Nanocrystalline Silicon Quantum Dot Light Emitting Diodes
Using Metal Oxide Charge Transport Layers

by

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A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
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Abstract

Silicon-based lighting show promise for display and solid state lighting use. Here we demonstrate a novel thin film light emitting diode device using nanocrystalline silicon quantum dots as an emission layer, and metal oxides as charge transport layers. Sputtering deposition conditions for the nickel and zinc oxides were explored in order to balance deposition rate with minimal roughness, optical absorption, and electrical resistivity. Devices displaying characteristic diode current-voltage behavior were routinely produced, although most showed significant reverse saturation current due to the presence of shunts. Current-voltage behavior of devices made in the same batch showed high repeatability, however variations in device performance was observed between batches while the parameters of synthesis were kept constant. Some devices were observed to emit orange-colored light, consistent with photoluminescence behavior of the silicon quantum dots. Photomultiplier tube measurements shows a turn-on voltage of 5V and an exponential increase in light emission with voltage increase.
Acknowledgments

First and foremost, I would like to thank my supervisor, Professor Kherani, for his support, encouragement, and guidance. It has been a privilege to be able to do research at the APD Lab. I also wish to extend my gratitude to Professor Ozin for facilitating access to the NanoMaterials Chemistry Labs - in aid of synthesizing the colloidal silicon nanocrystals. I would like to acknowledge the financial support of the Ontario Research Fund – Research Excellence program and the Department of Materials Science and Engineering at the University of Toronto.

I received generous help from numerous individuals throughout the course of this research. I would like to express my gratitude to Dr. Davit Yeghikyan Dr. Tome Kosteski for their technical assistance. Many thanks go to Keith Leong, Paul O’Brien, Zahidur Chowdhury, and Pratish Mahtani for always being there when I had questions. I would like to thank Jeffrey Castrucci for the photoluminescence studies; Michael Helander and Zhibin Wang for technical discussions; Mark Greiner for the XPS measurements; Yi-Lu Chang for help with the electroluminescence setup; Kitty Kumar for the AFM measurements; George Kretschmann for the XRD measurements; and Yang Yang for help with PMT measurements.

A special thanks goes to Dr. Danny Puzzo for sharing his expertise on the subject of nanocrystals. Many thanks also go to Dr. Eric Henderson, Laura Hoch, and Melanie Mastronardi for helping out with nanocrystal syntheses.

I would like to thank Jack, Hui-Lin, Paul, Keith, Bernie, Dave, and Yang for their companionship. You guys definitely made labbing more fun!

Last but not least, I would like to thank my parents for everything they have done for me. Thank you for believing in me.
# Table of Contents

Acknowledgments .......................................................................................................................... iii

Table of Contents ........................................................................................................................... iv

List of Tables ................................................................................................................................ vii

List of Figures .............................................................................................................................. viii

List of Acronyms, Abbreviations, and Chemical Formulae ........................................................ xiii

List of Symbols ............................................................................................................................ xvi

1 Introduction ................................................................................................................................ 1

1.1 Solid State Lighting using Light-Emitting Diodes (LEDs) ................................................ 1

1.2 Current State of Colloidal Quantum Dot LEDs ................................................................. 3

1.3 Silicon Nanocrystals and CQDs .......................................................................................... 5

1.4 Thesis Objective.................................................................................................................. 6

2 Nanocrystalline Silicon and Device Concept ............................................................................. 7

2.1 CQD ncSi Synthesis ............................................................................................................ 7

2.2 Quantum Confinement Effect and Quantum Dot Luminescence ....................................... 7

2.3 Device Concept ................................................................................................................. 10

3 Experimental Apparatus and Characterization Techniques ..................................................... 13

3.1 Sample Fabrication ............................................................................................................ 13

3.1.1 Sample Preparation ..................................................................................................... 13

3.1.2 RF Magnetron Sputtering ........................................................................................ 13

3.1.3 Electron Beam Deposition ..................................................................................... 15

3.1.4 Thickness Monitor During E-beam and Sputtering Deposition ........................... 16

3.1.5 Spincoating Deposition .......................................................................................... 17

3.2 Characterization Techniques ............................................................................................. 18

3.2.1 Spectroscopic Ellipsometry .................................................................................. 18
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.2</td>
<td>Profilometry</td>
<td>19</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Atomic Force Microscopy</td>
<td>19</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Photoluminescence</td>
<td>21</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Photoemission Spectroscopy (PES)</td>
<td>21</td>
</tr>
<tr>
<td>3.2.6</td>
<td>X-Ray Diffraction</td>
<td>24</td>
</tr>
<tr>
<td>3.2.7</td>
<td>Electroluminescence</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Experiments on Device Layers</td>
<td>26</td>
</tr>
<tr>
<td>4.1</td>
<td>Overview</td>
<td>26</td>
</tr>
<tr>
<td>4.2</td>
<td>TCO Layers Optimization</td>
<td>26</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Quartz Thickness Monitor Calibration</td>
<td>26</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Deposition Rates</td>
<td>29</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Absorption Studies</td>
<td>30</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Electrical Conductivity Studies</td>
<td>32</td>
</tr>
<tr>
<td>4.2.5</td>
<td>XPS Measurements</td>
<td>33</td>
</tr>
<tr>
<td>4.2.6</td>
<td>Bandgap Determination Using Tauc-Lorentz Model</td>
<td>35</td>
</tr>
<tr>
<td>4.2.7</td>
<td>X-Ray Diffraction</td>
<td>40</td>
</tr>
<tr>
<td>4.3</td>
<td>CQD ncSi Layer Experiments</td>
<td>41</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Spin-coating Rate</td>
<td>41</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Photoluminescence Studies</td>
<td>42</td>
</tr>
<tr>
<td>4.4</td>
<td>AFM Roughness Measurements</td>
<td>43</td>
</tr>
<tr>
<td>5</td>
<td>Device Fabrication, Results, &amp; Analysis</td>
<td>51</td>
</tr>
<tr>
<td>5.1</td>
<td>Device Fabrication</td>
<td>51</td>
</tr>
<tr>
<td>5.2</td>
<td>Current-Voltage Behavior and Stability</td>
<td>55</td>
</tr>
<tr>
<td>5.3</td>
<td>Oxide Experiments</td>
<td>60</td>
</tr>
<tr>
<td>5.4</td>
<td>Light Emission Characterization</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>Conclusion</td>
<td>66</td>
</tr>
</tbody>
</table>
6.1 Conclusions ................................................................................................................................. 66
6.2 Future Work ...................................................................................................................................... 67
References .............................................................................................................................................. 69
List of Tables

Table 4-1: Requirements for individual layers of a CQD ncSi LED. .................................................. 26

Table 4-2: Summary of thickness monitor parameters for TCOs after calibration. ......................... 29

Table 4-3: Effects on RF power and chamber pressure on the deposition rate of NiO and ZnO. 30

Table 4-4: Work functions of NiO and ZnO as measured by XPS. .................................................. 35

Table 4-5: Summary of Tauc Lorentz fitting of NiO ellipsometry data. ......................................... 35

Table 4-6: AFM investigation of average and RMS roughness of the deposited films in aid of examining the effects of RF deposition power on NiO film and studying the expected changes in the surface roughness with layer by layer growth of a actual device. ........................................ 45
List of Figures

Figure 1-1: Historical and Predicted Efficacy of Lighting Sources[1]. (HID: high intensity discharge; OLED: organic light emitting diode) ......................................................................................... 1

Figure 1-2: Typical design of an OLED. ........................................................................................................... 2

Figure 1-3: Three designs for generating white light using CQDs. Top: white light generation by mixing CQDs of various wavelength. Bottom left: direct white light generation from CQD emission layer. Bottom right: white light generation by mixing nanophosphors of different colors, with an excitation source due to a blue CQD LED [10]. ........................................................................... 3

Figure 1-4: Types of core-shell semiconductor nanocrystal structures [16]....................................................... 4

Figure 1-5: A typical architecture of a CQD-LED device, showing the anode (TCO), HTL, ETL, quantum dot (QD), and cathode (Al) layers on glass............................................................... 5

Figure 2-1: Physical representation of (a) bulk material - 3D, (b) sheet - 2D, (c) rod - 1D (d) crystal or quantum dot - 0D [34]. ................................................................................................. 8

Figure 2-2: Density of states for (a) 3D, (b) 2D, (c) 1D, and (d) 0D systems [34]. ................................. 8

Figure 2-3: Blue-shift of optical absorption peaks in CdS and CuCl (the horizontal scale represents light energy while the vertical scale represents the optical density) [35]. Crystal sizes for CdS: 1 - 320Å, 2- 23Å, 3 - 15Å, 4 - 12Å. Crystal sizes for CuCl: 1- 310Å, 2 - 29Å, 3 - 20Å. 9

Figure 2-4: X-ray photoelectron spectrum (XPS) of silicon nanocrystals [31]. The measurement was referenced to the valence band edge of bulk silicon................................................................. 10

Figure 2-5: Size-dependent photoluminescence of the silicon nanocrystals [31]. The peak centered at 685nm corresponds to nanocrystals of average size 3.2nm, whereas the peak centered at 645nm corresponds to nanocrystals of average size 3.0nm......................................................... 10

Figure 2-6: Proposed structure for ncSi LED using metal oxide charge transport layers. ............... 11

Figure 2-7: Band alignment of the various layers in the proposed ncSi LED device structure.... 12
Figure 3-1: A schematic diagram showing the setup of a sputtering system................................. 14

Figure 3-2: Photograph of the interior of the sputtering chamber, showing the location of the two targets, the gas ring, and thickness sensors................................................................. 15

Figure 3-3: Interior of the e-beam evaporation chamber............................................................... 16

Figure 3-4: Schematic diagram of an AFM [45]. ......................................................................... 20

Figure 3-5: Schematic diagram of an XPS setup [45]. ................................................................. 21

Figure 3-6: X-ray absorption and electron ejection during XPS [45]. ........................................... 22

Figure 3-7: Schematic diagram of PES processes, showing the location of the secondary edge [46]. ............................................................................................................................................... 23

Figure 3-8: A schematic diagram of the experimental setup for electrical and electroluminescence setup. A LabVIEW program controls the Keithley 2440 sourcemeter, which powers the sample, while simultaneously feeds current-voltage data back to LabVIEW. Luminance meter and spectrophotometer allows simultaneous optical data acquisition by LabVIEW. The light emission can also be sensed by naked eyes, and by a photomultiplier tube (PMT). A multimeter is used to collect emission strength, measured in PMT output voltage..... 25

Figure 4-1: Fitted ellipsometry data for a NiO thin film. Top plot shows fitted (green) curve for $\alpha$ (red). Bottom plot shows fitted (green) curve for $\beta$ (red). ................................................................. 27

Figure 4-2: Profilometry plot for a 1.7$\mu$m NiO thin film, used for calibration of the quartz sensor. ....................................................................................................................................................... 28

Figure 4-3: Profilometry plot for a 1.2$\mu$m ZnO thin film, used for calibration of the quartz sensor. ....................................................................................................................................................... 28

Figure 4-4: Transmission spectra of 20nm thick NiO films deposited on 0.7mm Corning 1737 glass substrate................................................................. 31

Figure 4-5: Absorption spectrum of 50nm ZnO film deposited on 0.7mm Corning 1737 glass.. 31
Figure 4-6: Effects of substrate heating during sputtering on the resistivity of NiO

Figure 4-7: XPS spectra in the vicinity of the secondary edge for NiO.

