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Quality of Aqueous Chemically Grown Zinc Oxide for Radiation Detection Applications

Ву

Austin L Tam

A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE in NUCLEAR SCIENCE AND ENGINEERING

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Committee Signature Page

To the Graduate Faculty:

The members of the Committee appointed to examine the thesis of Austin L Tam find it satisfactory and recommend that it be accepted.

Dr. Eric Burgett Major Advisor

Dr. Christopher McGrath Committee Member

Dr. David Beard Graduate Faculty Representative

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Table of Contents

List of Figures vii
List of Tables ix
Abstractx
CHAPTER 1. Background1
1.1 Physical Properties of ZnO1
1.2 ZnO Applications
1.3 Need for Detectors
CHAPTER 2. ZnO Growth Techniques9
2.1 Aqueous Growth Techniques9
2.2 Metalorganic Chemical Vapor Deposition10
2.3 Electrochemical Deposition
CHAPTER 3. Experimental13
3.1 Materials and Methods13
3.2 Process
3.3 Growth Parameters
CHAPTER 4. Results and Discussion

4.1	Powder X-Ray Diffraction Analysis18
	4.1.1 t-Test Analysis22
4.2	FIB Microscope Analysis24
4.3	Qualitative Analysis
4.4	Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy Analysis
4.5	Photoluminescence Measurements
4.6	Alpha Spectroscopy
CH.	APTER 5. Conclusion

List of Figures

Figure 1 - Wurtzite Structure Displayed by ZnO 1
Figure 2 - ZnO Scintillator Device
Figure 3 - Blank Sapphire with epitaxial ZnO layer
Figure 4 - Early Growth on Sapphire 2475-50 (24 hr, 75°C, 50mM) (not final sample). 14
Figure 5 - Hexamine ((CH_2) ₆ N_4) molecule
Figure 6 - Diffractogram Example Peak 002 (24 hr, 70°C, 50mM) 20
Figure 7 - The image was stitched together using open-source image analysis software,
ImageJ. Sample ZnO 2475-40 (24 hr, 75°C, 40mM)
Figure 8 - Well aligned planar surface (24 hr, 50°C, 30 mM)
Figure 9 - Mismatched lattice surface (24 hr, 65°C, 30mM)
Figure 10 - 1280-10 (12hr, 80°C, 10mM)
Figure 11 - ZnO 2475-50 (24 hr, 75 ^o C, 50mM) Cross Section at 45 ^o tilt
Figure 12 - ZnO 2475-50 (24 hr, 75 ^o C, 50mM) Cross Section at 0 ^o tilt
Figure 13 - EDS Data for 2485-50 (24hr, 85°C, 50mM)
Figure 14 - EDS DATA FOR 3685-50 (36hr, 85°C, 50mM)
Figure 15 - Optical Image of 2485-50 (24hr, 85°C, 50mM) Area of analysis highlighted
Figure 16 - Optical Images of 3685-50 (36hr, 85°C, 50mM) Area of analysis highlighted
Figure 17 - PL Measurement Experimental Setup

Figure 18 - Alpha Detection Setup	39
Figure 19 - Original ZnO Alpha Spectra	40
Figure 20 - Pu-239 Alpha Spectrum Composite from Detection Experiment Sample	
2475-50 (24 hr, 75 ^o C, 50mM)	40
Figure 21 - Burgett Alpha Spectra using Th-230	41

List of Tables

Table 1: XRD FWHM (arcseconds) for all samples	. 21
Table 2: Statistical Analysis of XRD Data for All Samples at Given Concentrations	. 23
Table 3: Statistical Analysis of XRD Data for All Samples at Times	. 23
Table 4: PL Intensity Data.	. 35
Table 5: Peak Wavelength on all samples	. 37
Table 6: t-Test Analysis of PL Intensity Data	. 37
Table 7: Table of alpha particle energies and corresponding probabilities for Pu-239	. 38

Abstract

This project was an experimental program to determine if aqueously grown zinc oxide (ZnO) crystal is pure enough to compete as a substitute for MOCVD-grown or bulk-melt-grown scintillator material. The aqueous ZnO is much cheaper and simpler to manufacture. The ZnO aqueous growth process was varied using a three-dimensional phase space of time, concentration, and temperature that allowed for a variety of growth features to be investigated. The growth process parameters of the experiment resulted in hexagonal rods that varied in diameter from micrometers to nanometers as well as other microgrowths and planar material growth.

The present work investigated ZnO as a metamaterial as well. The ability to produce repeating patterns using the aqueous growth of ZnO rods on a substrate with a chemical process would be very useful in creating metamaterial structures without the need to machine nanoscale features onto the surface. Hexagonal rod growths were desirable to create the metamaterial patterns. Planar growth was desirable for use as a detector material.

The crystalline properties of the aqueously grown ZnO were measured by x-ray diffraction measurements, photoluminescence spectroscopy measurements, scanning electron and focused ion beam imaging, and alpha-particle spectroscopy.

