample, specifically, the precursor which had aged for 9 days was used for spin-coating. All the precursors were stable, transparent and homogenous at the time of deposition. Highly conductive boron-doped silicon wafers (0.001~0.005 Ω.m) were oxidized, cleaned and used as substrates. The precursors were dropped on the substrates and spin-coated at 3000 rpm for 30 s. To evaporate the solvents, the wafers were calcined at 300 °C for 5 minutes. Precursor dropping, spin-coating and calcination processes were repeated 3 and 7 times for the 4L and 8L, respectively. The samples were then annealed at 800 °C for 1 hour to form uniform nanocrystalline ZnO thin films. To fabricate the bottom-gate TFTs, the wafers were cut into 1 cm² pieces and cleaned via acetone, methanol and deionized water (5 min each) in ultrasonic bath. Photolithography was then performed to achieve Corbino geometry (Figure 4.1 (left)). The outer ring \( R_2 = 200 \mu m \) was used as the source and the inner circle \( R_1 = 120 \mu m \) was used as the drain. Due to the Corbino geometry of the devices, the channel width-to-length ratio was defined through \( W/L \equiv 2\pi/\ln(R_2/R_1) \).\(^\text{20}\) The ZnO layers may contain 1 or multiple ZnO-ZnO interlayer-interfaces (Figure 4.1 (right)). In order to reach the highly-conductive boron-doped silicon body, acting as
the back gate, the bottom SiO$_2$ layer was scratched with a diamond pen and the silicon body was attached to a conductive supporting plate with silver paint.

![Figure 4.1: Left: Optical image of bottom-gate ZnO TFT with 4 channel layers (4L) with a mean film thickness of 100 nm on a 247 nm dry oxidized SiO$_2$. Right: The cross-section schematics of the Corbino bottom-gate ZnO TFTs.]

The source and drain contacts were deposited via magnetron DC sputtering. Titanium was used for the ohmic contact and was passivated by palladium. Mesa structure was formed by photolithography and wet chemical etching, using diluted hydrochloric acid. The ZnO layers were characterized by X-ray diffraction (XRD) with a Bruker D2 Phaser X-ray diffractometer and Raman spectroscopy with the 442 nm line of a He: Cd laser, using a Jobin Yvon spectrometer. Device current-voltage (I-V) and capacitance-voltage (C-V) measurements were performed with Keithly 2400 SourceMeter, and Keithly 590CV analyzer, respectively. For each sample, the data for a representative device is provided.

### 4.3 Results and Discussion

The ZnO thin films were grown on silicon dioxide and were analyzed with X-ray diffraction (XRD) and Raman spectroscopy. The XRD peak at 34.5 degrees exhibited the c-axis
(0002) orientation of the nanocrystalline thin films (Figure 4.2 (left)). The Raman shift (436.8 cm$^{-1}$) indicated a strong E$_2^{\text{High}}$ peak (Figure 4.2 (right)), corresponding to the oxygen vibration in the wurtzite structure.$^{21}$

Figure 4.2: Left: X-ray Diffraction pattern obtained from the 4L ZnO sample. The smaller peak at 33 degrees represents the silicon wafer. The inset shows the 34.5 degrees peak at a higher magnification. Right: Raman shift of the 8L sample. The 436.8 cm$^{-1}$ and 520 cm$^{-1}$ correspond to the ZnO E$_2^{\text{High}}$ (oxygen vibration) and the single crystal silicon wafer under the transparent silicon dioxide substrate, respectively.

Figure 4.3 presents the transistor output characteristics ($I_D$-$V_{DS}$) of the devices and Figure 4.4 shows the drain current ($I_D$) in a logarithmic scale and the transconductance $g_m \equiv \partial I_D / \partial V_{GS}$, in the linear region as a function of gate-source voltage bias ($V_{GS}$) for the three samples (1L, 4L and 8L). The devices are normally ON due to large background electron concentration. It is conjectured that the back channel starts to form just underneath the ZnO/ambient interface on top of the device as $V_{GS}$ surpasses the ON voltage ($V_{ON}$). The transconductance ($g_m$) for all of the devices increases with an increase in $V_{GS}$, which is believed to be attributed to the decrease of effective grain boundary potential barrier height$^{22}$, as well as the channel charge centroid receding from the ZnO/ambient interface and hence, reduction of surface roughness scattering.$^{23}$
4.4(a) shows $g_m$ of the single layer ZnO sample (1L), where $g_m$ reaches a maximum. As $V_{GS}$ increases, the channel charge centroid migrates toward the bottom gate, and due to carrier scattering caused by defects at the ZnO/SiO$_2$ interface, a decline in $g_m$ is observed.$^{22}$

In samples with higher number of layers (Figures 4.4(b) and 4.4(c)), however, a second peak is observed in $g_m$. The kink-effect is even more accentuated in 8L. We attribute the decline of the initial peak at $V_G = -10 \, \text{V}$ to the Coulombic and defect scattering of the carriers at the ZnO-ZnO interlayer-interfaces, due to the formation of depletion regions caused by trapped charges forming a negative space-charge sheet. In general, reactions at the grain boundaries of metal-oxide semiconductors result in the formation of depletion regions on the surface, with increasing its width as the surface area to volume ratio increases.$^{24}$ In a polycrystalline form of ZnO, the interfaces of neighboring ZnO grains form double Schottky barriers at the boundary$^{25}$ where oxygen vacancies are in the diamagnetic double positively charged oxygen vacancy ($V_O^{++}$) states.$^{26}$ Annealing the film results in grain growth and the grain boundary effects become less significant as the number of boundaries along the c-axis decreases.
Figure 4.3: Output characteristics of samples 1L (a), 4L (b), and 8L (c).
Figure 4.4: Drain current (black squares) and transconductance (blue stars) of samples 1L (a), 4L (b) and 8L (c) as a function of gate-source voltage bias. A kink effect can be observed in the transfer characteristics, as well as local maxima in the multiple layer samples.
The rationale behind the formation of the depletion layers (causing a decline in $g_m$ and creating the first peak) comes from the adsorption of molecules from the ambient on the surface, capturing an electron from the ZnO lattice and becoming negatively charged, and creating a charge sheet. Surface defects, such as oxygen vacancies, act as active adsorption sites for ambient gas molecules. Reversible behavior (physisorption) and irreversible behavior (chemisorption) can be observed during the resistance measurement of ZnO films in vacuum/ambient cycles. During the sol-gel spin-coating growth process, calcination may result in a temporary reduction of physisorbed surface trapped molecules. However, physisorption and chemisorption recur before the next spin-coating process, introducing surface states.

Oxygen is one of the significant surface-adsorbed gases from the ambient. Oxygen reacts with neutral ($V_0^-$) and positively charged oxygen vacancies ($V_0^+$) on the surface, capturing a conduction band electron from the ZnO lattice. This creates deep levels in the band gap and forms strongly bonded chemisorbed ions such as $\text{O}^-$, $\text{O}_2^-$ or $\text{O}_2^-$ on the surface. The only stable surface ion below $650 \text{ K}$, however, is $\text{O}_2^-$. An $\text{O}_2^-/\text{O}^-$ system reacting with $V_0^{++}$ and $V_0^+$ ensues upon photoexcitation, based on radiative and nonradiative recombinations.

Besides oxygen, H$_2$O may also be chemisorbed and form $\text{OH}^-$ on the surface while other gases may capture electrons and form negatively charged species on the surface as $aG + xe = A^{x-}$, where $G$ is the gas molecule and $A$ is the adsorbed specie. Moisture is omnipresent in sol-gel processing. At ambient temperature, water molecules are adsorbed and cannot be fully desorbed from ZnO surface. This is due to the positive Gibbs free energy difference of the water molecules adsorbed to the surface. Subthreshold swing (SS) measurements suggest that the defect levels are created inside the band gap as a result of oxygen and moisture adsorption.
All aforementioned species remain on the surface during the subsequent spin-coating process and will form a two-dimensional depletion layer at the ZnO-ZnO interface. Although annealing increases the grain size decreases the grain boundary surface to volume ratio and eliminates a portion of mid-gap states, the chemisorbed oxygens at these boundaries create extra stable deep level trapping centers at the ZnO-ZnO interfaces.\textsuperscript{35} In multiple layered samples, these depletion layers induce Coulomb scattering as the carriers move toward the bottom gate when $V_{GS}$ increases.