Figure 4-8: XPS spectra in the vicinity of the secondary edge for ZnO.

Figure 4-9: Fitting of ellipsometry data for 20nm NiO film, deposited at 50W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).

Figure 4-10: Fitting of ellipsometry data for 20nm NiO film, deposited at 100W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).

Figure 4-11: Fitting of ellipsometry data for 20nm NiO film, deposited at 125W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).

Figure 4-12: Attempted fitting of ellipsometry data for a 20nm ZnO film. Green curve is a fit of raw data (pink).

Figure 4-13: XRD pattern for NiO.

Figure 4-14: XRD pattern for ZnO.

Figure 4-15: Thickness versus spincoating RPM for ncSi layer fabrication.

Figure 4-16: Photoluminescence curves of two batches of CQD ncSi, designated by letters A and B. The number on the legend represents frequency of excitation.

Figure 4-17: AFM surface profile of Corning 1737 glass.

Figure 4-18: AFM surface profile of NiO deposited at 25W RF power.

Figure 4-19: AFM surface profile of NiO deposited at 50W RF power.

Figure 4-20: AFM surface profile of NiO deposited at 100W RF power.

Figure 4-21: AFM surface profile of NiO deposited at 125W RF power.

Figure 4-22: AFM surface profile of NiO deposited at 150W RF power.
Figure 4-23: AFM surface profile of ZnO deposited at 100W RF power. ................................... 49

Figure 4-24: AFM surface profile of NiO/ncSi structure. ............................................................ 49

Figure 4-25: AFM surface profile of NiO/ncSi/ZnO structure. .................................................... 50

Figure 4-26: SEM micrograph of the cross-section of a 2μm NiO, deposited on a crystalline silicon substrate............................................................................................................................ 50

Figure 5-1: ITO contact strip design, showing dimensions of ITO strips (black) and glass (white). ....................................................................................................................................................... 51

Figure 5-2: Cross section of ITO strips, measured by profilometry. ............................................. 52

Figure 5-3: Top view of a fabricated structure, showing a matrix of devices. One end of the ITO strips, shown vertically, was exposed for contacting. Al contact strips, shown horizontally, were placed perpendicular to the ITO strips. Each intersection point between the ITO strips and the Al strips is an independent LED device. The yellow arrows show the contact points needed to drive the device at the top left corner........................................................................................................ 54

Figure 5-4: Photo of a fabricated structure. The circle centers on a single device. ....................... 55

Figure 5-5: I-V characteristics typical of unsuccessful LED devices........................................... 56

Figure 5-6: Current-voltage curve of an LED device showing typical diode-like behavior. ....... 56

Figure 5-7: An I-V comparison of devices on three sample substrates (substrates A, B, and C) that are fabricated simultaneously, showing consistency between samples within each sample fabrication run. Numbering after A, B, and C distinguishes between individual device number on each substrate (i.e. five different devices were tested for substrate A, in the order of A1, A2, A3, A4, and A5). ........................................................................................................................................ 57

Figure 5-8: Comparison of I-V curves between devices fabricated in different fabrication runs but while using identical layer thicknesses of 20nm/30nm/55nm for NiO/ncSi/ZnO. D1 to D7 represent dark diodes (not visible to the naked eye), while E1 and E2 represent devices capable of producing light visible to the naked eye................................................................. 58
Figure 5-9: Current density and luminance as a function of bias voltage for an OLED using ncSi and organic transport layers [31]. ................................................................. 59

Figure 5-10: Deterioration of device during measurement from voltage scanning from -2 to 10V. ................................................................................................................................. 60

Figure 5-11: I-V characteristics of a device with an SiO₂ layer. .................................................. 61

Figure 5-12: I-V characteristics of a second device with an SiO₂ layer. ...................................... 61

Figure 5-13: PMT measurement of device luminescence (blue) and current density (red) with respect to bias voltage. .................................................................................................................. 63

Figure 5-14: Log plot of PMT measurement of luminescence strength and current density of a device with respect to bias voltage. ........................................................................................................ 63

Figure 5-15: Current and luminescence behavior as a function of applied bias for the best device reported by Cheng et al. [40]. ........................................................................................................ 64
<table>
<thead>
<tr>
<th>Acronym/Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum Oxide</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>Boron Oxide</td>
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<tr>
<td>CaO</td>
<td>Calcium Oxide</td>
</tr>
<tr>
<td>C₁₀</td>
<td>Decyl</td>
</tr>
<tr>
<td>CH₃CH₂OH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>CPL</td>
<td>Compact Fluorescent Lighting</td>
</tr>
<tr>
<td>CQD</td>
<td>Colloidal Quantum Dot</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DI</td>
<td>De-Ionized</td>
</tr>
<tr>
<td>E-Beam</td>
<td>Electron Beam</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron Transport Layer</td>
</tr>
<tr>
<td>ILED</td>
<td>Inorganic Light Emitting Diode</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>HSiCl₃</td>
<td>Trichlorosilane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Term</td>
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<td>--------------</td>
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<tr>
<td>HTL</td>
<td>Hole Transport Layer</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage</td>
</tr>
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<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>Na$_2$O</td>
<td>Sodium Oxide</td>
</tr>
<tr>
<td>ncSi</td>
<td>Nanocrystalline Silicon</td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>NiO</td>
<td>Nickel Oxide</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Polyethylenedioxythiophene</td>
</tr>
<tr>
<td>PES</td>
<td>Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PLED</td>
<td>Polymer Light Emitting Diode</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
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<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>PVK</td>
<td>Poly(vinylcarbazole)</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic Ellipsometry</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SMOLED</td>
<td>Small Molecule Organic Light Emitting Diode</td>
</tr>
<tr>
<td>SSL</td>
<td>Solid State Lighting</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent Conducting Oxide</td>
</tr>
<tr>
<td>TPBi</td>
<td>$2,2',2''$-(1,3,5-phenylene)tris-[1-phenyl-1H- benzimidazole]</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
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<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
</tbody>
</table>
List of Symbols

\( a \)  \quad \text{Lattice Constant}

\( a_e \)  \quad \text{Electron Bohr Radius}

\( a_E \)  \quad \text{Exciton Bohr Radius}

\( a_h \)  \quad \text{Hole Bohr Radius}

\( \AA \)  \quad \text{Angstrom}

\( C \)  \quad \text{Coulomb}

\( d \)  \quad \text{Interplanar Spacing}

\( E_b \)  \quad \text{Binding Energy}

\( E_F \)  \quad \text{Fermi Energy}

\( E_{SC} \)  \quad \text{Secondary Cut-Off Energy}

\( E_{sp} \)  \quad \text{Energy}

\( h \nu \)  \quad \text{Light Energy or X-Ray Energy}

\( k \)  \quad \text{Extinction Coefficient}

\( \lambda \)  \quad \text{Wavelength}

\( n \)  \quad \text{Refractive Index}

\( \rho \)  \quad \text{Mass Density or Electrical Resistivity}

\( \theta \)  \quad \text{Diffraction Angle}

\( q \)  \quad \text{Elementary charge, or } 1.602 \times 10^{-19} \text{ C}
\( \bar{R} \)  Average Crystal Size

\( R_a \)  Average Roughness

\( R_q \)  Root Mean Square Roughness

\( R_s \)  Sheet Resistance

\( \Phi_s \)  Sample Work Function

\( \Phi_{sp} \)  Spectrometer Work Function

\( t \)  Film Thickness

\( V_a \)  Applied Bias

\( Z_m \)  Acoustic Impedance of Material

\( Z_q \)  Acoustic Impedance of Quartz Crystal
1 Introduction

1.1 Solid State Lighting using Light-Emitting Diodes (LEDs)

As our energy intensive lifestyles continue to put pressure on the sustainability of our environment, more efficient use and production of energy is being pursued in all areas of human activity. Renewable energy sources such as wind and solar have begun to gradually replace traditional fossil fuel-based energy production. At the same time, as incandescent light sources are being phased out of domestic and public usage and being replaced by fluorescent lighting, research has been ongoing to develop and optimize high-efficiency future generations of lighting devices. Solid-state lighting (SSL) and display technologies that employ light emitting diode (LED) technology have attracted much interest for their potential in efficient conversion of electricity to light.

![Image of historical and predicted efficacy of lighting sources](image1)

**Figure 1-1**: Historical and Predicted Efficacy of Lighting Sources[1]. (HID: high intensity discharge; OLED: organic light emitting diode)

As shown in Figure 1-1, compact fluorescent lighting (CPL) sources currently hold the edge in being the most prevalent efficient electricity-to-light conversion lamps. However, the luminous efficiency of SSL devices using LED technology is projected to overtake fluorescent technologies before 2020 [1]. Furthermore, LED technology boasts additional benefits over CPL,
which include improved durability, absence of mercury toxicity, shorter warm-up time, increased longevity, as well as an improved ability to sustain brightness throughout its operational lifetime [2].

LED lighting devices can be roughly divided into two classes: inorganic light emitting diodes (ILEDs or often simply LEDs) and organic light emitting diodes (OLEDs). Traditionally, ILEDs are made using heterostructures of nitrides such as gallium nitride (GaN), indium nitride (InN), aluminum gallium nitride (AlGaN), and indium gallium nitride (InGaN) [2]. Commercial LEDs require high quality crystalline nitride layers produced using organometallic vapor phase epitaxy (OMVPE). These layers are deposited on substrates such as sapphire and silicon carbide (SiC). Various challenges, such as poor-lattice matching, difficulty in dicing, and differences in thermal expansion constants, increase production costs [3]. In addition, indium (In) and gallium (Ga) present additional materials’ cost disadvantage compared to organic materials and the common microelectronic semiconductor silicon (Si).

There has been considerable interest in OLEDs as a candidate for solid state lighting and in display technologies. OLEDs can be further divided into two groups: small molecule light-emitting diodes (SMOLEDs) and polymer light-emitting diodes (PLEDs). SMOLEDs use complexed metal centres for light generation [4-5]. PLEDs use $\pi$-conjugated polymers with good conductivity and fluorescence efficiency [5]. Both share a common design for a typical device, as shown in Figure 1-2. The substrate is usually a high transmission glass for optical applications. The anode is usually a transparent conducting oxide (TCO) such as indium tin oxide (ITO). Hole injection layer or hole transport layer (HIL/HTL) injects the holes into the emission layer (EML) where light is generated. The electron injection layer or electron transport layer (EIL/ETL) injects electrons supplied from the cathode, typically a metal having a suitable work function.