This work has resulted in a simple and cost effective process for developing the ZnO material in multiple forms. However, for nuclear detection applications, ZnO fails when compared to other traditional detectors.

CHAPTER 1. Background

1.1 Physical Properties of ZnO

ZnO can be found in three different crystal structures: rock salt, zinc blende, and wurtzite. Rock salt is a rare form that can be created at high pressures (around 10 GPa). The other two forms are much more common, though the cubic structure of the zinc blende is only stable if it is grown on cubic substrates. The wurtzite structure is hexagonal and the most stable form of ZnO. It is also the preferred form for many reasons. The structure is stable at room temperatures and pressures and many growth conditions favor it over the other forms. The ZnO wurtzite form has lattice constants of A=3.25 angstroms and C=5.2 angstroms which gives a C/A ratio of approximately 1.6 which is nearly an ideal lattice for hexagonally structured material, the perfect lattice ratio being 1.6333(Yang).



Figure 1 - Wurtzite Structure Displayed by ZnO

The bonding of ZnO is almost entirely ionic in nature as would be expected with Zn^{2+} and O^{2-} . This bonding accounts for the preferential formation of the wurtzite structure over the cubic zinc blende, as well as the strong piezoelectric effect of ZnO. The polar bonds of the ZnO make the zinc and oxygen planes electrically charged. In order to achieve electrical neutrality, the planes reconstruct at an atomic level in most materials; however, with ZnO this is not the case. The surfaces are atomically flat, stable and exhibit no reconstruction. This characteristic is an anomaly of ZnO and is not completely understood (Baruah).

The hexagonal structure of ZnO makes the material relatively soft with an approximate hardness of 4.5 on the Mohs scale (Burgett). This makes it ideal for thin, flexible material growth. The hexagonal structure also makes ZnO ideal for ceramics since it has a high heat capacity, high thermal conductivity and low thermal expansion and high melting point. ZnO also demonstrates a smaller elastic constant as well as the highest piezoelectric tensor of similar semiconductors such as GaN (Dal Corso). In addition, ZnO demonstrates strong pyroelectric properties (Vasudevan). These properties make it an important material for a variety of piezoelectric and pyroelectric applications, which require large electromechanical couplings.

The structural and chemical properties of ZnO also give it unique electrical traits. These include its relatively large band gap of approximately 3.37 eV and an exciton binding energy of 60 meV at room temperature (Schmidt-Mende). The large band gap provides the advantages of higher breakdown voltages, the ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. When ZnO's exciton-binding energy is compared to those of other semiconductor materials such as ZnSe (22 meV), ZnS (40 meV), and GaN (25 meV) it is clear that ZnO is a better candidate for more energy intensive applications, *e.g.* UV laser fabrication and nuclear detector work (Vasudevan). Pure ZnO also demonstrates transparency to wavelengths between 380nm and 2500nm (Morkoc). The thermal energy at room temperature of 26 meV ensures efficient exciton emission at room temperature under low excitation energy. Thus, ZnO is a promising photonic material in the blue-UV region (Wang). This bandgap and transparency together make it an ideal candidate for future work as a metamaterial and as a photonic device in a matrix for detection work.

1.2 ZnO Applications

ZnO has a variety of applications due to these unique chemical properties. These range from uses as paint and medical ointment, as a treatment for various skin conditions, to the modern applications of ZnO nanostructures. Its wide band gap, excellent chemical and thermal stability, as well as electric properties allow ZnO to be superior to other chemical compounds in an assortment of roles. Lasers, transparent conducting oxides and thin film transistors, piezoelectric devices, gas sensors, biosensors, and solar cells are all examples of applications for which ZnO has shown promise. This includes radiation detection as a scintillator. However, since ZnO is competing against very mature GaN semiconductor technology, it is largely limited to niche applications, where its specific properties are required. GaN devices have been long established due to their very hard, durable nature, mechanically stable wide bandgap, 3.4 eV, and high heat capacity and thermal conductivity. Even with these properties, ZnO can be used in devices that GaN cannot. For example, ZnO's piezoelectrical properties, which produce a very high electrical response for a semiconductor, have been used successfully in thin film devices

such as bulk acoustic wave and Surface Acoustic Wave (SAW) devices (Ozgur). SAW filters are common in many consumer items such as TV signal filters and wireless communication systems (Ozgur).

With the advent of nanoscale growth techniques and machining processes in the late 1990s, ZnO once again was thoroughly studied. Semiconductor manufacturers continued to look for viable ZnO semiconductor applications but also incorporated nanostructures to change the optical, mechanical, and electrical properties of the material. A prime example of the difference in macroscale ZnO versus nanoscale ZnO is seen in its use as an ultraviolet light blocking agent in sunscreen. Traditionally, sunscreen has appeared white after it is applied to skin since it scatters visible light. However, new sunscreens use ZnO nanoparticles and, while they still block UV light, they do not scatter visible light and thus appear clear once applied. Manipulation of nanostructures has allowed for many different phenomena to be investigated.