When $V_{GS} < V_{ON}$, charge carriers are repelled from the bottom gate into the top metal contacts (source and drain) and ZnO channel layers are fully depleted. When $V_{GS}$ surpasses $V_{ON}$, carriers are injected into the layers from the top. As $V_{GS}$ increases, the channel charge centroid moves away from the ZnO/ambient interface, followed by reduction in carrier scattering. In multiple-layer samples, as the centroid go through the ZnO-ZnO interface, mobility decreases due to Coulomb scattering. This results in a kink in the transfer characteristics and a local maximum in $g_m$ (Figures 4.4(b) and 4.4(c)). As $V_{GS}$ increases further, the depletion region shrinks due to an increase in the donor concentration $N_D$ ($V_o^+ / V_o^+ \rightarrow V_o^\times$).\textsuperscript{36} Moreover, the conduction band minimum (CBM) just below the potential barrier gets closer to the fermi level as a result of the gate-induced depletion region shrinkage. At a certain critical voltage ($V_c$) These two factors facilitate tunneling, the carriers penetrate deeper into the channel layers and $g_m$ increases once more before its decline due to the centroid reaching the ZnO/SiO$_2$ interface. Band bending as a function of $V_{GS}$ at the ZnO/SiO$_2$ interface was approximated in a previous study.\textsuperscript{37} It is believed that the local peak at $V_g = 15 \, V$ in the transconductance for 4L sample may be associated with a depletion layer close to the ZnO/SiO$_2$ interface while a kink observed at $V_g = -15 \, V$ may be related to a depletion layer closer to the upper surface (Figures 4.4(b)). This indicates that the
uniformity and the effective area of the O$_2^-$ surface charge density may differ from a depletion layer to another, depending on the time interval the surface is exposed to the ambient during fabrication. As the number of layers increases, e.g. the 8L, the possibility of the formation of uniform 2D potential barriers is enhanced (Figures 4.4(c)).

Figure 4.5 presents the normalized capacitance-voltage (C-V) measurements of the samples. The gate bias ($V_g$) ranges in the C-V measurements which correspond to $V_{GS}$ in the I-V measurements are all shifted to the left due to electrical gate stressing of the I-V measurements. Figure 4.5 (a) shows C-V for 1L sample. Although a kink-like feature is observed at $V_g = 30$ V, but the data is fairly noisy or possible mobile charges in the insulator or at the ZnO/SiO$_2$ interface. For 4L, a kink can be seen at $V_g = -20$ V (inset of Figure 4.5 (b)), which is believed to be associated with a depletion region in the upper part of the ZnO layer. The location of the kink in C-V can be directly related to that in $g_m$ (Figure 4.4(b)). The corresponding effect of the 2 local peak in $g_m$ of 4L at $V_g = 15$ V was subtle in the C-V characteristics and could not be distinguished. The kink-effect is apparent in 8L (Figure 4.5 (c)), occurring at the same $V_g$ range at which the local maximum transconductance occurs (Figure 4.4(c)). In this negative $V_g$ range, one or several depletion regions hinder the carrier injection toward the oxide interface. With a surge in $V_g$, carriers are able to tunnel through the barriers and accumulate on lower surfaces.
Figure 4.5: Normalized quasi-static capacitance-voltage measurements for samples 1L (a), 4L (b) and 8L (c). The insets exhibit the specific region with a higher magnification to distinguish the kink-effect in 4L (b) from a possible noise in 1L (a).
The carrier concentration \((N_D)\) was calculated to be \(2 \times 10^{18} \text{ cm}^{-3}\) via linear extrapolation of the inverse of capacitance per unit area squared versus gate bias \((V_G)\) plot of the 4L sample based on the following expression;

\[
N_D = -2[q\varepsilon_{ZnO}\varepsilon_0\frac{\partial}{\partial V_G}\frac{1}{C^2}]^{-1}
\]

where \(C\) is capacitance per unit area, \(q\) is the carrier charge, \(\varepsilon_0\) is permittivity of vacuum, and \(\varepsilon_{ZnO}\) is the static dielectric constant of ZnO \((\varepsilon_{ZnO} \approx 8.656)^{39}\). The interlayer-interface built-in potential \((\varphi_{l-i})\) was then calculated to be 0.72 \(\text{V}\) based on the following relation;

\[
\varphi_{l-i} \approx \frac{k_B T}{q} \ln \frac{N_D}{n_i}
\]

where \(n_i\) is the intrinsic carrier concentration \((10^6 \text{ cm}^{-3} \text{ at room temperature})^{27}\), \(k_B\) is Boltzman’s constant, and \(T\) is temperature. Our value for \(\varphi_{l-i}\) obtained in this study is higher than the results reported by Liao et al.\(^{40}\) The width of a single Schottky barrier \((W_D)\) and the screening Debye length \((\lambda_D)\) can be calculated from the following equations;

\[
W_D = (2\varepsilon_{ZnO}\varepsilon_0 \varphi_{l-i}/ q N_D)^{1/2}
\]

\[
\lambda_D = (k_B T \varepsilon_{ZnO}\varepsilon_0 / N_D q^2)^{1/2}
\]

where \(W_D\) and \(\lambda_D\) are 18.5 \(\text{nm}\) and 2.46 \(\text{nm}\), respectively. The obtained value for \(W_D\) explains the normally OFF behavior of the 1L ZnO sample. The ZnO surface of 1L is exposed to the ambient for an extended time (considering the transistor fabrication processes) and more oxygen molecules are chemisorbed at the surface, compared to the ZnO-ZnO interlayer-interfaces of other samples where another layer is deposited on the previous layer in around 5 minutes. Therefore, \(W_D\) becomes larger for 1L and the single layer becomes fully depleted at zero gate bias.
Figures 4.6, 4.7, 4.8 and 4.9 present the potential barriers at the interlayer-interfaces in the energy band diagram, as well as the cross-section schematics of the device at different gate biases.

Depletion layer formation caused by surface oxygen chemisorption has been studied in other metal oxides such as TiO$_2$ and SnO$_2$.\textsuperscript{41,42} Hence, the interlayer-interface barriers observed in this study may exist in the aforementioned WBGS thin films deposited via the sol gel spin coating method as well.\textsuperscript{43,44}

### 4.4 Conclusion

In this experiment, ZnO TFTs with different number of spin-coated channel layers were fabricated. A kink or additional local maxima were observed from the transfer curve and corresponding transconductance of the TFT with multi-layered channel layers, respectively. A model was presented to explain the observed phenomena by considering formation of the depletion layer at the ZnO-ZnO interlayer-interfaces due to the oxygen chemisorption on the surface during the fabrication process. The deep level traps created due to the oxygen chemisorption are not removed by annealing at 800 °C. The effects become more apparent as the number of layers increase. It was hypothesized that transconductance increases as the channel charge centroid moves away from the ZnO/ambient interface toward the bottom gate, followed by the decline in transconductance as the charge centroid go through the ZnO-ZnO interlayer-interface depletion regions due to Coulomb scattering. Subsequently, the transconductance increases once more as the channel charge centroid moves away from the depletion regions and the depletion width becomes smaller, and then decreases as the centroid hits the ZnO/SiO$_2$ interface.
Figure 4.6: Device cross-section schematics of representation the ZnO-ZnO interlayer-interfaces with gate bias at depletion mode (left). The red arrows represent the electric field applied by the bottom gate, fully depleting the active layer (hatched area). Energy band diagram representation of the channel layer with gate bias lower than $V_{ON}$ (right).

Figure 4.7: Device cross-section schematics of representation the ZnO-ZnO interlayer-interfaces with gate bias just above $V_{ON}$ (left). The red arrows represent the electric field applied by the bottom gate, partially depleting the active layer (hatched area). Energy band diagram representation of the channel layer with gate bias just above $V_{ON}$, allowing carriers to form a back channel (right).
Figure 4.8: Device cross-section schematics of representation the ZnO-ZnO interlayer-interfaces (left). The red arrows represent the electric field applied by the bottom gate, depleting (hatched area) parts of the active layer just below the potential barrier at the interface. Energy band diagram representation of the channel layer with gate bias just below the critical voltage ($V_c$) just before the hot carriers can tunnel through the barrier (right).

Figure 4.9: Device cross-section schematics of representation the ZnO-ZnO interlayer-interfaces (left). The red arrows represent the electric field applied by the bottom gate, depleting (hatched area) parts of the active layer well below the potential barrier at the interface. Energy band diagram representation of the channel layer with gate bias just above the critical voltage ($V_c$), allowing the hot carriers to tunnel through the barrier (right).
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Chapter 5

Gamma Irradiation Effects on Sol-Gel Derived

Thin Film Transistors

5.1 Introduction

Solution-based bottom-gate zinc oxide thin film transistors (TFTs) were successfully fabricated, remaining functional and demonstrating stability under extreme gamma irradiation conditions. Zinc oxide was used as the active channel layer and was kept unpassivated. The devices were fabricated on samples with different number of layers grown via sol-gel spin coating technique. The devices were then measured before and after being exposed to 1.2 MGy (120 Mrad (air)) and an additional 1 MGy (total 2.2 MGy) of gamma irradiation on the same devices. Device characteristics were extracted from the current-voltage measurements. The zinc oxide films were characterized by photoluminescence and Atomic Force Microscopy (AFM) before and after irradiation. The degradation/enhancement of device characteristics such as saturation mobility, drain current on/off ratio and threshold voltage shift before and after irradiation is discussed.