![Figure 1-2](image-url): Typical design of an OLED.
OLEDs have numerous advantages, including low driving voltage, potential for high external quantum efficiency, and potential for streamlined processing methods such as inkjet printing [6]. However, there are also challenges at the present. Organic charge transport layers are inherently very resistive compared to inorganic conductive oxides. This prevents high-current-density operation, which is needed to achieve high population inversion for optimal brightness [7]. Shelf-life and stability also need improvement before large-scale commercialization is possible, because unfavorable ambient conditions such as moisture, oxygen, and temperature often rapidly degrade device performance [8-9].

1.2 Current State of Colloidal Quantum Dot LEDs

In recent years, much research has been done on inorganic colloidal quantum dot (CQD)-based LEDs as a candidate for SSL applications [10]. Inorganic CQDs emit light that is tunable by varying material composition [11] or crystal size [12]. Unlike organic dyes, inorganic nanocrystals show considerable resistance towards photo-oxidation [10]. Three popular designs for generating white light are shown in Figure 1-3: white light can be generated from nanocrystals of different color (top), from white light-emitting nanocrystals (bottom left), or from down conversion of blue light using nanophosphors (bottom right).

![Figure 1-3](image-url)

**Figure 1-3:** Three designs for generating white light using CQDs. Top: white light generation by mixing CQDs of various wavelength. Bottom left: direct white light generation from CQD emission layer. Bottom right: white light generation by mixing nanophosphors of different colors, with an excitation source due to a blue CQD LED [10].
Much of the work done in white light generation by mixing CQDs of various colors was done by the use of metal chalcogenide nanocrystals. Binary, tertiary, and even quaternary chalcogenide nanocrystals such as ZnS, ZnSe, PbS, PbSe, CdZnS, CdSe, ZnCdSe, ZnCuInS were often employed in a core-shell structure to produce the blue, green, and red colors needed to produce white light [11, 13-15]. There are three basic types of core-shell structures, as shown in Figure 1-4 [16]. In the figure, each box spans the bandgap of a given material, the outer boxes represent the bandgap of the shell, while the inner box represents that of the core. Type I structure is mostly commonly used, as the shell acts as a barrier to trap the carriers and passivate the surface of the nanocrystal it surrounds [16]. In Type II core-shell structures, the staggered placement of the bands causes significant red-shift in emission, as the effective bandgap is reduced [16]. Reverse Type I allows control over emission by varying shell thickness [16].

![Figure 1-4: Types of core-shell semiconductor nanocrystal structures [16].](image)

The common device structure for a CQD-LED bears much resemblance to that of an OLED device. As shown in Figure 1-5, the structure is virtually identical to a typical OLED structure, which was shown in Figure 1-2, the primary difference being that the organic-based emitter is now replaced by the quantum dot (QD) emission layer.
1.3 Silicon Nanocrystals and CQDs

Silicon (Si) has inherent advantages over other materials for SSL applications. It is significantly less expensive compared to materials such as germanium or gallium that are used in today's commercial SSL devices. Si is also relatively non-toxic compared to heavy metals such as Cd or Pb. In the nanocrystalline form, so far there has been no studies of toxicity of Si. One issue with Si is that it is not a direct bandgap semiconductor in its bulk state. At the nano length scale, however, Si nanostructures are capable of emitting light at room temperature due to quantum confinement effect [17-18].

Numerous 2-D and 3-D nanometer-scale silicon structures capable of luminescence have been demonstrated, including porous silicon, silicon nanocrystals (ncSi), silicon nanopillars, and super-lattices of silicon embedded in an insulator matrix [19-30]. Among these choices, ncSi has the advantages of allowing closer packing, as well as possibilities of further processing for higher monodispersity and further functionalization from encapsulation with organic ligands [31]. The potential of ncSi as a thin film LED device was demonstrated recently in a structure where organic transport layers were used for ETL and HTL [31].

**Figure 1-5**: A typical architecture of a CQD-LED device, showing the anode (TCO), HTL, ETL, quantum dot (QD), and cathode (Al) layers on glass.
1.4 Thesis Objective

In this research we propose and demonstrate a thin film LED structure based on colloidal ncSi using nickel oxide (NiO) and zinc oxide (ZnO) as charge transport layers. A systematic study of electronic, structural, and optical properties of the metal oxides was done, in order to identify the optimum process conditions for device fabrication. This constitutes the first demonstration of thin film LED using solution-processed ncSi CQDs and inorganic charge transport layers. Smooth NiO and ZnO layers were found to be electrically more conductive than organic charge transport layers in a device setting, providing an alternative to organic charge transport layers in OLEDs. Nanocrystalline silicon quantum dots showed tunable luminescent colors, and therefore present themselves as an environmentally friendly choice for display and lighting applications.

The structure of the thesis is organized as follows: Chapter 2 gives an introduction to nanocrystalline silicon as well as the structural elements constituting the proposed device. Chapter 3 describes various fabrication and characterization techniques and associated facilities/instrumentation. Chapter 4 presents the results of the experiments on structural, electronic, and optical properties of NiO, ZnO, as well as ncSi layers, thereby identifying optimal deposition conditions in preparation for first device fabrication. Chapter 5 concludes with a summary of the results of this research, highlighting the electrical and optical performance of ncSi LED devices, and a discussion of the challenges encountered and potential future directions.
2 Nanocrystalline Silicon and Device Concept

2.1 CQD ncSi Synthesis

A detailed account of the processes involved in nanocrystal synthesis is reported by Henderson et al [31-32]. Here for simplicity we only present the synthesis procedure. Sol-gel polymers were first synthesized by rapid addition of deionized water into trichlorosilane (HSiCl₃) at 0°C under an Argon (Ar) atmosphere. Resulting polymers were heat-treated at 1100°C in a slightly reducing atmosphere of 5%H₂/95%Ar for 1 hour to produce silicon nanocrystals embedded in a matrix of silicon oxides. Prior to liberation of the embedded nanocrystals, sodium chloride (NaCl) salt (2:1 mass ratio of NaCl: composite) was added and the mixture ground into fine powder. The salt was then removed from repeated washing. The resulting powder is then added to an etching solution which consisted of a 1:1:1 mixture of 49% HF(aq):H₂O:CH₃CH₂OH. The resulting freestanding hydrophobic, hydride-terminated silicon nanocrystals were extracted using hexanes. The nanocrystals were capped with decyl (C₁₀) groups by reaction with decene at 150°C under N₂ atmosphere.

2.2 Quantum Confinement Effect and Quantum Dot Luminescence

Nanostructures are typically defined to be structures having feature sizes smaller than 100nm in length [33]. Nanostructures with one or more dimensions confined to a length comparable to the exciton Bohr radius, typically less than tens of nanometers, experiences quantum confinement effect, which results in a widening of energy level spacing. Figure 2-1 gives a physical picture of a bulk material versus confinement in one, two, and three dimensions. The bulk material is often referred to as a 3D system, whereas confinement in one, two, and three dimensions are often referred to as 2D, 1D, and 0D systems, respectively. Figure 2-2 shows the resulting density of states for these systems. Note how each restriction within an additional dimension reduces total density of states.
A classic example was demonstrated by Ekimov et al. [35], as shown in Figure 2-3. CdS and CuCl nanocrystals embedded in a silicate glass matrix, showed blue-shifting of their optical absorption peaks as the crystal size decreased from greater than 300Å down to less than 20Å.
Figure 2-3: Blue-shift of optical absorption peaks in CdS and CuCl (the horizontal scale represents light energy while the vertical scale represents the optical density) [35]. Crystal sizes for CdS: 1 - 320Å, 2 - 23Å, 3 - 15Å, 4 - 12Å. Crystal sizes for CuCl: 1- 310Å, 2 - 29Å, 3 - 20Å.

The magnitude of the increase in band gap energy depends not only on the crystal size, but also on the material under consideration. For every material, the exciton Bohr radius $a_B = a_e + a_h$, where $a_e$ and $a_h$ are electron and hole Bohr radii, respectively. For crystals of size $R$, where $R \approx R$, one begins to observe the quantum confinement effect. As $R$ further decreases, further energy shifts are observed [34].

For silicon, the exciton Bohr radius $a_E$ is approximately 5nm. Therefore, for nanocrystals of sizes 5nm and lower, one would expect to observe visible shifts in its optical emission peaks due to the change in valence and conduction band energy levels. This was shown recently by Puzzo et al. [31]. Figure 2-4 shows an x-ray photoelectron spectrum of silicon nanocrystals measured against bulk silicon, showing a down shift of the valence band edge by 0.40eV due to quantum confinement [31]. The size-dependent photoluminescence of the silicon nanocrystals from quantum confinement was also demonstrated in the same study, shown in Figure 2-5, where crystals of average diameter 3.0nm yielded a peak centered at 645nm and crystals of average diameter 3.2nm yielded a peak centered at 685nm.
Figure 2-4: X-ray photoelectron spectrum (XPS) of silicon nanocrystals [31]. The measurement was referenced to the valence band edge of bulk silicon.

Figure 2-5: Size-dependent photoluminescence of the silicon nanocrystals [31]. The peak centered at 685nm corresponds to nanocrystals of average size 3.2nm, whereas the peak centered at 645nm corresponds to nanocrystals of average size 3.0nm.

2.3 Device Concept

The proposed device is shown in Figure 2-6. ITO serves as the anode, from where holes are injected. The holes traverse through the hole transport layer, nickel oxide (NiO), and into the ncSi layer. Aluminum (Al) serves as the cathode, from where electrons are injected. The
electrons traverse through the electron transport layer, zinc oxide (ZnO), and into the ncSi layer. Electrons and holes combine radiatively in the ncSi layer, thus producing light.

![Diagram](image)

**Figure 2-6**: Proposed structure for ncSi LED using metal oxide charge transport layers.

The band alignment is shown in Figure 2-7, where the band energy positions of ncSi, NiO, and ZnO are taken from Ref. [7, 31, 36] respectively. The work function of ITO is taken from reported values of between 4.3 to 4.7eV [37-39]. The potential barrier from NiO to the valence band of ncSi is very small (0V), facilitating efficient hole injection into the ncSi layer. Likewise, the voltage barrier from ZnO to the conduction band of ncSi is very small as well (0.3V), facilitating efficient electron injection. The potential difference between the conduction band energies of NiO and ncSi is approximately 1.9eV, which traps injected electrons. Likewise, the valence band energies of ZnO and ncSi differ by 1.8eV, trapping injected holes. This symmetrical formation of energy level alignment will ensure balanced charge injection, which is important in avoiding undesirable problems such as excessive background current and luminescence quenching due to quantum dot charging [7]. Additionally, it is also important that the charge transport layers be mechanically smooth and structurally amorphous, in order to minimize possibilities of current shorting pathways and formation of preferred current channels within the device [7].
A similar structure was reported by Cheng et al. [40], using free standing nanocrystalline silicon produced by plasma synthesis from silane gas. Cheng’s study also reported the use of sputter deposited NiO layers and ZnO layers deposited by atomic layer deposition. There are several key differences that warrants this present study. First, nanocrystals used in the present study are synthesized using a solution-based synthesis method, which may yield different material properties. Second, quantum dots with capped ligands are used in this study, in contrast to free-standing silicon nanocrystals. Lastly, the use of sputter deposition for the ZnO layer is expected to result in a more straightforward deposition procedure, compared to atomic layer deposition.
3 Experimental Apparatus and Characterization Techniques

3.1 Sample Fabrication

3.1.1 Sample Preparation

Corning 1737 glass of 0.7mm thickness was used as the substrate for a variety of experimental syntheses as well as device fabrication. Corning 1737 is a boro-aluminosilicate glass, with typical compositions of 55.0% SiO$_2$, 7.0% B$_2$O$_3$, 10.4% Al$_2$O$_3$, 21.0% CaO, and 1.0% Na$_2$O. All glass substrates were cut into squares of 24mm in side length. Cut glass substrates were subjected to the following cleaning procedure: i) washing in de-ionized (DI) water, ii) 5 minutes sonication in acetone, followed by 1 minute dip in DI water, iii) 5 minutes sonication in isopropyl alcohol, iv) blow dry with a gentle nitrogen stream. The cleaning procedure removes organic surface contaminants. This cleaning procedure was also followed for Si substrates of various sizes; silicon substrates were used for ellipsometry studies.

3.1.2 RF Magnetron Sputtering

Sputtering is a deposition process where a plasma is used to knock atoms/clusters off the surface of a bulk material source, where the source material is also referred to as a sputtering target. Figure 3-1 shows the schematic diagram for typical sputtering setup. The system used for in this study was manufactured by Kurt J. Lesker. After evacuation of the chamber to a base vacuum of $<10^{-7}$ Torr, a working gas, typically Ar, is introduced. The chamber pressure during deposition is typically a few to hundreds of millitorrs [41]. The bulk material, or the target, is held at a positive bias with respect to the gas ring, from which the working gas is introduced. Once a glow discharge is ignited at a sufficiently high DC voltage, net charge flows from the target in the direction of the substrate with subsequent deposition of neutral and charged atoms and clusters. It is the energetic positive gas ions in the discharge that strike the cathode and thus knock-on energy is transferred to the atoms in the target material. Atoms with sufficient energy are ejected from the target and traverse to the substrate where deposition occurs. Temperature control over the substrate during deposition is possible with use of a radiative heater coil placed behind the substrate holder. In an RF setup, an RF matching network alternates the field at 13.56MHz. Figure 3-2 shows the interior of the sputtering chamber. In this study, RF magnetron sputtering
was used to deposit NiO and ZnO layers, as well as patterned ITO (indium tin oxide) contact strips. The sputtering system and the electron-beam deposition system, described in detail later, both employ a common load-lock chamber. Samples inserted into the load-lock chamber are pumped down using a turbomolecular vacuum pump to a pressure of $10^{-5}$ Torr, before being transferred into the deposition chamber. This minimizes environmental contamination from the atmosphere and also helps to remove gas molecules adsorbed on the surface of the substrate before deposition.

![Rotating Substrate Holder](image)

**Figure 3-1:** A schematic diagram showing the setup of a sputtering system.
3.1.3 Electron Beam Deposition

Electron beam (e-beam) deposition is a physical vapor deposition (PVD) technique commonly used for metal thin film depositions. During e-beam deposition, the metal source, usually in the form of pellets, is held in a crucible under high vacuum. An electron beam is focused by magnets onto the metal source. As the metal absorbs the electrons, kinetic energy is transferred to the metal, causing it to heat up rapidly. As the metal reaches the vaporization point, metal atoms evaporate into the vacuum and thus diffuse to the substrate sample where the film growth process occurs. In this study, Al contacts on the devices were formed using e-beam deposition. Figure 3-3 shows the interior of the e-beam evaporation chamber.

**Figure 3-2**: Photograph of the interior of the sputtering chamber, showing the location of the two targets, the gas ring, and thickness sensors.
3.1.4 Thickness Monitor During E-beam and Sputtering Deposition

Thickness during e-beam and sputtering deposition is monitored using a quartz crystal sensor. The quartz crystal oscillates at a resonant frequency that changes as the material is deposited on
the exposed side. Critical parameters for accurately monitoring film growth are the material density, the crystal tooling constant, and the \( z \)-factor [42]. Material density, or \( \rho \), is readily available from the manufacturer. The relative location of the crystal sensor with respect to the location of the sample determines the crystal tooling constant. This quantity is expressed as a percentage value, and should be constant for a particular deposition system even when different materials are used. The \( z \)-factor is used to match the acoustic impedance of the deposition material to that of the quartz crystal, as shown in Eq. 3-1, where \( Z_q \) is the acoustic impedance of the quartz crystal, and \( Z_m \) is the acoustic impedance of the deposition material [42].

\[
z \text{- factor} = \frac{Z_q}{Z_m} \quad \text{(Eq. 3-1)}
\]

The crystal tooling constant can be determined by referencing the quartz crystal oscillator measurement against the thickness of a given film measured by another method, such as profilometry or spectroscopic ellipsometry; this is done using a new quartz sensor, when the \( z \)-factor is approximately equal to 1 [42]. Once the crystal tooling factor is known, the accurate \( z \)-factor can be determined by referencing with the thickness of a known film, using a well-used crystal.

### 3.1.5 Spincoating Deposition

Spincoating is a deposition method commonly used to deposit a solution-based precursor onto a substrate. A substrate is secured to a rotating stage by vacuum and spun at typical speeds of 500-6000 revolutions per minute (RPM) while a solution-based precursor is dropped onto the substrate. The ability for the solution to adhere to the substrate is termed the wettability of the substrate. As the solution is dropped onto a spinning, wettable substrate, it spreads outwards, coating the entire substrate. Due to the rapid rate of substrate rotation, liquid solution on the substrate quickly solidifies in two stages. First, excess liquid is expelled from the surface toward the outer edge with decreasing thickness of the liquid solution on the substrate, often resulting in the formation of a film of uniform thickness on the substrate. Second, rapid evaporation of the solvent occurs, which further solidifies the film.
3.2 Characterization Techniques

3.2.1 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a non-destructive, optical technique where polarized light is measured after its reflection from a sample substrate. From SE measurement data for a thin film along with a bench-marked optical model, one can extract parameters such as refractive index, thickness, optical bandgap, and other useful information through regression fitting of the data. In this study, SE measurements were used to measure thickness of TCO films for quartz thickness sensor calibration, as well as provide bandgap data for NiO and ZnO.

The Cauchy model approximates the index of refraction $n$ using three parameters $A$, $B$, and $C$, as shown in Eq. 3-2 [43]. The model assumes that the material is non-absorbing in the range of $\lambda$ modeled.

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + ... \text{ (Eq. 3-2)}$$

The Tauc-Lorentz model can be used to model the absorption behavior of amorphous semiconductors in order to extract the band gap [43]. The Tauc-Lorentz method is based on the Tauc plot [44], which models the imaginary part of the dielectric function near the band edge for an amorphous semiconductor using the expression shown in Eq. 3-3. Here $\varepsilon_2$ represents the imaginative part of the dielectric function, $E_g$ the band gap energy, $A_T$ a constant, and $\Theta$ the Heaviside function. $\varepsilon_2$ is related to the refractive index $n$ and the extinction coefficient $k$ by Eq. 3-4, while the absorption coefficient $\alpha$ is related to the extinction coefficient $k$ by Eq. 3-5.

Therefore when one plots $\alpha^{1/2}$ against photon energy $E$, the extrapolated intercept on the $E$ axis yields the magnitude of $E_g$ [45].
\[ \varepsilon_2(E) = A_r \frac{(E - E_g)^2}{E^2} \Theta(E - E_g) \quad (Eq. 3-3) \]

\[ \varepsilon = \varepsilon_1 + i \varepsilon_2 = \varepsilon \varepsilon_2 = (n + ik)^2 \quad (Eq. 3-4) \]

\[ \alpha = \frac{4 \pi k}{\lambda} \quad (Eq. 3-5) \]

### 3.2.2 Profilometry

Profilometry is a physical method that profiles a surface by use of a stylus-type probe. An Alphastep 200 profilometer was used in this study. For this profilometer, a stylus tip is gently brought into contact with the sample surface by use of a spring mechanism. The stylus is dragged across the sample surface along an axis during measurement. Scanning speeds may be set from 40nm/s up to 5μm/s, to suit roughness and the desired scanning length of the sample. For thin films from 20 to 100 nm in thickness, the profilometry provides a first order estimate of thickness, which is needed as initial estimates to ellipsometry data fitting. For samples of thickness on the order of microns, measurement from profilometry serves as a quick, and reliable replacement for ellipsometry and electron microscopy techniques. For this reason, profilometry was used for the calibration of quartz thickness monitors.

### 3.2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a physical probing method that provides surface profile details over a small area. Surface roughness is an important property to be monitored in thin film depositions. Figure 3-4 shows a schematic diagram of a typical AFM. In contact mode, used in this study to profile roughness of the TCO films, the cantilever is placed in light, physical contact with the sample, and is drawn across the sample as the measurement is made. A laser is positioned to reflect off the top of the cantilever, to be captured by a photo diode. By segmenting the photodiode into distinct areas and by sensing the deflected light in different areas of the photodiode, the system can sense the direction and magnitude of the deflection of the cantilever, which is then processed by computer software to show topological mapping of an area.
There are two commonly used quantification methods for roughness, average roughness and root mean squared roughness.

**Average roughness** $R_a$, which is a numerical average of measured roughness, is defined as:

$$R_a = \frac{1}{n} \sum_{j=1}^{n} |y_j| \quad \text{Eq. 3-6}$$

where $n$ is the number of data points, and $y_j$ is the vertical distance from the mean line to the $i^{th}$ point.

**Root mean squared (RMS) roughness** $R_q$ is a weighted average of measured roughness, which is defined as:
\[ R_q = \sqrt{\frac{1}{n} \sum_{i=1}^{n} y_i^2} \text{ (Eq. 3-7)} \]

\( R_q \) gives a better picture of the magnitude of roughness variation.

### 3.2.4 Photoluminescence

Photoluminescence (PL) involves the creation of an electron-hole pair by the absorption of energetic incident radiation, and then detecting the subsequent radiative recombination of the electron-hole pair that results in characteristic photon emission. High energy resolution makes the method a reliable measurement in applications such as impurity identification in semiconductors [45]. In this study, a Perkin-Elmer LS 55 fluorescence spectrometer was used to characterize the shape and the location of emission peak for ncSi CQDs using PL. A monochromator was used to isolate the excitation wavelength, in order to distinguish it from the emission spectrum.