Wide band gap semiconductor (WBGS) devices are of great interest in high power electronics due to their high breakdown voltage and efficiency. Due to its high device efficiency at room temperature ($k_B T = 26$ meV) among other direct WBGS exciton binding energies, such as 4H-SiC (20 meV), GaN (25 meV) and ZnSe (22 meV), ZnO is an exemplary candidate for
excitonic emission applications.\textsuperscript{1,2,3} ZnO has been exploited in power electronics\textsuperscript{4}, transparent electronics\textsuperscript{5}, sensing applications\textsuperscript{6,7,8}, UV-visible down-shifting applications\textsuperscript{9}, and nano-sized piezotronics\textsuperscript{10}, generators\textsuperscript{11} and modifiers\textsuperscript{12,13,14}.

Radiation-resistant devices are utilized in various research areas such as space applications and high energy accelerators. Research on structural stability and device characteristics of different semiconductors under gamma irradiation is a growing field, in the search for a radiation-hard substitution for silicon.\textsuperscript{15,16,17,18,19,20} Silicon based devices indicate drastic decline under gamma irradiation (with doses as small as 20 kGy)\textsuperscript{21,22} and therefore, radiation-hard silicon devices have been scrutinized in the past couple of decades.\textsuperscript{23,24,25} Yet, the intrinsic radiation-hardness of ZnO is superior to hardened-silicon or other robust materials such as gallium nitride.\textsuperscript{26} Despite the fact that investigations on structural hardness and stability of ZnO devices against irradiation by energetic particles such as electrons\textsuperscript{27,28,29,30,31}, protons\textsuperscript{32,33}, neutrons\textsuperscript{34,35} and ions\textsuperscript{36,37,38} have been reported, the gamma ray irradiation is far from being mature and further research is required. High energy irradiation introduces point defects, as a consequence of Compton scatterings, if the particle energy surpasses displacement energy of lattice atoms.\textsuperscript{39} Atomic displacement damage for zinc and oxygen (in wurtzite ZnO) has been reported by several groups. Locker and Meese reported the threshold energies of incoming particles to initiate displacement damage for oxygen and zinc atoms, in wurtzite ZnO, to be 310 keV and 900 keV, respectively.\textsuperscript{40} They also claimed the atomic displacement energy (\(E_d\)) of 57 eV for both zinc and oxygen atoms. Lorenz \textit{et al.}\textsuperscript{41} estimated \(E_d\) (Zn)=65 eV and \(E_d\) (O)=50 eV. These values are well above the average atomic displacement energies of other WBGSs such as: \(E_d\) (Si)=12.9 eV, \(E_d\) (Ge)=14.5 eV, \(E_d\) (GaAs)=9.5 eV, \(E_d\) (GaN)=19.5 eV and \(E_d\) (4H-SiC)=21.3 eV.\textsuperscript{42}
The energies of the gamma rays from $^{60}\text{Co}$ decay, 1.17 and 1.33 MeV, surpass the displacement threshold energy required for both atoms and therefore, introduction of vacancies and interstitial point defects is expected. Jackson et al.\textsuperscript{43} reported several successful gamma ray irradiation experiments on bottom-gate ZnO TFTs fabricated via pulsed laser deposition (PLD) and plasma-enhanced atomic layer deposition (PEALD). The group reported functional transistors with a slight negative threshold voltage shift after being irradiated by 1 MGy gamma irradiation without being electrically biased during irradiation. An improvement was observed after annealing at 200\(^\circ\)C for 1 minute, removing the radiation induced voltage shifts.\textsuperscript{44} The experiment was repeated under electrical bias during irradiation, confirming the radiation resistance of ZnO TFTs.\textsuperscript{45,46} This experiment further investigates the radiation-hardness of ZnO thin films and ZnO-based TFTs under gamma irradiation. Atomic force microscopy (AFM) and photoluminescence (PL) were conducted on the films and current-voltage (I-V) measurements of the TFTs were employed. The ZnO TFTs were fabricated via sol-gel spin coating technique. Despite the disadvantages of the sol-gel derived devices such as high operating voltages\textsuperscript{47}, the growth process is an attractive deposition method among researchers due to its simplicity and cost-effectiveness. Unlike growth processes which require ultra-high vacuum and/or high deposition temperature, sol-gel spin-coating technique can be utilized in the ambient. Sol-gel spin coating technique was utilized by Nishio et al.\textsuperscript{48} to deposit transparent conductive Al-doped ZnO thin films, and by Natsume et al.\textsuperscript{49} to grow undoped ZnO films, for the first time. Norris et al.\textsuperscript{50} reported the fabrication of fully transparent thin film transistors (TTFTs) on a glass substrate by spin coating zinc nitrate solution, using indium tin oxide as the transparent bottom-gate contact and a superlattice of Al$_2$O$_3$ and TiO$_2$ (ATO) deposited via Atomic Layer Deposition (ALD) as the gate insulator. In this project, to best of our knowledge, the gamma-ray irradiation of sol-gel derived
bottom-gate ZnO TFTs was performed for the first time. Fabricated TFTs were characterized before irradiation, were then radiated via $^{60}$Co radiation source (rate of $388.3$ mGy/s) with a total dose of $1.2$ MGy, and were characterized again. After characterization, the devices were radiated by an additional $1$ MGy (total $2.2$ MGy) radiation dose, surpassing the highest doses previously reported for irradiation of ZnO TFTs fabricated via other growth methods. The devices were characterized once more to evaluate the ionization and displacement damage effects on the TFTs induced by irradiation.

5.2 Experimental

The semiconductor was grown using the sol-gel spin-coating method by dropping the solution on the substrate followed by calcining the wafer. The precursor was prepared as mentioned in Chapter 3, to yield a clear, homogenous and stable solution. As the conductive substrate, two heavily-boron-doped silicon wafers ($0.01 – 0.02$ ohm.cm) were cleaned by acetone, methanol and deionized (DI) water, followed by hydrofluoric (HF) acid to remove possible redundant surface oxide. The wafers were then dry oxidized in order to achieve the bottom gate oxide layers ($170$ nm silicon dioxide). The precursor was then dropped on the oxidized wafers and rotated at $3000$ rpm for $30$ s. The coated wafers were then calcined at $285$ ºC for $5$ minutes to remove the organic residuals through evaporation. The dropping process was repeated $3$ times on one wafer (resulting in a 4-layer ZnO film) and $7$ times on the other wafer (resulting in an 8-layer ZnO film). The wafers were then annealed at $800$ ºC in ambient air for $1$ hour to accommodate the formation of ZnO nanocrystallines through coalescence. The film thicknesses were measured to be ranging from $90$ nm to $105$ nm by profilometry for the 4-layer wafer (4L), and from $183$ nm to $196$ nm for the 8 layer wafer (8L). A single $1$ cm x $1$ cm piece was chosen from the center of each wafer for circular TFT fabrication (central circle for drain and outer ring for source). Circular
source and drain (S/D) patterns were achieved by photolithography on the samples. Titanium, passivated by molybdenum and palladium, was deposited as the ohmic source and drain (S/D) contacts via DC magnetron sputtering. The rationale behind the S/D metallic structure emerged from the deterioration of titanium/aluminum contacts in a previous study. The deterioration may come from the lower atomic displacement threshold energy for aluminum (~16 eV) compared to palladium (~34 eV). The devices on each sample where then isolated via wet-etching by using hydrochloric acid (HCl), forming a mesa structure, in order to minimize the gate oxide leakage current. To reach the conductive silicon bottom gate contact, the backside of the wafer was simply scratched with a diamond pen and silver paint was applied to attach the bottom gate to a metallic substrate for a convenient measurement. The samples were irradiated by gamma rays through exposure to cylindrical ⁶⁰Co rods to achieve total doses of 1.2 MGy and 2.2 MGy. Device measurements and analysis were conducted before and after irradiation to compare the irradiation effects in the ambient. The ZnO film on each wafer was characterized by room temperature photoluminescence (PL) with a 325 nm laser line (20mW) from a He-Cd laser. Current-voltage (I-V) measurements of the devices were acquired with a Keithley 2400 SourceMeter.

### 5.3 Results and Discussion

Several TFT devices from each sample (one sample from the 4L wafer and another from 8L wafer) were measured before and after irradiation for output and transfer characteristics. Two devices were chosen from each sample to represent the general behavior of the set. Devices from the 4L wafer (4L-1 and 4L-2) were measured before irradiation (referred to as Un-4L-1 and Un-4L-2 hereafter) and measured again after being irradiated by gamma irradiation doses of 1.2 MGy (referred to as 120-Irr-4L-1 and 120-Irr-4L-2 hereafter) and 2.2 MGy (referred to as 220-Irr-4L-1 and 220-Irr-4L-2 hereafter). Similarly, the unirradiated devices measured from the 8L wafer will
be referred to as Un-8L-1 and Un-8L-2. These devices will be referred to as 120-Irr-8L-1 and 120-Irr-8L-2 after 1.2 MGy irradiation, and 220-Irr-8L-1 and 220-Irr-8L-2 after 2.2 MGy irradiation.