### 3.2.5 Photoemission Spectroscopy (PES)

Photoemission spectroscopy (PES) is an analytical technique performed in vacuum, that is primarily used to identify chemical species at a sample surface [45]. Both x-ray and ultraviolet rays may be used as the incoming radiation. X-rays (x-ray photoelectron spectroscopy, XPS) causes emission of core electrons, whereas UV light (ultraviolet photoelectron spectroscopy, UPS) interacts with valence electrons. Figure 3-5 shows the schematic diagram of an XPS setup: the x-ray source generates x-rays that strikes the sample and results in electron emission, which in turn are captured and counted by appropriate electronics. Electrons can be emitted from any orbital by the process of photoemission when the energy of the x-ray exceeds the electron binding energy. The process is surface sensitive, because the emitted electrons are from the top 0.5-5 nm surface of the sample.

*Figure 3-5: Schematic diagram of an XPS setup [45].*
Figure 3-6: X-ray absorption and electron ejection during XPS [45].

Figure 3-6 demonstrates the process of x-ray absorption and electron emission. The binding energy $E_b$ of an emitted electron, referenced to the Fermi energy $E_F$, can be calculated from Eq. 3-8,

$$E_b = h\nu - E_{sp} - q\phi_{sp} \quad \text{(Eq. 3-8)}$$

where $h\nu$ is the energy of the x-ray, $E_{sp}$ the measured energy of the emitted electron, $\phi_{sp}$ the work function of the spectrometer, and $q$ an elementary charge or $1.602\times10^{-19}$C. As we can see from the equation, it is important that the x-ray source be monochromatic so that an accurate $E_b$ can be extracted.
Figure 3-7: Schematic diagram of PES processes, showing the location of the secondary edge [46].

Figure 3-7 shows the PES process. As can be seen, the onset of electron emission occurs at the secondary edge, where the minimal net energy input of $\Phi_s$, or the sample work function, causes electron emission. Mathematically, $\Phi_s$ can be calculated by

$$\Phi_s = E_{SC} + V_a - h\nu \quad (\text{Eq. 3-9})$$

where $E_{SC}$ is the binding energy at secondary edge, $h\nu$ the photon energy of the system, and $V_a$ the applied bias, an extra parameter used during measurement (not shown in the figure). In this study, monochromatic Al Kα ($h\nu = 1486.7$ eV) was used as source x-ray for XPS measurements.
3.2.6 X-Ray Diffraction

X-ray diffraction (XRD) is often used to determine crystallinity and phases within a solid. The measurement process involves exposing a solid sample to a source of x-rays of a known wavelength $\lambda$, and accordingly sensing the diffracted signal. The angle of incidence of the source equals the angle of reflection of the detector. A spectrum is generated as the source and the sensor go through a range of angles. Eq. 3-10 shows the relationship between angle of the detector $\theta$, wavelength of the x-ray source $\lambda$, with interplanar spacing $d$ [41]. Here $n$ can be any integer. Eq. 3-10 states that for any set of $n$, $d$, and $\theta$ for which the equation is valid, constructive interference will occur and the detector will sense an amplified diffracted signal.

$$n\lambda = 2d \sin \theta \quad \text{(Eq. 3-10)}$$

The interplanar spacing $d$ is related to the lattice constant of the material $a$, and the Miller indices of the diffracting plane, $h$, $k$, and $l$, by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{(Eq. 3-11)}$$

Thus, by knowing $\lambda$, $\theta$, and $n$, one can calculate $d$ for a diffraction pattern, which in turn allows us to identify the diffracting plane and verify that the correct phases and materials are in the sample.

The setup used was a Philips XRD system consisting of the following basic components: a PW 1830 HT generator, a PW 1050 goniometer, PW3710 control electronics, and X-Pert system software. Copper (Cu) Kα1 radiation ($\lambda=0.154\text{nm}$) was used as x-ray source. A nickel (Ni) filter was used to block off Cu Kβ radiation, so that the resulting x-ray emission is monochromatic.

3.2.7 Electroluminescence

In this study, Electroluminescence (EL) measured photon output as the LED device was driven by a voltage source. A Keithley 2440 source meter was controlled by a LabVIEW program to drive the device by using regularly timed step increases in a voltage range from -40V to +40V. 100mA was set as the compliance current. The meter has a noise background on the order of 1nA, which was at least two orders of magnitude below the lowest device current measured during experiments.
Two types of detectors were used in this study: a photometer and a photomultiplier tube (PMT). A photometer typically measures intensity of the light that is visible to the human eye, while the PMT is capable of sensing light below the visibility threshold and also infrared (IR) emissions. A schematic diagram of the electrical and electroluminescence setup is shown in Figure 3-8.

**Figure 3-8:** A schematic diagram of the experimental setup for electrical and electroluminescence setup. A LabVIEW program controls the Keithley 2440 sourcemeter, which powers the sample, while simultaneously feeds current-voltage data back to LabVIEW. Luminance meter and spectrophotometer allows simultaneous optical data acquisition by LabVIEW. The light emission can also be sensed by naked eyes, and by a photomultiplier tube (PMT). A multimeter is used to collect emission strength, measured in PMT output voltage.
4 Experiments on Device Layers

4.1 Overview

Optimization of the individual layers of the CQD ncSi LED was necessary before fabrication of complete devices. Table 4-1 outlines the requirements for the various layers. The focus of this chapter is to present detailed experimental results of all the materials studies. Device integration, characterization and analysis are presented in chapter 5.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Requirements</th>
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<tbody>
<tr>
<td>ITO</td>
<td>• low surface roughness</td>
</tr>
<tr>
<td>NiO</td>
<td>• low absorption over visible wavelengths</td>
</tr>
<tr>
<td></td>
<td>• low surface roughness</td>
</tr>
<tr>
<td></td>
<td>• sufficient electrical conductivity</td>
</tr>
<tr>
<td>CQD ncSi</td>
<td>• low surface roughness</td>
</tr>
<tr>
<td>ZnO</td>
<td>• low absorption over visible wavelengths</td>
</tr>
<tr>
<td></td>
<td>• low surface roughness</td>
</tr>
<tr>
<td></td>
<td>• sufficient electrical conductivity</td>
</tr>
</tbody>
</table>

Table 4-1: Requirements for individual layers of a CQD ncSi LED.

4.2 TCO Layers Optimization

4.2.1 Quartz Thickness Monitor Calibration

The quartz thickness monitor can be calibrated by carrying out measurements with the ellipsometer and the profilometer. A thin film of thickness 20-100nm was first deposited. The film thickness was then determined using the Cauchy model fitting of the ellipsometry data, for photon energies in the range of 1.5eV to 2.0eV. Figure 4-1 shows a fitted data set, the top curve showing an α plot and bottom curve showing a β plot, both quantities measured by ellipsometry.
There is good fit with $R^2 = 0.999$ for a thickness of $28.81 \pm 0.02$ nm, and a refractive index of $n = 2.01$. Using the known crystal tooling factors that correspond to the two target locations, the $z$-factors for NiO and ZnO that yield the correct thickness were determined. The correct calibration was confirmed by monitoring thick film depositions that were confirmed by profilometry. The parameters used for subsequent experiments and device fabrication are listed in Table 4-2.

**Figure 4-1:** Fitted ellipsometry data for a NiO thin film. Top plot shows fitted (green) curve for $\alpha$ (red). Bottom plot shows fitted (green) curve for $\beta$ (red).
Figure 4-2: Profilometry plot for a 1.7μm NiO thin film, used for calibration of the quartz sensor.

Figure 4-3: Profilometry plot for a 1.2μm ZnO thin film, used for calibration of the quartz sensor.
4.2.2 Deposition Rates

The effects of varying chamber pressure and RF power on the deposition rates of NiO and ZnO were investigated. The NiO and ZnO sputtering targets in stoichiometric ratios were supplied by Kurt J. Lesker. For all TCO depositions, the sputtering chamber was pumped down to $10^{-7}$ Torr or lower after sample loading, in order to minimize the impurity content in the films. All test samples were timed and deposited to a thickness of 20nm, as confirmed by ellipsometry. The sputtering gas (Ar) flow rate was kept constant at 20sccm. The results are shown in Table 4-3.

<table>
<thead>
<tr>
<th>Material</th>
<th>NiO</th>
<th>ZnO</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Location</td>
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<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$\rho$</td>
<td>7.45</td>
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</tr>
<tr>
<td>Crystal Tooling</td>
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<td>45.7</td>
<td>33.3</td>
</tr>
<tr>
<td>Z-Factor</td>
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<td>0.556</td>
<td>1</td>
</tr>
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</table>

*Table 4-2: Summary of thickness monitor parameters for TCOs after calibration.*
<table>
<thead>
<tr>
<th>Material</th>
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<th>Chamber Pressure (mTorr)</th>
<th>Rate (Å/min)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td></td>
<td>100</td>
<td>3</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>3</td>
<td>8.34</td>
</tr>
<tr>
<td>ZnO</td>
<td>50</td>
<td>3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5</td>
<td>7.8</td>
</tr>
</tbody>
</table>

**Table 4-3**: Effects on RF power and chamber pressure on the deposition rate of NiO and ZnO.

As Table 4-3 shows, over all, both NiO and ZnO tend to deposit at slow rates, even at powers of 100W and 125W. Also notable is that changing chamber pressure from 3mTorr to 5mTorr has little effect on the deposition rates of both oxides at 100W RF power. Further, increasing the power directly results in an increased deposition rate.

### 4.2.3 Absorption Studies

Using a Perkin-Elmer Lambda 18 UV/VIS spectrometer, transmission of NiO and ZnO films were measured. For the deposition of both materials the chamber pressure was maintained at 3mTorr. In both cases, 20nm-thick films on 0.7mm Corning 1737 glass substrates were used. A reference curve of the glass substrate is also shown in the transmission plot for NiO in Figure 4-4. The rapid decline in transmission with decreasing wavelength starting at approximately 350nm is expected and confirms reports in the literature [47-48]. Of interest to this study is the limited absorption at 600-700nm, specifically showing transmission of greater than 70%. This is important as it is expected that the emission peak of the CQD ncSi will fall in this range. The data also indicates that the RF power used in the deposition has little effect on absorption properties.
A similar set of experiments was done for ZnO. The data is shown in Figure 4-5. The cause of the transmission dip or absorption peak at approximately 360nm is unclear, as the optical and electronic properties of ZnO are highly sensitive to slight changes in deposition conditions and often vary between different deposition systems [49-52]. However, as the graph shows, there is excellent transmission of greater than 80% for light of wavelengths of 600-700nm.

Figure 4-4: Transmission spectra of 20nm thick NiO films deposited on 0.7mm Corning 1737 glass substrate.

Figure 4-5: Absorption spectrum of 50nm ZnO film deposited on 0.7mm Corning 1737 glass.
4.2.4 Electrical Conductivity Studies

For a thin film of isotropic material, sheet resistance $R_s$ is related to electrical resistivity $\rho$ by:

$$R_s = \frac{\rho}{t} \text{ (Eq. 4-1)}$$

where $t$ stands for film thickness. Therefore, by knowing $R_s$ and $t$, one may calculate $\rho$. $R_s$ was measured using a FOUR DIMENSIONS 101C 4-point probe station, and $t$ was measured using ellipsometry. For ITO contacts used in this study, we relied on previous experimental work in the group which has established a good recipe for ITO with resistivity of $6 \times 10^{-3} \, \Omega \text{.cm}$. Figure 4-6 shows the effects of sputtering gas and deposition temperature on the resistivity of NiO films. As the figure shows, the resistivity of the sample sputtered in pure Ar at room temperature held steadily at $125 \, \Omega \text{.cm}$. Resistive TCO layers may contribute to heating and also higher turn-on voltage for the devices. For this reason, attempts were made to decrease the resistivity of the NiO layer by increasing the oxygen content. By increasing the oxygen-to-nickel ratio, it was reported that the conductivity was found to be enhanced due to increases in Ni$^{3+}$ concentration [53]. By substituting the Ar sputtering gas with a 5% O$_2$-Ar mixture, additional oxygen was introduced. The orange line in Figure 4-6 shows the resistivity for a sample deposited at room temperature. As shown in the figure, although the resistivity showed an immediate improvement of two orders of magnitude at the time of deposition, within 24 hours, the resistivity quickly surpasses that of the film sputtered in Ar. By heating the substrate, during NiO deposition, to temperatures of 150, 175, 200, and 225°C, the deterioration in electrical conductivity can be delayed significantly, as shown in Figure 4-6. This confirms published reports on improved electrical stability of NiO films prepared at deposition temperatures ranging from 200 to 300°C [54]. However, because the electrical resistivity of the oxygen-doped NiO film cannot be held at a stable value, NiO sputtered in pure Ar was used for actual device fabrication.
Sheet resistance measurements on room temperature deposited ZnO was also performed. Over a course of ten days, the resistivity was stable at 1.06kΩ cm. This value is acceptable, considering it is within one order of magnitude of the resistivity of NiO deposited at room temperature (125Ω cm). Because ZnO is the last step in the fabrication process and further heat treatment may negatively impact the entire device, heat treatment studies were not conducted.

### 4.2.5 XPS Measurements

XPS measurements were performed on both ZnO and NiO to determine the location of the Fermi energy. In order to minimize surface contamination, ZnO and NiO films were deposited on n-type crystalline silicon substrates immediately before measurement. The sample spent less than ten minutes in air during sample preparation and transfer into the XPS measurement chamber. Using Eq. 3-9, mentioned in the previous chapter, $\Phi_s$ was calculated for NiO and ZnO, using an applied bias $V_a$ of 15V and an x-ray energy $h\nu$ of 1486.7eV. Figure 4-7 and Figure 4-8 show the
XPS spectra in the vicinity of the secondary edge for NiO and ZnO, respectively. The work functions for both materials are shown in

$$\Phi_s = E_{SC} + V_d - h\nu \quad \text{(Eq. 3-9)}$$

**Figure 4-7**: XPS spectra in the vicinity of the secondary edge for NiO.

**Figure 4-8**: XPS spectra in the vicinity of the secondary edge for ZnO.
Material Work Function $\Phi_s$ (eV) (±0.1 eV)

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Phi_s$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>4.9</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 4-4: Work functions of NiO and ZnO as measured by XPS.

Comparing the measured work function to previously reported values of conduction and valence band energies [7, 36] for NiO (1.8eV and 5.5eV) and ZnO (4.0eV and 7.3eV), it is clear that the majority carrier in NiO in this study is p-type and that of ZnO is n-type. These characteristics are important since NiO is in charge of hole transport and ZnO electron transport.

4.2.6 Bandgap Determination Using Tauc-Lorentz Model

For 20nm thin films of NiO and ZnO, ellipsometry measurements were made with photon energies spanning from 1.5eV up to 5eV. Good fits of ellipsometry data for NiO films were obtained using initial estimates of 20nm for film thickness and 3.6eV for bandgap energy $E_g$. The fitted curves are shown in Figure 4-9, Figure 4-10, and Figure 4-11. Table 4-5 summarizes extracted bandgap energies $E_g$ and the fitting error, measured in $R^2$. Note that $E_g$ stays relatively constant at 3.1 eV, relatively independent from deposition power. On the other hand, no good fits of data for the ZnO film were achieved, as shown in Figure 4-12. This is likely due to the ZnO film being more crystalline in nature, whereas the Tauc-Lorentz model is more suitable in modeling amorphous semiconductors.

<table>
<thead>
<tr>
<th>Deposition RF Power (W)</th>
<th>Extracted $E_g$ (eV)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.04 ± 0.04</td>
<td>0.999680</td>
</tr>
<tr>
<td>100</td>
<td>3.16 ± 0.04</td>
<td>0.999681</td>
</tr>
<tr>
<td>125</td>
<td>3.17 ± 0.04</td>
<td>0.999624</td>
</tr>
</tbody>
</table>

Table 4-5: Summary of Tauc Lorentz fitting of NiO ellipsometry data.
Figure 4-9: Fitting of ellipsometry data for 20nm NiO film, deposited at 50W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).
Figure 4-10: Fitting of ellipsometry data for 20nm NiO film, deposited at 100W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).
Figure 4-11: Fitting of ellipsometry data for 20nm NiO film, deposited at 125W RF power, using Tauc Lorentz model. Green curve is a fit of raw data (pink).
Figure 4-12: Attempted fitting of ellipsometry data for a 20nm ZnO film. Green curve is a fit of raw data (pink).
4.2.7 X-Ray Diffraction

Thick films of NiO and ZnO of 1.5μm thickness were deposited on 0.7mm Corning 1737 glass for XRD analysis. Copper (Cu) Kα1 radiation (λ=0.154nm) was used. Figure 4-13 shows the diffraction pattern for NiO, the peaks for the planes (111) and (200) are found as expected, confirming past reports in literature [53-54]. Because Ni is just below Cu on the periodic table, Cu x-rays can excite or fluoresce Ni x-rays. This contributed to the noisy baseline of the measurement for the NiO sample. Similarly, Figure 4-14 shows the diffraction pattern for ZnO, the peaks for the planes (002) and (101) are found as expected, confirming literature findings [51-52]. The diffraction signals for ZnO are clearly visible, which shows that the ZnO film was somewhat crystalline in nature, rather than amorphous. This may help to explain why the Tauc-Lorentz model successfully fitted $E_g$ for NiO, whereas the model failed to provide a fitting for $E_g$ for ZnO based on ellipsometry data, since Tauc-Lorentz model assumes that the material is amorphous.

![XRD for NiO](image)

**Figure 4-13: XRD pattern for NiO**
4.3 CQD ncSi Layer Experiments

4.3.1 Spin-coating Rate

The rate of rotation of the spincoater, stated in revolutions per minute (RPM), affects the thickness of films fabricated using the spin-coater. On the other hand, the film thickness was also affected by the viscosity and precursor concentration in the solution, namely, the concentration of ncSi CQDs in the hexane solution. Because the concentration of ncSi CQD varied between batches and cannot be precisely determined, it was necessary to calibrate the RPM versus film thickness for each batch, to ensure repeatability of ncSi layer thickness in consecutive experiments. Each spin-coated ncSi sample was heat-treated at 110°C in a N₂ glovebox in order to remove excess solvent while being in an environment that does not promote surface oxidation of the quantum dots. This calibration was done for each new batch of ncSi CQD, and sometimes repeated within the same batch in order to ensure consistency. Figure 4-15 shows typical curves for spincoating rate versus film thickness. As the figures show, typically by 2000RPM the film thickness reaches a stable value. There is typically a 10-15nm range in film thickness that can be tuned by changing the spincoating rate. During the study, when the viscosity of the solution was incapable of producing the right film thickness, hexane was carefully added to dilute the solution or the solution was subjected to evaporative concentration by gently blowing a nitrogen stream over the solution until the viscosity attained was able to produce films of desired thickness.
4.3.2 Photoluminescence Studies

As mentioned in the previous chapter, emission peaks of the ncSi films from PL are related to the bandgap of the quantum dots. Emission peaks from PL give a good indication of the emission when the device is driven in an EL mode. Figure 4-16 shows the PL data for thin films made from two batches of CQD ncSi that are capped with decyl (C10) groups, designated by the letters A and B. As the plot shows, for Batch A, at all three excitation frequency (400, 420, and 440nm) the film photoluminescence peaked at 594nm. Similarly, for batch B, the ncSi films showed photoluminescence behavior that peaked at 628nm. Both wavelengths correspond to orange color in the visible spectrum.
Figure 4-16: Photoluminescence curves of two batches of CQD ncSi, designated by letters A and B. The number on the legend represents frequency of excitation.

4.4 AFM Roughness Measurements

Roughness of the device is an important parameter to note as each layer is deposited, because excessive roughness can cause current leakage pathways, since each functional layer is only tens of nm in thickness. AFM measurements of a number of films are summarized in Table 4-6. Corning 1737 glass substrate (Figure 4-17), cleaned by the standard cleaning procedure outlined earlier, yields an $R_a$ value of 3.00nm, which provides a baseline for subsequent measurements. 20nm of NiO deposited at RF powers of 25W (Figure 4-18) and 50W (Figure 4-19) only slightly increases $R_a$ to 3.5nm and 4.0nm, respectively. At 100W (Figure 4-20) and 125W (Figure 4-21), $R_a$ increases to moderate levels of 8.6nm and 10.5nm. At 150W (Figure 4-22), $R_a$ increases substantially to 41.3nm, due to increased deposition rate. 50nm ZnO deposited at 100W (Figure 4-23) shows a very low $R_a$ of 2.8nm, essentially unchanged from the roughness of the glass. Layered structures of 50nm NiO/30nm ncSi/20nm ZnO were made to study roughness as each layer was added. 100W RF power was used for NiO depositions in order to balance roughness with an acceptable deposition rate. The NiO/ncSi (Figure 4-24) bilayer structure, measured prior
to ZnO deposition, yielded $R_a$ of 3.4nm, showing that the ncSi layer served to smoothen the underlying NiO layer. This is a reflection of the small crystal size of ncSi, expected to be between 2 to 3nm. $R_a$ of the trilayer NiO/ncSi/ZnO structure (Figure 4-25) was satisfactorily low at 3.6nm. Note that while $R_a$ gives some indication of the magnitude of roughness fluctuations, these values may be over-estimated due to the presence of dust considering that the AFM scans were not carried out in a cleanroom environment.