Figure 5.1: Characteristics of the devices from 4L wafer before irradiation. Top: Output (right) and saturation transfer (left) curves for Un-4L-1. Bottom: Output (right) and saturation transfer (left) curves for Un-4L-2.

Figure 5.1 presents the output curves (drain current $I_D$ vs. drain-source voltage bias $V_{DS}$) and transfer curves (drain current $I_D$ vs. gate-source voltage bias $V_{GS}$) for Un-4L-1 and Un-4L-2.
After 1.2 MGy irradiation, the characteristic curves for these devices (120-Irr-4L-1 and 120-Irr-4L-2) are represented in Figure 5.2. The output characteristic curves indicate stability of the devices after irradiation in the saturation region.

Figure 5.2: Characteristics of the devices from 4L wafer after 1.2 MGy irradiation. Top: Output (right) and saturation transfer (left) curves for 120-Irr-4L-1. Bottom: Output (right) and saturation transfer (left) curves for 120-Irr-4L-2.

After 1.2 MGy additional irradiation dose (2.2 MGy total), the 4L devices (220-Irr-4L-1 and 220-Irr-4L-2) became dysfunctional, plausibly due to active layer thickness reduction caused by
displacement damage to the surface atoms. After 2.2 MGy irradiation, the remaining thin ZnO film becomes fully depleted due to surface oxygen chemisorption. The device could not be turned ON at low gate biases, and higher biases (~60 V) caused the gate insulator to permanently break down.

A few device characteristics such as threshold voltage ($V_{th}$), drain current ON-OFF ratio ($I_{ON}/I_{OFF}$) and maximum saturation mobility ($\mu_{sat}$) were extracted from the saturation transfer region. Saturation mobility ($\mu_{sat}$) was obtained at $V_{DS} = 45\,V$ from

$$\mu_{sat}(V_{GS}) = \frac{2}{C_{ox}} \times \left(\frac{W}{L}\right)^{-1} \times m_{sat}^2$$

where $C_{ox}$ is the gate oxide capacitance per unit area, $\frac{W}{L}$ is the channel’s width-to-length ratio and $m_{sat} \equiv \partial \sqrt{I_{D,sat}} / \partial V_{GS}$ with $I_{D,sat}$ being the drain current in saturation region. Due to the circular shape of the devices, $\frac{W}{L} \equiv \frac{2\pi}{\ln R_2}$ where $R_1$ is the drain radius (inner circle) and $R_2$ is the inner radius of the source (outer ring). $I_{OFF}$ in this work is defined by the average drain current at voltages below the ON voltage ($V_{ON}$) and $I_{ON}$ is defined by the average saturated current measured in transfer characteristics in saturation region. Despite the ambiguity during the extraction of the threshold voltage ($V_{th}$) for ZnO TFTs, $V_{th}$ was roughly approximated by linear extrapolation from the $\sqrt{I_{D,sat}}$ vs. $V_{GS}$ curve. In the subthreshold region of the unirradiated devices (Figure 5.1), an abnormality was observed. This abnormality is rectified after 1.2 MGy irradiation (Figure 5.2). We relate this phenomenon to the formation of depletion layers at the ZnO-ZnO interlayer-interfaces caused by oxygen chemisorption during fabrication. Oxygen is an avid ambient adsorbent on ZnO surfaces and by forming negative surface ions, the height of Schottky barrier at the ZnO/ambient interface is further increased. The potential barriers
formed at the ZnO-ZnO interlayer-interfaces have been seemingly distorted due to displacement
damage occurred in the bulk after irradiation.

Table 5.1 summarizes the data results for devices 4L-1 and 4L-2 for an
unirradiated/irradiated sample comparison. Both devices from the 4L wafer indicated similar
trends. $V_{th}$ in the fabricated TFTs is unstable, seemingly due to shallow trap states at the
insulator/semiconductor interface proximity or the unpassivated semiconductor/ambient interface
which may cause a positive shift (acceptor-like traps)\textsuperscript{60} or a negative shift (depopulation of donor-
like traps).\textsuperscript{61}

Table 5.1: Device characteristics of 4L-1 and 4L-2 before and after irradiation. The arrows
indicate the enhancement/decline of the value compared to the unirradiated sample.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_{sat}$ (cm$^2$/V.s)</th>
<th>$I_{ON}/I_{OFF}$</th>
<th>$V_{th}$ (V)</th>
<th>$I_{ON}$ (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-4L-1</td>
<td>0.173</td>
<td>2.6 $\times$ 10$^7$</td>
<td>$-12.4$</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>120-Irr-4L-1</td>
<td>0.0657 ↓</td>
<td>6.1 $\times$ 10$^5$ ↓</td>
<td>$-23.8$ ↓</td>
<td>$2.2 \times 10^{-5}$ ↓</td>
</tr>
<tr>
<td>220-Irr-4L-1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Un-4L-2</td>
<td>0.164</td>
<td>3.2 $\times$ 10$^7$</td>
<td>$-19.8$</td>
<td>$5.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>120-Irr-4L-2</td>
<td>0.0518 ↓</td>
<td>1.2 $\times$ 10$^6$ ↓</td>
<td>$-22.5$ ↓</td>
<td>$1.9 \times 10^{-5}$ ↓</td>
</tr>
<tr>
<td>220-Irr-4L-2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

After irradiation, $V_{th}$ was shifted toward negative, suggesting the creation of gate-oxide
states by ionization damage, acting as hole traps in the oxide bulk. These states inside oxide bulk
trap holes and create fixed positive charges inside the oxide, shift the Fermi level in the gate metal
contact and cause a band bending at the SiO$_2$/ZnO interface. These fixed charges can only be
detraped \textit{via} thermal annealing. Whereas these trap states may have been originated by the
creation of point defects, the radiation damage was not sufficient to affect $I_G$ after 1.2 MGy
irradiation dose, even through high $V_{GS}$ biases. The average $I_{OFF}$ remained unchanged, implying
the stability of the source-drain and gate-channel leakage currents.\textsuperscript{62} A decrease in $I_{ON}$ in all 4-
layer devices was observed, resulting in an overall exacerbation in $I_{ON}/I_{OFF}$. Displacement damage dealt by gamma rays towards the surface layer reduces the thickness of the film as well as increasing the surface roughness and the surface area by gradually deforming or even removing the surface atoms from the structure.\textsuperscript{63,64,65} Surface defects in ZnO, specifically oxygen vacancies, act as active adsorption sites for ambient gas molecules.\textsuperscript{66} Consequently, in addition to the thinning of the channel, the total depletion region below the exposed surface area increases due to additional chemisorption of oxygen ions and the channel resistance becomes higher due to electron concentration reduction.\textsuperscript{67} Noting the formation of the back-channel at the ZnO/ambient interface in the subthreshold region, the surface roughness and Coulomb scattering (by the depletion region formed at the ZnO/ambient interface) are the primary causes of carrier scattering and hence, the decline in saturation mobility ($\mu_{sat}$). These issues prevail in 4-layer devices, due to the lower thickness of the channel layer, but are overshadowed by aspects in the 8-layer devices, after 1.2 MGy. After an additional 1 MGy (2.2 MGy), the 8-layer devices experience the mechanisms in the 4-layer devices, due to the active layer etching.

Figure 5.3, Figure 5.4 and Figure 5.5 represent the output and transfer curves for the devices from the 8-layer wafer before irradiation (Un-8L-1 and Un-8L-2), and after 1.2 MGy irradiation (120-Irr-8L-1 and 120-Irr-8L-2), and after 2.2 MGy irradiation (220-Irr-8L-1) respectively. Device properties of the 8-layer devices (8L-1 and 8L-2) are summarized in Table 5.2 for an overall comparison between device performances before and after irradiation. After 2.2 MGy irradiation, the second 8L sample (220-Irr-8L-2) became dysfunctional after the insulator breakdown at a gate bias of -60 eV.
Figure 5.3: Characteristics of the devices from 8L wafer before irradiation. Top: Output (right) and saturation transfer (left) curves for Un-8L-1. Bottom: Output (right) and saturation transfer (left) curves for Un-8L-2.
Figure 5.4: Characteristics of the devices from 8L wafer after 1.2 MGy irradiation. Top: Output (right) and saturation transfer (left) curves for 120-Irr-8L-1. Bottom: Output (right) and saturation transfer (left) curves for 120-Irr-8L-2.
Figure 5.5: Characteristics of the devices from 8L wafer after 2.2 MGy irradiation. Top: Output (right) and saturation transfer (left) curves for 220-Irr-8L-1. The gate insulator of the other device, 220-Irr-8L-2, experienced a permanent break down due to the high gate voltage bias.