An SEM cross-sectional view of a 2μm NiO film on crystalline silicon substrate, grown at 100W RF power, is shown in Figure 4-26. It is interesting to note that NiO grew into columns. As the thickness increased, the columns, initially about 10 nm in diameter, increased to about 100nm in diameter as the film surpassed 300nm in thickness. At 20nm thickness, the film was made up of fine columns of about 10nm in diameter. This confirmed our roughness measurement of 20nm NiO films sputtered at 100W, which had an average roughness of 8.6nm. The SEM image shows that the NiO was columnar in structure at 20nm thickness, with column diameter in the nanometer range. The presence of columns was not ideal in the context of this device, since voids and grain boundaries may cause the formation of preferential current pathways inside the device during operation [7].
<table>
<thead>
<tr>
<th>Material</th>
<th>Average roughness $R_a$ (nm) (± 0.5nm)</th>
<th>RMS roughness $R_q$ (nm) (± 0.5nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corning 1737 glass substrate</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>NiO (20nm, 25W)</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td>NiO (20nm, 50W)</td>
<td>4.1</td>
<td>5.4</td>
</tr>
<tr>
<td>NiO (20nm, 100W)</td>
<td>8.6</td>
<td>11.1</td>
</tr>
<tr>
<td>NiO (20nm, 125W)</td>
<td>10.5</td>
<td>22.9</td>
</tr>
<tr>
<td>NiO (20nm, 150W)</td>
<td>41.3</td>
<td>51.4</td>
</tr>
<tr>
<td>ZnO (50nm, 100W)</td>
<td>2.8</td>
<td>3.4</td>
</tr>
<tr>
<td>NiO (20nm, 100W)/ncSi (30nm)</td>
<td>3.4</td>
<td>5.1</td>
</tr>
<tr>
<td>NiO (20nm, 100W)/ncSi (30nm)/ ZnO (50nm, 100W)</td>
<td>3.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

**Table 4-6**: AFM investigation of average and RMS roughness of the deposited films in aid of examining the effects of RF deposition power on NiO film and studying the expected changes in the surface roughness with layer by layer growth of a actual device.
Figure 4-17: AFM surface profile of Corning 1737 glass.

Figure 4-18: AFM surface profile of NiO deposited at 25W RF power.
Figure 4-19: AFM surface profile of NiO deposited at 50W RF power.

Figure 4-20: AFM surface profile of NiO deposited at 100W RF power.
Figure 4-21: AFM surface profile of NiO deposited at 125W RF power.

Figure 4-22: AFM surface profile of NiO deposited at 150W RF power.
**Figure 4-23:** AFM surface profile of ZnO deposited at 100W RF power.

**Figure 4-24:** AFM surface profile of NiO/ncSi structure.
**Figure 4-25**: AFM surface profile of NiO/ncSi/ZnO structure.

**Figure 4-26**: SEM micrograph of the cross-section of a 2μm NiO, deposited on a crystalline silicon substrate.
5 Device Fabrication, Results, & Analysis

5.1 Device Fabrication

Corning 1737 glass was cut into squares of 24mm in length and cleaned as outlined in Section 3.1.1. 300nm of ITO, which has a sheet resistance of $20\,\Omega/\square$, was deposited in a pattern of strips as shown in Figure 5-1.

![Figure 5-1: ITO contact strip design, showing dimensions of ITO strips (black) and glass (white).](image)

A shadow mask was used for fabrication of the patterned ITO strips. The shadow mask was made by laser-scribing of 280µm crystalline Si wafer pieces. The cross-sectional view of the
contact strip was measured by profilometry, shown in Figure 5-2. As the cross-section shows, the contact strip shows gradual sloping of thickness at the edges, this was likely due to the thickness of the shadow mask. Although photolithography processing will give sharper drop-offs at the edges of the contacts, for LED devices in this study, gradual sloping may be beneficial, since it may reduce possibilities of current shorting between layers.

![Graph](image)

**Figure 5-2**: Cross section of ITO strips, measured by profilometry.

The glass samples with the patterned ITO strips were washed with isopropyl alcohol and dried using a nitrogen stream, before loading into the sputtering chamber. NiO was deposited at 50W RF power and 3mTorr chamber pressure, in order to ensure minimal roughness. Using spincoating, 30nm films of ncSi were then deposited. The films were heated treated for 40 minutes at 110°C inside a nitrogen glovebox. After removal from the glovebox, the sample was quickly loaded into the sputtering chamber with minimal exposure to dust and air. ZnO was then deposited at 50W RF power and 3mTorr, in order to minimize roughness and sputtering of the ncSi layer underneath.

Aluminum (Al) strips were deposited on top of the ZnO layer, using the same pattern as those used to make the ITO contact strips. The Al strips were deposited perpendicular to the direction of the ITO strips. The criss-cross arrangement of the ITO and Al contact strips enables fabrication of a number of devices on each substrate. At each intersection between an ITO contact line and an Al contact line, a single device can be found. The fabrication processes,
starting from NiO depositions and ending with Al depositions, took 10-14 hours to complete, depending on the rates of deposition. Patterned ITO strips on glass substrates were batch produced and cleaned before each device fabrication using isopropyl alcohol. Fifty fabrication runs were carried out in total. Through numerous experiments, best practices for device fabrication which led to successful devices were identified. Aside from limiting exposure of the sample substrate to dust at all times, it was crucial that the device be fabricated with each step in close succession, i.e. each device fabrication started early in the morning and finished late into the night of the same day.

Figure 5-3 shows a diagram representing the top view of a fabricated structure, where yellow arrows show possible placement locations for electronic probes that would power the sample. Each intersection point between the Al strips and the ITO strips is an LED device. Each individual device may be driven by placing contact probes on the Al and ITO strip responsible for the device. Care was taken to ensure that the contact probes are not placed directly onto the devices, in order to minimize mechanical damage from contact pressure. Picture of a sample substrate with a matrix of sample devices is shown in Figure 5-4.
Figure 5-3: Top view of a fabricated structure, showing a matrix of devices. One end of the ITO strips, shown vertically, was exposed for contacting. Al contact strips, shown horizontally, were placed perpendicular to the ITO strips. Each intersection point between the ITO strips and the Al strips is an independent LED device. The yellow arrows show the contact points needed to drive the device at the top left corner.
5.2 Current-Voltage Behavior and Stability

Processing conditions played a crucial role in the current-voltage (I-V) behavior and the stability of the LED devices. None of the devices whose ncSi layer was spincoated outside the cleanroom showed diode characteristics. A typical I-V curve is shown in Figure 5-5, indicating a resistance of about 250Ω which was observed for unsuccessful devices. To maximize the yield of successful devices after fabrication, it was imperative that: i) the ncSi layer is deposited in the cleanroom, ii) the quantum dot solution is filtered using 0.2μm PTFE membrane filters to remove dust and other solid particles immediately before spincoating, and iii) each stage of sample fabrication is carried out in close succession. Following the processing conditions outlined above, diode-like I-V behavior was observed, as shown in Figure 5-6, for a device having NiO/ncSi/ZnO thicknesses of 20nm/30nm/55nm. However, there is evidence of some leakage current as seen when a negative bias is applied.
Figure 5-5: I-V characteristics typical of unsuccessful LED devices.

Figure 5-6: Current-voltage curve of an LED device showing typical diode-like behavior.
Figure 5-7: An I-V comparison of devices on three sample substrates (substrates A, B, and C) that are fabricated simultaneously, showing consistency between samples within each sample fabrication run. Numbering after A, B, and C distinguishes between individual device number on each substrate (i.e. five different devices were tested for substrate A, in the order of A1, A2, A3, A4, and A5).

Figure 5-7 shows I-V curves of thirteen devices fabricated on three glass substrates, denoted A, B, and C, during a single fabrication run, with the structure NiO/ncSi/ZnO and layer thicknesses of 20nm/30nm/55nm. As the graph shows, the turn-on voltage and the current levels are fairly consistent between the devices. Note that all the devices tested in this fabrication run (A, B, and C) were capable of light-emission.

Figure 5-8 shows devices made using identical parameters (20nm/30nm/55nm of NiO/ncSi/ZnO) as that of the devices presented above. However, each device was made in a separate fabrication
run. Devices D1 to D7 are for devices that did not emit light readily observable by the human eye, while devices E1 and E2 emitted light visible to the naked eye. As the graph shows, although the fabrication parameters were kept constant, the I-V curves of the devices were not very repeatable. The device current at 0 V and at 10V for some of the devices differs by as much as two orders of magnitude. Note that the current density of an emitting device (E2) at 10V is greater than 1A/cm², significantly higher than that achieved by using organic transport layers [31], as shown in Figure 5-9. This is important as it was one of the reasons why inorganic metal oxides were chosen as charge transport layers for this study.

Figure 5-8: Comparison of I-V curves between devices fabricated in different fabrication runs but while using identical layer thicknesses of 20nm/30nm/55nm for NiO/ncSi/ZnO. D1 to D7 represent dark diodes (not visible to the naked eye), while E1 and E2 represent devices capable of producing light visible to the naked eye.
Figure 5-9: Current density and luminance as a function of bias voltage for an OLED using ncSi and organic transport layers [31].

The I-V curves for D1 and D2 in Figure 5-8 showed a clear point where the diode switches on: approximately 2V for D2 and 2.8V for D1. The curves for D1 and D2 also shows a transition to the series resistance limiting region spanning from 4 to 5V. For all the other devices except D3, there did not appear to be a distinct point where the diode switches on, but the curves for all of these devices tail off in the 4 to 5V range in to the series resistance limiting region. It is interesting to note that D3 seems to be in between the two types of behaviors, showing a turn-on point at approximately 3.3V, before tailing off to the series resistance limiting region. It is interesting that both emitting devices, E1 and E2, did not have a clear turn-on point. This suggests that in order to produce light, ideal diode-like behavior was not essential. The devices that did not show a clear turn-on point typically received significantly larger currents compared to those that did, likely in part due to a shunting current, related to the reverse current observed before, shown in Figure 5-6. Since all the devices were made using identical device thickness parameters, and efforts were made to deposit the layers under identical conditions, it can be concluded that unknown environmental/device conditions, such as humidity and/or the presence of dust/surface-interface imperfections, are the cause(s) of this unrepeatability.

Similarly, the lifetime or longevity between devices fabricated from different runs tend to vary. Most devices retained their diode IV behavior for approximately a week, although some broke down rather quickly following a few measurement scans immediately after fabrication. The most
The extreme case is shown in Figure 5-10, where the device deteriorates into a resistor after 4 voltage scans. The varying device longevity could be affected by the same unidentified factor(s) that caused the disparities in device performance.

![Figure 5-10: Deterioration of device during measurement from voltage scanning from -2 to 10V.](image)

5.3 Oxide Experiments

In an attempt to minimize the shunting current that seemed to exist in most of the devices, 5nm of silicon oxide (SiO₂) was deposited immediately after the ncSi layer, with the aim that the oxide layer would act as a barrier and thus inhibit shunting.

An Oxford Plasmalab PECVD system was used in a cleanroom setting. The deposition chamber was cleaned for 10 minutes using 80% CF₄/O₂ at 90sccm. The chamber was then pumped down to less than 10mTorr. The chamber was then purged with 1000sccm N₂ for 3 min, at 1500mTorr chamber pressure. SiO₂ was deposited using a previously established recipe, at 40W RF power and 400mTorr chamber pressure, with a gas mixture of 30sccm 5% SiH₄/N₂ and 700sccm N₂O. For 5nm of SiO₂, 80 seconds of deposition at 170°C was needed. The SiO₂ fabrication step was inserted into the fabrication procedure right after ncSi layer deposition, with all other steps remaining unchanged.