Although less apparent in the 8-layer devices, the aforementioned abnormality in the subthreshold region in the unirradiated samples can be noticed (Figure 5.3). After irradiation, interlayer-interface effects become less significant and the abnormality can hardly be recognized (Figure 5.4 and Figure 5.5).

After 1.2 MGy gamma irradiation, similar to the 4-layer devices, $V_{th}$ is shifted for all 8-layer devices confirming the formation of radiation-induced oxide interface hole trap states, created by point defects. A boost in $I_{ON}$ is present in all 8-layer devices, increasing $I_{ON}/I_{OFF}$ in all devices. The creation of new point defects such as zinc interstitials (Zn$_i$) and neutral oxygen vacancies (V$_O$), caused by displacement damage, could contribute to shallow donor concentration and therefore be a conceivable reason for the enhancement of $I_{ON}$. Effects such as electron-hole pair generation caused by high energy radiation can also enhance conductivity. The origin behind intrinsic n-type conductivity of ZnO has been controversial and has been attributed to shallow donors such as oxygen vacancies (V$_O$), zinc-interstitial nitrogen-antisite (Zn$_i$-No) complexes.
hydrogen impurities in interstitial sites\textsuperscript{71} and in oxygen vacancy sites\textsuperscript{72}, and also to other possible impurities.\textsuperscript{73}

Furthermore, in all 8-layer sample devices, mobility has increased after irradiation. This signifies induced effects in the bulk, which are dominated by surface effects in the thinner film (4-layer) sample. The carriers are significantly depopulated in the 4-layer sample, imposed by the depletion region under the surface. A strongly viable candidate for the mobility enhancement is the distortion of the potential barriers at ZnO-ZnO interlayer-interfaces. These barriers hinder the carriers and cause Coulomb scattering, reducing the carrier mean-free-path.

After the additional 1 MGy radiation (2.2 MGy total dose), the trend observed in the 4-layer sample devices after 1.2 MGy radiation can be observed in the 8-layer sample (220-Irr-8L-1): a decline in \( \frac{I_{ON}}{I_{OFF}} \) and \( \mu_{sat} \). This is expected since the thickness of the channel layer has been reduced is such a way that surface effects now dominate the bulk effects. Also, \( V_{th} \) experienced a positive shift, suggesting creation of more ZnO/SiO\(_2\) interface states acting as acceptor-like traps. When filled, acceptor-like states become negatively charged. The electric field of filled acceptor-like traps compensates the electric field caused by positive charges in the gate insulator induced by gamma-rays’ ionization damage.

Table 5.2: Device characteristics of 8L-1 and 8L-2 before and after irradiation. The arrows indicate the enhancement/decline of the value compared to the unirradiated sample.

<table>
<thead>
<tr>
<th></th>
<th>( \mu_{sat} ) (cm(^2)/V.s)</th>
<th>( \frac{I_{ON}}{I_{OFF}} )</th>
<th>( V_{th} ) (V)</th>
<th>( I_{ON} ) (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-8L-1</td>
<td>0.576</td>
<td>1.1 \times 10^7</td>
<td>-34.5</td>
<td>8.6 \times 10^{-5}</td>
</tr>
<tr>
<td>120-Irr-8L-1</td>
<td>1.789 ↑</td>
<td>2.7 \times 10^7 ↑</td>
<td>-50.5 ↓</td>
<td>4.4 \times 10^{-4} ↑</td>
</tr>
<tr>
<td>220-Irr-8L-1</td>
<td>0.007 ↓</td>
<td>1.7 \times 10^4 ↓</td>
<td>-40.0 ↑</td>
<td>3.41 \times 10^{-6} ↓</td>
</tr>
<tr>
<td>Un-8L-2</td>
<td>0.338</td>
<td>1.6 \times 10^7</td>
<td>-41.5</td>
<td>9.1 \times 10^{-5}</td>
</tr>
<tr>
<td>120-Irr-8L-2</td>
<td>2.194 ↑</td>
<td>2.9 \times 10^7 ↑</td>
<td>-55.0 ↓</td>
<td>7.0 \times 10^{-4} ↑</td>
</tr>
<tr>
<td>220-Irr-8L-2</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Figure 5.6 depicts the morphology of the devices after being irradiated (compare with the unirradiated sample in Figure 4.1 (left) in Chapter 4), taken by a KEYENCE High Resolution Digital Optical Microscope. The ZnO/SiO₂ step is more distinguished in the 8L sample due to its larger thickness. In addition to the etching mechanism described shortly, the deterioration of the films can be linked to two major factors: (i) the films are not passivated and (ii) the crystalline size is small as an outcome of the deposition method; whereas unexposed films\textsuperscript{74} and single crystals\textsuperscript{75} are expected to be more radiation-resistant.

Crude profilometry measurements suggested an increase in the overall surface roughness after irradiation. Therefore, Atomic Force Microscopy (AFM) was conducted on samples, acquiring a fine texture. Figure 5.7 exhibits the surface topology of the sample from the 4L wafer before irradiation, as well as the ZnO/SiO₂ step.

Figure 5.6: Optical microscope top view of irradiated circular TFTs from the samples: 4L sample after 1.2 MGy (Top Left), 4L sample after 2.2 MGy (Top Right), 8L sample after 1.2 MGy (Bottom Left), 8L sample after 2.2 MGy (Bottom Right).
Figure 5.7: AFM of the ZnO/SiO$_2$ edge (left) and ZnO film surface topography (right) of pristine sample from 4L wafer.

Figure 5.8: AFM of the 4L sample after 1.2 MGy gamma irradiation. The ZnO/SiO$_2$ edge (left) and the ZnO film surface topography (right).
Figure 5.9: AFM of the 4L sample ZnO/SiO$_2$ edge after 2.2 MGy gamma irradiation from 2 different regions (left and right). The faint tilted-vertical border line at the center of the image (left) is the ZnO/SiO$_2$ edge.

Figure 5.10: AFM images of the sample from the 8L wafer after 1.2 MGy gamma irradiation dose: the ZnO/SiO$_2$ edge (left) and the surface topography (right).
Figure 5.8 shows the 4L sample after 1.2 MGy gamma irradiation. The ZnO/SiO₂ edge deterioration and the roughening of ZnO film surface suggest the removal of surface atoms. In the AFM images of the 4L sample after the additional irradiation and total dose of 2.2 MGy gamma irradiation (Figure 5.9), the ZnO/SiO₂ edge becomes hard to identify in some regions (Figure 5.9 (left)), confirming the reduction of film thickness.

Figure 5.10 presents the topography of the 8L sample and the ZnO/SiO₂ step after 1.2 MGy irradiation. Considering the similarity of the pristine 8L surface topography to the pristine 4L sample, the deformation and the increase in surface roughness is noticeable after 1.2 MGy gamma irradiation. The ZnO/SiO₂ step is more distinguishable due to the higher thickness of the film. Gamma irradiation effects on layer and device characteristics depend on the total dose, as well as the crystal quality. For low gamma ray irradiation doses (< 30 kGy), in addition to an increase in surface roughness, mobility enhancement has been observed in indium zinc oxide (IZO) polycrystalline films.⁷⁶,⁷⁷,⁷⁸

Here, an etching mechanism is proposed as one of the consequences of displacement damage. When high energy photons (gamma rays) with energies as high as 1.17 and 1.33 MeV penetrate the ZnO film, the photon “collide” with an electron through Compton scattering. If the photon is scattered at an angle $\theta$ from its initial path, the outgoing photon’s energy ($E_{\text{out}}$) can be obtained from the scattering angle $\theta$ and the incoming photon’s energy ($E_{\text{in}}$) via

$$E_{\text{out}} = \frac{E_{\text{in}}}{1 + \varepsilon(1 - \cos \theta)}$$

where $\varepsilon$ is a constant, defined by

$$\varepsilon \equiv \frac{E_{\text{in}}}{m_e c^2} \approx \frac{E_{\text{in}}}{511 \, \text{eV}}$$
where $m_e$ is the stationary mass of an electron, and $c$ is the universal constant for speed of light in vacuum. The scattered electron acquires the rest of the remainder of the energy (Figure 5.11), which can also be derived from the four-momentum conservation law to be

$$E_{c,K}(E_i, \theta) = E_{in} \frac{2\epsilon \sin^2 \frac{\theta}{2}}{1 + 2\epsilon \sin^2 \frac{\theta}{2}}.$$

where $E_{c,K}(E_i, \theta)$ is the outgoing electron’s energy. As a result, the maximum energy transferred to the outgoing electron is

$$E_{c,K,\text{max}} = E_{in} \frac{2\epsilon}{1 + 2\epsilon}.$$

As the magnitude of $\epsilon$, which is directly proportional to $E_{in}$, increases, the ratio $\frac{2\epsilon}{1+2\epsilon}$ gets closer to 1. Therefore, the maximum energy an electron can acquire through Compton scattering can approach 1.17 and 1.33 MeV if the scattered photons angle $\theta \approx \pi$.