Figure 5-11 and Figure 5-12 show two devices made separately with 5nm of SiO₂. Device A showed a mostly resistor-like behavior whose current at 10V is about one-tenth that of previous
devices. Device B shows a diode-like I-V behavior. However, its current densities of tens of microamperes per square centimeter is far too low for these types of devices. No visible emission was seen. While the behavior of device A was likely due to plasma damage to the ncSi layer, device B showed promise for SiO$_2$ as a barrier layer to prevent device shunting. However, the oxide also drastically decreased the device current, which was likely too small to cause visible luminescence, given the limited efficiency of the devices at this early stage of research.

![Device A with SiO$_2$ Layer](image1)

**Figure 5-11:** I-V characteristics of a device with an SiO$_2$ layer.

![Device B with SiO$_2$ Layer](image2)

**Figure 5-12:** I-V characteristics of a second device with an SiO$_2$ layer.
5.4 Light Emission Characterization

The light from emitting ncSi LED devices was visible by naked eye starting at a bias of approximately 8V. It has a distinct orange color, indicative of the size of quantum dots used, which was centered at approximately 700nm. An attempt was made to capture the light intensity using a Minolta LS-110 Luminance meter and the spectral distribution using an Ocean Optics USB2000 fiber spectrometer. However, in both cases, the light was not strong enough to be detected. Hence a Hamamatsu R928 photomultiplier tube (PMT) was used. The PMT had a spectral response of 185nm to 900nm, and was biased at 1000V during measurement.

Figure 5-13 shows the device luminescence and current density as a function of device bias. The luminescence strength indicated by the signal voltage in mV. It shows that the device is clearly luminescing under applied bias. The log plot, as Figure 5-14 shows, clearly indicates that the emission starts at 6V, and that to first order, the luminescence strength varies exponentially with applied bias ($y = ae^{bx}$, where $y$ is the luminescence, $x$ is the applied bias, and $a$ and $b$ are constants). From the turn-on point at 5V, up until the largest bias achieved before device breakdown, 17V, the device emission increased by a factor of hundred, as measured by the PMT setup. On average, the device emission gains an order of magnitude for every 6V increase in bias voltage. In Figure 5-14, it can be observed that on a log scale, the current density can be separated into two distinct regimes. At $V < 4V$, the I-V curve follows a sharper slope compared to the slope of the curve for $V > 6V$, with a transition region centered at $V = 5V$. It is interesting to observe that it is at a bias of 5V that emission starts to occur, as shown by the change in PMT signal voltage. We noted earlier from analyzing Figure 5-8 that some degree of current shunting could be occurring inside the device during its operation. Therefore a likely three-stage mechanism for the emission behavior can be proposed. First, at initial turn-on (bias less than 4V), the bulk of the current observed in the device were shunting currents. Second, sufficient bias voltage (between 4V and 6V) activated the LED with respect to light emission, likely by the creation of band offsets at interfaces adjacent to the ncSi layer, favorable for charge injection into the ncSi layer. Finally, for biases greater than 6V, the device emits orange light from the ncSi layer and the emission gains brightness exponentially as a function of bias voltage.
It is worth mentioning that under a large reverse bias, i.e. 9V or larger, a few devices emitted a weak but discernible blue color, seen by the naked eye. In this case, the blue color is likely from the emission of one of the oxide layers, because of their larger band gap energies.

**Figure 5-13**: PMT measurement of device luminescence (blue) and current density (red) with respect to bias voltage.

**Figure 5-14**: Log plot of PMT measurement of luminescence strength and current density of a device with respect to bias voltage.
Overall, compared to the recent report by Cheng et al. [40], which used freestanding ncSi as emission layer, NiO and ZnO as charge transport layers, several improvements were observed. Figure 5-15 shows the device with the brightest emission, reported by Cheng. Optically, the device in the current study showed continuous exponential increase in emission strength from turn-on bias at 5V up to 17V, compared to a turn-on voltage of 7V, a luminescence maximum at 9V before decreasing to 66% of the maximum value at 10V, as reported by Cheng [40]. The device in the current study was capable to function at a 17V bias, whereas in the previous report, 10V was the maximum bias tested. A comparison of emission brightness could not be made, because in the previous report, arbitrary units were used for luminescence intensity. The quantum dots used in the previous study had an emission peak at $\lambda = 653$nm, close to the emission peaks (594nm and 628nm) of the ncSi quantum dots in the present study. However, the emission layer used by Cheng were fabricated using plasma deposition, which produced ncSi layers of 250nm and 1500nm in thickness, compared to an emission layer of only 30nm used in the current study.

Figure 5-15: Current and luminescence behavior as a function of applied bias for the best device reported by Cheng et al. [40].

In terms of current-voltage performance, in Cheng's report the current showed immediate increase for a positive bias as observed in Figure 5-15, similar to that observed in this study. The analyzer used in the previous study saturated at 0.1A, which prevented tests to see if the device
could have withstood high currents. However, the almost vertical increase in current at approximately 7.9V, combined with the decrease in the rate of luminescence gain from 7.5V up to 9V, as shown in Figure 5-15, showed that there was likely a shunting pathway, which worked against electroluminescence, as suggested by the authors [40]. Indeed, the decrease in luminescence as the bias increased from 9V to 10V further supports this explanation. However, in the current study, although there were evidences that a shunting current exists in positive biased operation of the device, the device showed no sign of deterioration due to shunting up to a high bias voltage of 17V. This was supported by the continuous exponential gain in emission from bias voltages of 5V to 17V.

Comparisons can also be drawn with the recent study by Puzzo et al. [31], whose devices used CQD ncSi synthesized by the same method, but with organic charge transport layers. One of the goals of this study was to show the potential of metal oxides as materials capable of supporting high current densities inside an LED structure. This was successfully achieved: the highest current density attained by Puzzo was approximately 430mA/cm² at a bias of 15V, for a device using polyethylenedioxythiophene (PEDOT) as HTL and 2,2',2''-(1,3,5-phenylene)tris-[1-phenyl-1H- benzimidazole] (TPBi) as charge transport layers. In the current study, the device using metal oxide charge transport layers reached a current density of approximately 1A/cm² at 15V, and eventually reached 6A/cm² at 17.5V. As discussed earlier, the bulk of the current attained at high biases (>6V) should have contributed to charge injection, rather than shunting, an argument supported by the continuous exponential increase in electroluminescence.

On the other hand, the brightness of the devices in this study could only be measured using a PMT setup and could not be sensed by a Minolta LS-110 Luminance meter, which was used in Puzzo's study to measure a luminescence of 57cd/m² for the device using poly(vinylcarbazole) (PVK) as HTL and TPBi as ETL. Yet, this drop in electroluminescence performance should not be taken as a conclusion that metal oxides are inferior candidates for thin film LEDs. There has been extensive experience in the research community with the usages of polymer charge transport layers in OLEDs, whereas studies using metal oxides as charge transport layers have just started to gain momentum.
6 Conclusion

6.1 Conclusions

In this study, we have proposed and demonstrated a proof-of-concept thin film LED device based on nanocrystalline silicon quantum dots as an emission layer and the metal oxides NiO and ZnO as the hole and electron charge transport layers, respectively. The silicon nanocrystals were prepared using a solution-based method that is based on HF liberation of nanocrystals produced by thermal treatment of a silicon-rich oxide precursor.

Low optical loss thin films of NiO and ZnO were developed as transparent charge transport layers. Key film properties of the films are as follows:

- At 100W RF sputtering power, both films were relatively smooth, having average roughnesses of 8.6nm and 2.8nm for NiO and ZnO, respectively.
- NiO films exhibited p-type charge carriers and had a stable resistivity of 125\,\Omega\cdot\text{cm}.
- ZnO films exhibited n-type charge carriers and had a stable resistivity of 1.06k\,\Omega\cdot\text{cm}.

Through repeated experimentation, best practices which maximized the success rate of device fabrication were established. It was observed that dust exposure should be kept to a minimum and that each step in fabrication should be carried out in close succession. Fabrication runs of 10-14 hours in length had to be carried out within a single day. Through these best practices, several ncSi based devices capable of light emission were successfully fabricated with the following results:

- The observed orange light of the emitting devices matched the observed photoluminescence peaks of the ncSi quantum dots.
- Owing to a low emission intensity, the emitted spectrum could only be detected using a photomultiplier tube, and thus an emission spectrum was not measured.
- The photomultiplier signal, providing an integrated luminescence signal, detected a device emission turn-on at 6V. The luminescence increased exponentially with bias
voltage. The emission brightness of the device increased by a factor of 10 for every 6V increase in bias voltage.

Compared to the recent report by Cheng et al. using freestanding ncSi and metal oxide charge transport layers [40], this study demonstrated a higher operating bias voltages without deterioration in luminescence (17V compared to 9V). Limited shunting was not visible at biases of greater than 6V, compared to shunting-related device deterioration which occurred at 10V in the Cheng et al.’s study.

Compared to the recent study using organic charge transport layers by Puzzo et al. [31], significantly higher current densities were achieved (6A/cm² compared to 0.43A/cm²), demonstrating the ability for metal oxides to operate under high current regimes. However, decrease electroluminescence was observed in the present study, which can be attributed to the relative inexperience in using metal oxide charge transport layers in an OLED setting.

This proof-of-concept study points to the potential of silicon nanocrystal quantum dots as a potential environmentally friendly material for display and lighting technology. The dependence of emission behavior on the crystal size, based on the quantum confinement effect, can be utilized in fine tuning the emission color and/or in color mixing applications such as the production of white light. Metal oxide transport layers based on NiO and ZnO show promise as robust charge carriers capable of withstanding higher current densities compared to organic charge transport layers commonly found in OLEDs.

6.2 Future Work

Improved devices using the same materials and design are possible with further studies, which include:

i. Identification of structural/environmental factors causing decreased device fabrication success rate and decreased longevity.

ii. Further optimization of charge carrier layers in order to provide more balanced charge injection. This can be explored through the doping of ZnO by small amounts of Al in order to increase its conductivity. Balanced charge injection could play a role in minimizing background current.
iii. Explore the range of colors that can be achieved by varying the size of the ncSi quantum dots, by incorporating ncSi of different average sizes into the structure.

iv. The effects of the size and electronic nature of ligands on optical and electronic characteristics of the devices needs to be investigated. Aromatic rings or conjugated chains are alternative possibilities that also could be considered.

v. Introduction of hole and/or electron blocking layers to further trap the charges within the nanocrystalline silicon layer may further improve device performance.

vi. The use of inorganic capping compounds using atomic layer deposition, appropriately infiltrating the nanoparticle films, could be used in further enhancing the electronic properties of the nanocrystal silicon emission layer.
References