![Figure 5.11: Compton scattering inside ZnO lattice. The orange and blue sphere represent O and Zn atoms. The incoming photons (violet arrows) collide with electrons inside the lattice. The outgoing photons (red arrows) have a smaller energy, transferring momentum to energetic electrons (green arrows).](image)
For maximum effect on the lattice, we will consider that the maximum energy is transferred to the Compton-scattered electron (photoelectrons). These energetic photoelectrons may then collide with the nuclei in the lattice and displace a chain of atoms (Figure 5.12). Due to their high velocity, the collision is relativistic and the transferred energy to a nucleus \((E_T)\) can be obtained from

\[
E_T = \frac{2E_{in}' (E_{in}' + m_e c^2)}{M c^2}.
\]

where \(E_{in}'\) is the incoming relativistic electron’s energy and \(M\) is the atomic mass of the nucleus. The displaced atoms then collide with other lattice atoms, causing a displacement chain. The transferred energy to an outgoing nucleus \((T_E)\) from an incoming non-relativistic nucleus is

\[
T_E = \frac{4 M_{Zn} M_O}{(M_{Zn} + M_O)^2} E_T
\]

where \(E_T\) is the incoming nucleus’ energy, \(M_{Zn}\) is the atomic mass of zinc and \(M_O\) is the atomic mass of oxygen. In order for atomic displacement to occur, the incoming particle’s energy must surpass the threshold atomic displacement energy discussed earlier \((E_d \sim 57 \text{ eV})\). But also, if the number of displaced atoms is small \((n \leq 2)\), the displaced atoms can migrate to a vacancy and the damage can be “healed”. If multiple atoms \((n \geq 5)\) are displaced, the defects will be stable. As a result, in order to observe a stable defect in a sublattice, the incoming particles, photons in this case, must have a threshold energy. To initiate stable displacement damage (green circle in Figure 5.13) to the oxygen (zinc) sublattice in wurtzite ZnO, incoming particles with energies higher than 310 keV (900 keV) are required. And if the displacement chain occurs near the surface, there is a possibility of surface atoms going through a ballistic ejection, leaving the lattice (red circle in Figure 5.13). As the radiation dose increases, the number of electrons acquiring energies above 900 keV, as well as the number of chain displacement occurring close to the surface, increases. Eventually, the active layer will be etched atom by atom and the surface effects, such as depletion
region below the surface due to surface chemisorption, become dominant against the bulk effects, such as the distortion of the potential barriers at the ZnO-ZnO interlayer-interfaces.

Figure 5.12: Energetic electrons go through inelastic collisions with the lattice atoms. The outgoing nuclei collide with other atoms inelastically. The displacement chain stops when the last nucleus’ energy is smaller than the threshold atomic displacement energy of other atoms.

Figure 5.13: Stable distortions (inside the green circle) require higher number of displacements (\( n \geq 5 \)). If the atom being displaced is a surface atom, it might leave the lattice (the atom inside the red circle).

PL spectroscopy was conducted on both wafers before and after irradiation (Figure 5.14). Peculiarly, the spectra from the wafers show different behaviors and yet, they confirm and clarify
the performance degradation in one wafer against the enhancement of the other. In Figure 5.14 (a),
the 4L sample indicates a shift from the green luminescence to a very broad blue-violet
luminescence, followed by a peak in the UV range. The reduction of the layer thickness of the 4L
sample after 2.2 MGy irradiation is further confirmed by the decline in the UV luminescence
amplitude. Although the area ratio of the UV luminescence over the visible luminescence is an
indication of an improved crystal quality79, the excitonic emissions close to 3–3.2 eV have been
attributed to different transitions. Noting the existing controversy over different aspects of point
defects in ZnO, such as the origin of the green luminescence and the n-type/p-type conductivities,
the UV-violet-blue luminescence can be attributed to several energy states. Zinc interstitial (Zn\(_{\text{i}}\))\(^{80}\)
state transitions to valence band minimum (VMB), conduction band maximum (CMB) transitions
to deep acceptor levels such as zinc vacancies (V\(_{\text{zn}}\))\(^{81}\) and to negatively charged zinc vacancies
(V\(_{\text{zn}}^{-}\))\(^{82}\) have been attributed to blue-violet luminescence. UV luminescence can be attributed to
V\(_{\text{zn}}^{-}\) weekly perturbed by neighborhood zinc atoms (i.e. V\(_{\text{zn}}'\))\(^{83}\), as well as deep acceptor-bound
exciton level transitions caused by nitrogen replacing oxygen sites (N\(_{\text{O}}\))\(^{84,85}\). Fu et al. reported an
intensification of the UV photoluminescence (PL) emission of ZnO-SiO\(_{2}\) nanocomposites grown
via sol gel process compared to ZnO. They deduced the formation of Zn–O–Si bonds at the ZnO-
SiO\(_{2}\) interface.\(^{86}\)

The PL for 8L sample (Figure 5.14 (b)) indicates a slight shift from the green luminescence
toward blue luminescence after 1.2 MGy and a very broad blue/violet/UV luminescence after 2.2
MGy, suggesting the creation of V\(_{\text{zn}}\) and V\(_{\text{zn}}^{-}\) complexes as well as Zn\(_{\text{i}}\). The nanocrystalline ZnO
films contain a significant number of point defects, mainly at the grain boundaries. The cascade
caused by ionization damage of gamma irradiation can create and alter the charge of the defects
which might have been unstable during the growth process due to high formation energies or very
small migration energies such as $Zn_l$. A similarity can be noticed between the photoluminescence transitions of Un-4L to 120-Irr-4L, and of 120-Irr-8L to 220-Irr-8L; and that is the decline in green luminescence (mainly attributed to positively charged $V_{\delta}^+$ and an enhancement of broad blue/violet/UV luminescence ($V_{zn}$ and $Zn_l$ related defects, as well as the creation of Zn–O–Si bonds possibly due to displaced silicon atoms).

![Figure 5.14: PL spectra of the sample from the 4L wafer (a) and the 8L wafer (b) before and after irradiation.](image)

The gate leakage current ($I_G$) measured for all devices (from 4L and 8L wafers) remained in the $1 \sim 50$ pA range before and after 1.2 MGy irradiation dose, indicating the damage effect on $I_G$ to be negligible. After the additional 1 MGy, however, the leakage current in 8L-1 sample was magnified by an order of magnitude (Figure 5.15).
Figure 5.15: Gate current as a function of gate-source voltage after different irradiation doses for 8L-1 (i.e. Un-8L-1, 120-8L-1 and 220-8L-1). The inset indicates the magnified leakage current for the unirradiated sample.

Finally, the devices were re-measured after 18 months to examine the improvement and the self-healing of the ZnO devices at room temperature. No recovery was observed in room temperature, proposing the formation of stable point defect clusters\(^8\) and permanent damage due to the etching of the surface due to ballistic ejection of the surface atoms.

5.4 Conclusion

Thin film transistors were fabricated \(\text{via}\) the sol-gel spin-coating technique and were measured before and after gamma irradiation doses of 1.2 MGy and 2.2 MGy. The output measurements confirmed the stability of the devices. Slight saturation mobility degradation (enhancement) was observed in the 4-layer (8 layer) ZnO devices after 1.2 MGy irradiation.
Further radiation dose of 1 MGy degraded the mobility and $I_{ON}/I_{OFF}$ of the 8-layer device and the 4-layer devices became dysfunctional. Measurements indicated a negative shift of threshold voltages in all devices after 1.2 MGy irradiation. An abnormality in the subthreshold regime was observed which was removed after irradiation. AFM indicated a reduction of ZnO layer thickness. A model was proposed based on the displacement damage occurred to the surface atoms. Photoluminescence indicated a broad blue/violet/UV shift of the visible spectrum. The enhancements and degradations of devices were in agreement with PL spectra.
References


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57 This abnormality exists in transconductance and mobility measurements of all devices fabricated by our sol gel spin coating method and is currently under investigation. The justified results will be published elsewhere.


Chapter 6

ZnO Nanoparticle Inclusions as Refractive Index Modifiers

6.1 Introduction

The following work has been published in the Journal of Nanoscience and Nanotechnology as “Simulation of the Refractive Index of Ga Doped ZnO Nanoparticles Embedded in PEDOT: PSS Using Effective Medium Approximations”. The author wants to primarily acknowledge the help of Fei Tong for her great contribution. This study was also facilitated by Dewang Song, Yoonsung Chung, Burcu Ozden, Kosala Yapabandara, Michael C. Hamilton, Dong-Joo Kim, Helen Koo, Kyeong K. Lee, and Minseo Park. We have theoretically investigated the change of refractive index of nanocomposites composed of Ga-doped ZnO nanoparticles (Ga-ZnO NPs) dispersed in conductive polymer Poly(3,4-ethylenedioxythiophene) and Poly(styrene sulfonic acid) (PEDOT:PSS) matrix by tuning the fraction of the Ga-ZnO NP inclusions and concentration of Ga dopant in Ga-ZnO, by using Maxwell-Garnet, Bruggeman and Lorentz-Lorenz effective medium theories. The dependence of the effective refractive index of Ga-ZnO NPs embedded in PEDOT:PSS composite on the Ga doping concentration and its volume fraction of the inclusions are presented. Ga-ZnO NPs can increase the effective refractive index. This can be used to engineer a desired effective index of refraction for the enhancement of light extraction and absorption efficiency in optical devices such as organic light emitting diodes (OLEDs) and organic solar cells.
(OSC). It is crucial to match the refractive indices of conductive anode electrode and the emissive layer.

Nanoparticles dispersed in a polymer or polymer-nanoparticle composites have recently attracted great attention in the potential optoelectronic applications in band gap alteration for organic solar cells (OSC)\(^2,3\) and enhancing electroluminescence (EL) properties in organic light emitting diodes (OLED)\(^4,5\). Electrical and optical properties of the composite can be tuned by using nano-inclusions. Several researchers have reported modification of the refractive index of the polymer-nanoparticle composites by adjusting the size and concentration of NPs. Obreja \textit{et al.}\(^6\) reported the increase of the refractive index of poly(methyl methacrylate) (PMMA), 2-hydroxyethyl methacrylate (HEMA) and polyvinyl alcohol (PVA) by doping them with oxide NPs such as TiO\(_2\), ZrO\(_2\), SiO\(_2\). Modification of the refractive index of the nanocomposites based on poly(methyl methacrylate) (PMMA) and zinc oxide (ZnO) NPs was reported by Demir \textit{et al.}\(^7\) In addition, Englebienne \textit{et al.}\(^8\) reported an increase in refractive index of composite composed of encapsulated colloidal gold NPs and water-soluble conductive polymer poly(aniline-2-carboxylic acid) (PANI-COOH).

Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT:PSS) remains to be a popular conductive organic polymer which is widely used as the anode electrode (hole transport layer) in flexible organic optoelectronic devices such as OLEDs\(^9,10\) and OSC\(^11,12\). In the case of OLEDs, it is desired to adjust the refractive index of PEDOT:PSS (n = 1.42)\(^13\) to match that of the organic polymer emissive layer whose refractive index is usually in the range of 1.7~1.8\(^14\). Due to the inherent high refractive index of ZnO (n=2.0)\(^15\), embedding ZnO NPs in PEDOT:PSS will increase the refractive index of the polymer-composite matrix, improving the
light extraction efficiency of the OLED. For solar cells, impedance matching of the photoactive layer with the transparent conductive layer can increase the efficiency.\textsuperscript{16,17}

Although the modification of the electrical conductivity of PEDOT:PSS by the incorporation of ZnO NPs has been investigated by a few research groups\textsuperscript{18,19}, the theoretical study of the modification of the refractive index of such nanocomposites have not been conducted. Among the group III dopants applied to alleviate the resistivity of ZnO, Ga is one of the most efficient elements, has the closest electronegativity and the atomic radius to zinc\textsuperscript{20}, and increases the mobility in ZnO\textsuperscript{21}. Therefore, the focus of this work will be on the investigation of the modification of the refractive index of Ga doped ZnO (Ga-ZnO) NPs embedded in PEDOT:PSS (hereafter to be referred to as Ga-ZnO/PEDOT:PSS) by simulation based on Bruggeman (BG), Maxwell-Garnett (MG) and Lorentz-Lorenz (LL) effective medium approximations\textsuperscript{22}. These theories were frequently applied for modeling of optical properties of nanocomposites\textsuperscript{23,24,25}. Wong \textit{et al.}\textsuperscript{26} and Janicki \textit{et al.}\textsuperscript{27} used Maxwell-Garnet’s, Bruggeman’s, Lorentz-Lorenz’s and other effective medium theories to model the refractive index profiles of ZnO quantum dots dispersed in Poly(methyl methacrylate), and of the dielectric inhomogeneous coatings, respectively.

\subsection*{6.2 Simulation Details}

Among many effective medium approximations (EMA), BG’s, MG’s and LL’s theories were used since Ga-ZnO NPs inside PEDOT:PSS form a two-phase nanocomposite\textsuperscript{28}. In BG’s approach, the ratio of both constituents’ volumes in the homogenous blend are comparable (between 1/3 and 2/3).\textsuperscript{29} Thus, the effective dielectric constant and the refractive index are equally affected by the two media in BG’s method. In MG’s approximation, a smaller constituent is
dispersed in a main medium, negligibly affecting the dominant electric field inside. In the cases where the inclusions’ fraction approaches zero, and/or the constituents’ refractive index approaches the refractive index of the host, the two theories (BG and MG) become equivalent.\textsuperscript{30} In both cases, the wavelength of the incoming radiations must be much larger than the size of the inclusions since these approximations are based on considering particles in a uniform electric field. In LL’s approximation, the effects of the neighboring dipoles are also taken into account.\textsuperscript{31} Spherical inclusions are considered being affected by the outer electric field as well as the dipole field from the neighboring polarized inclusions. It should be noted that the geometrical shapes of the inclusions are considered to be spherical for all the effective medium theories mentioned above. Depending on the structure of the mixture and the comparative filling factors, one approach is more accurate than others.

By using the effective medium approximations, the resultant effective refractive indices \( n_{\text{eff}} \) of the Ga-ZnO/PEDOT:PSS were calculated. \( n_H \) (higher index) and \( n_L \) (lower index) are denoted for the refractive indices of Ga-ZnO and PEDOT:PSS, respectively. In general, \( n^2 = \varepsilon \mu \), where \( \varepsilon \) is the relative permittivity and \( \mu \) is the relative permeability. Since the inclusions and the matrix are both non-magnetic in this study, it was assumed that \( \mu \rightarrow 1 \). The volume fraction of the inclusions (Ga-ZnO) is denoted by \( f_{\text{H}} \), and the volume fraction of PEDOT:PSS is denoted by \( f_{\text{L}} = 1 - f_{\text{H}} \). The effective refractive indices of the mixtures were calculated using the following equations for (1) BG\textsuperscript{32}, (2) MG\textsuperscript{33} and (3) LL\textsuperscript{23} effective medium approximations, respectively:

\[
\text{BG} \quad f_H \frac{n_H^2 - n_{\text{eff}}^2}{n_H^2 + 2n_{\text{eff}}^2} + (1 - f_H) \frac{n_L^2 - n_{\text{eff}}^2}{n_L^2 + 2n_{\text{eff}}^2} = 0 \tag{1}
\]

\[
\text{MG} \quad \frac{n_{\text{eff}}^2 - n_H^2}{n_{\text{eff}}^2 + 2n_H^2} = (1 - f_H) \frac{n_L^2 - n_H^2}{n_L^2 + 2n_H^2} \tag{2}
\]

\[
\text{LL} \quad \frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = f_H \frac{n_H^2 - 1}{n_H^2 + 2} + (1 - f_H) \frac{n_L^2 - 1}{n_L^2 + 2} \tag{3}
\]
6.3 Results and Discussion

Figure 6.1 shows the schematics of the embedded Ga doped ZnO nanoparticles in PEDOT:PSS polymer matrix. The refractive index of PEDOT:PSS \((n_L = 1.42)\) can be increased by embedding ZnO NPs \((n=2.0)\) in the polymer matrix to match that of the organic polymer emissive (active) layer \((n=1.7\sim1.8)\) in order to increase the light extraction efficiency. In addition, Ga doping of the ZnO NPs can be applied for fine tuning of the refractive index of the layer.

![Figure 6.1: Schematics of the embedded Ga doped ZnO nanoparticles in PEDOT:PSS polymer matrix.](image)

The refractive index is wavelength dependent, thus the calculations were performed for three different wavelengths. The maximum index of refraction for pure ZnO occurs at \(\lambda= 403\) nm according to the experimental data we collected from an article by D.-T. Phan et al.\(^ {34,35}\) We have also calculated the effective refractive indices for \(\lambda= 550\) nm since tris-8-hydroxyquinoline aluminum (Alq3)\(^ {36}\) is widely used in green OLEDs for its high electron mobility and efficiency. In addition, \(\lambda= 650\) nm was also used for the red OLEDs.\(^ {37}\) Table 6.1 summarizes effective
refractive indices of Ga-ZnO NPs ($n_{hi}$) with different Ga doping percentages, for each aforementioned wavelength.

Figures 6.2, 6.3, and 6.4 show the effective refractive index of Ga-ZnO/PEDOT:PSS for $\lambda = 403$ nm simulated by BG, MG and LL effective medium approximations, respectively. Figures 6.5, 6.6, and 6.7 indicate the simulated effective refractive index of the composite determined at $\lambda = 550$ by the BG, MG, and LL theories, respectively. Figures 6.8, 6.9, and 6.10 show the effective refractive index simulated at $\lambda = 650$ nm by the BG, MG, and LL equations, respectively. The effective refractive index of Ga-ZnO/PEDOT:PSS was affected by the doping concentration of Ga, the fraction of inclusion, and the wavelength of the light.

Since the maximum refractive index for pure ZnO occurs at $\lambda = 403$nm, the Ga dopants’ contribution to the effective refractive index at this wavelength is more apparent, as is shown in Figures 6.2, 6.3, and 6.4. As for higher wavelengths, the contribution of the dopant becomes less evident.

Table 6.1: Refractive Index of Ga-ZnO [Ref. 34, 35]

<table>
<thead>
<tr>
<th>Ga weight % →</th>
<th>0 weight %</th>
<th>1 weight %</th>
<th>2 weight %</th>
<th>3 weight %</th>
<th>4 weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>403nm</td>
<td>2.03524</td>
<td>1.97737</td>
<td>1.96884</td>
<td>1.97202</td>
<td>1.97002</td>
</tr>
<tr>
<td>550nm</td>
<td>1.97614</td>
<td>1.96506</td>
<td>1.96591</td>
<td>1.96673</td>
<td>1.97052</td>
</tr>
<tr>
<td>650nm</td>
<td>1.96638</td>
<td>1.96272</td>
<td>1.96198</td>
<td>1.96403</td>
<td>1.96572</td>
</tr>
</tbody>
</table>
Figure 6.2: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by BG at 403nm.

Figure 6.3: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by MG at 403nm.
Figure 6.4: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by LL at 403nm.

Figure 6.5: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by BG at 550nm.
Figure 6.6: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by MG at 550nm.

Figure 6.7: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by LL at 550nm.
Figure 6.8: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by BG at 650nm.

Figure 6.9: Effective Refractive Index of Ga-ZnO/PEDOT:PSS determined by MG at 650nm.
As stated before, the MG approximation is applied for relatively small inclusion volume fractions. Our calculated volume fraction, required for the effective index matching, exceeds 1/3. The result is valid since $n_L \approx n_H$ and therefore the MG and BG theories conclude an analogous result.

Light extraction efficiency can be increased by matching the refractive indices of the emissive layer and the hole transport layer (Ga-ZnO/PEDOT:PSS) in OLEDs. The matching of different active layers with their corresponding transparent conductive layers (Ga-ZnO/PEDOT:PSS) can decrease light reflection, thus increasing the efficiency of multijunction OSCs. In addition, gradual tuning of refractive index, by manipulating the inclusion volume fractions of the Ga-ZnO NPs, can be used in graded-refractive-index-structured solar cells to considerably suppress the reflectance via impedance matching.\textsuperscript{38}
6.4 Conclusion

Bruggeman, Maxwell-Garnett and Lorentz-Lorenz effective medium approximations were used to simulate the refractive index of Ga-ZnO NPs dispersed in conductive polymer PEDOT:PSS. We have demonstrated how the refractive index of Ga-ZnO/PEDOT:PSS is modified by tuning the fraction of the NPs and the concentration of Ga in ZnO NPs. It was found that if the refractive index of Ga-ZnO/PEDOT:PSS is to be matched with that of the organic emissive layer (n=1.7~1.8), the desired volume fraction of the Ga-ZnO should occur between 45% and 71% when the concentration of Ga in ZnO NPs varies between 0 and 4 percent.
References


28 J. C. M. Garnett, Phil. Trans. R. Soc. Lond. 203, 385 (1904).


35 Private Email communication with F. Yakuphanoglu, co-author of [33].


Chapter 7

Summary and Future Work

7.1 Summary

This research was mostly devoted to characterization of ZnO films and the TFTs employing the films as active channel layers synthesized via the sol-gel spin-coating deposition method. Zinc acetate dehydrate was mixed with monoethanolamine, diluted with isopropanol, and stirred on a hot plate to obtain a transparent, stable and homogenous precursor. The precursor was spin-coated on oxidized boron-doped silicon wafers as substrates and calcined afterwards. The spin-coating process was repeated to obtain different thicknesses on different samples. The samples were then annealed at different temperatures and the films were characterized. Despite the Raman spectroscopy and photoluminescence showing a qualitative crystal quality increase as the annealing temperature increased, SEM images revealed gaps being formed between grains as the annealing temperature reached 900 °C and therefore, 800 °C was chosen as the post-annealing temperature.

An abnormality in the transfer characteristics, transconductance and the mobility of the TFTs was observed. Hypothesizing that surface oxygen chemisorption occurs during the time interval between the spin-coating processes, an experiment was designed and implemented to examine the hypothesis. ZnO films with different number of spin-coating repetition were used to fabricate TFTs. The I-V and C-V measurements hinted to the possibility of depletion layers being
formed at the ZnO-ZnO interlayer-interfaces. A “kink effect” (or “hump effect”) was observed in transfer characteristics of devices with higher number of ZnO layers and multiple peaks were apparent in their transconductance and mobility. These devices also exhibited abnormality in their C-V characteristics, resembling parasitic capacitance effects in parallel with the main capacitor. This effect, however, was absent in the single layer ZnO sample, lowering the possibility of an edge effect to be the cause of this effect in C-V measurements. Furthermore, the single layer ZnO TFT did not show any kink in its transfer characteristics. More rigorous study is advised to achieve a strong conclusion on this matter.

The radiation hardness of ZnO was corroborated by measuring gamma irradiated ZnO TFTs, using $^{60}$Co tubes as the radiation source, before and after irradiation. Two samples with different thicknesses were fabricated for this experiment: one with 4 layers of ZnO, and one with 8 layers. The output characteristics indicated the functionality of the devices from both samples after gamma irradiation dose of 1.2 MGy (120 MRad). The transfer characteristics in the saturation region of transistors from the 4 layer sample indicated a reduction in saturation mobility and current ON/OFF ratio ($I_{ON}/I_{OFF}$), whereas the same properties were enhanced in devices from the 8 layer sample. It was conjectured that the enhancement was related to higher influence of ZnO-ZnO interlayer-interface distortion in the bulk of the 8 layer sample compared to surface effects, while the latter becomes more significant in the thinner 4 layer sample. The kink effect observed in both samples before irradiation, caused by ZnO-ZnO interlayer-interfaces, was absent in the measurements conducted after gamma irradiation dose of 1.2 MGy. AFM and High Resolution Digital Optical Microscopy images confirmed diminishing of the ZnO channel layers as the irradiation dose increased. A model was proposed based on the displacement damage occurring at the surface, due to photon-electron Compton scattering, to explain the gradual etching of the film.
The rise in the blue/violet/UV luminescence of the samples after irradiation implied a surge in zinc vacancies and zinc interstitials.

In addition to the aforementioned research on ZnO TFTs, modification of the refractive index of PEDOT:PSS by gallium doped ZnO nanoparticle inclusions based on volume fraction was studied. Three effective medium approximations (Bruggeman, Maxwell-Garnett and Lorentz-Lorenz) were used to find the appropriate volume fraction of the doped nanoparticle inclusions \((n≈2)\) in PEDOT:PSS \((n_L = 1.42)\) to match the index of refraction for organic polymer emissive layer \((n=1.7~1.8)\) in OLEDs. It was found that for gallium doped ZnO nanoparticles, with doping concentration ranging from 0% to 4%, the volume fraction of inclusions inside the PEDOT:PSS matrix should vary between 45% and 71%.

### 7.2 Future Work

The effect of ZnO-ZnO interlayer-interfaces was investigated by exploiting the number of ZnO layers deposited \(\textit{via}\) sol-gel spin-coating method. The claim can be further investigated by drastically elongating the time interval between the spin-coating processes, exposing the top ZnO surface to the ambient even further before the next deposition. If the deposition process (spin-coating and calcination processes) is realized inside an isolated environment with non-reactive ambient, such as an argon filled glovebox, the absence of a depletion layer at the ZnO-ZnO interlayer-interfaces can be investigated.

Radiation hardness of ZnO was highlighted in this work, approving previous reports, with TFTs having unpassivated channel layers as thin as 200 microns functioning after being exposed to a relatively high gamma irradiation dose. The malfunction of transistors with a smaller channel thickness was credited to the consequences of displacement damage on the surface, causing
ballistic ejection of surface atoms. Passivating the ZnO active layer may affect the etching process and the carrier mobility. This passivation layer may, however, introduce impurities into the ZnO layer. Annealing the passivation layer after deposition and the irradiation effects on device performance can be further investigated. Finally, C-V measurements before and after irradiation offer insightful material for scrutinizing the displacement damage, the ZnO/SiO₂ interface traps and the induced SiO₂ positive charges in the bulk.