One of particular interest in recent years is the photonic crystal. Photonic crystals are nanostructures, in a repeating pattern, that are smaller than the wavelength of the electromagnetic radiation being influenced. The patterned nanostructures preferentially affect light or other EM radiation of a specific wavelength, determined by the size of the nanostructure. This has been demonstrated in previous work using silicon machined to manipulate infrared radiation (Lee). Since it has been shown that ZnO can be grown into nanostructures (Burgett), there has been a great deal of interest in attempting to control the patterning of ZnO through various growth techniques. This includes incorporating these nanostructures into ZnO scintillators to improve optical clarity and performance. In the market today, ZnO has an advantage over other traditional semiconductor material since it is obtained fairly easily. In the thin-film transistor market, ZnO has the potential to become an important material. This is due to the prospective worldwide shortage of indium in the face of growing demand for indium tin oxide, the most common thin-film transistor type. Even with the interest in ZnO in many markets, much more research and development is needed before it can become a viable semiconductor, competitive with more established technologies and methods.

ZnO has been tested as a scintillator in nuclear detection work. A scintillator material absorbs ionizing radiation and converts the incident energy into light. The light is typically visible or ultraviolet and can be detected using a PhotoMultiplier Tube (PMT). Since the development of the PMT in the 1940s, a wide variety of inorganic materials have been used as scintillators. Lehmann explored the use of ZnO as a detector material with donor impurities (Lehmann), and found that its scintillation decay times were less than a nanosecond. This is extremely fast for a scintillator. Thus, it showed great promise as a detector at the time. However, during the 1960s only powdered forms were available for experimentation. Many different ZnO growth processes, including aqueous growth, were explored in the following years. The 1990s saw renewed interest in the material as scientists looked for ever more efficient LEDs. It was also investigated for use in calorimetry for high-energy physics and scientific industrial applications (Rodnyi; Derenzo).

An understanding of the scintillation process can be found in the literature (Rodnyi; Derenzo). It can be broken down into four stages:

5

- The absorption of the incident radiation and subsequent creation of energetic primary electrons and inner shell holes. This happens in 10⁻¹⁵ to 10⁻¹³ seconds.
- Relaxation of the energetic electrons and inner shell holes through intraband transitions and electron-phonon interactions. This takes 10⁻¹² to 10⁻¹¹ seconds, and results in lower energy electrons and holes.
- 3. Secondary electrons and holes thermalize and then form electron-hole pairs with energies on the order of the potential energy of the system. Energy is then transferred to light emitting atoms leaving them in excited states. The type of atom dictates the time this process takes. This time ranges from 10^{-12} to 10^{-8} seconds, thus giving the intrinsic rise time of scintillation light.
- 4. The emission of scintillation light from the light emitting atoms. This fast radiative process can be as short as 10⁻⁹ seconds for recombinations involving free electrons and holes, free and bound excitons, and core-valence recombination. Slower radiative processes can take seconds or minutes for forbidden transitions.

Since Lehmann's experiments in the 1960's, zinc oxide scintillator investigations have focused on utilizing a variety of dopants. While dopants are not necessary for scintillation in ZnO, they can shift the output wavelength or time required for scintillation. For scintillator applications Gd, B, and Li are most common (Burgett). Lehmann had proposed that the introduction of Ga in place of some zinc would result in a degenerate donor band overlapping the bottom of the conduction band. The donor band electrons would recombine with ionization holes in the valence band, resulting in nearband edge emission and a decay time of 0.65 nanoseconds (Lehmann). At the time, Lehmann had only powdered ZnO for use, and, thus his results were fairly limited, never reaching his theorized decay times. When improved material production techniques became common, single crystalline material dramatically enhanced these results. ZnO:Ga has demonstrated sub-nanosecond photoluminescence, cathodoluminescence, and X-ray excited luminescence (Lehmann; Derenzo; Lorenz). With improved production methods ZnO is a suitable candidate for scintillator applications requiring super-fast response and high energy resolution.

1.3 Need for Detectors

With recent advances in growth techniques for ZnO, it is now viewed as a viable detector material and a candidate to replace some of the older technologies that are still being used from the Cold War. Since 2001, the Department of Homeland Security has spent millions of dollars on developing better technology for detecting smuggled nuclear weapons but has since had to stop deploying new detectors due to a lack of helium-3 (Wald). Helium-3 has been a vital component for neutron detection devices since they were first developed fifty years ago. It produces ionized tritium and a proton when struck by a neutron allowing for detection of the neutron. The world's supply of helium-3 comes as the byproduct of nuclear weapons programs looking to maintain tritium in nuclear warheads or as the byproduct of nuclear reactors. Thus, as the world's nuclear-weapon stockpiles have decreased, so has the world's supply of helium-3. This consequently led to the 2009 global shortage and the halting of the deployment of additional detectors. The nuclear physics community also uses helium-3 as a cryogenic

liquid to cool MRI magnets and superconducting magnets at the world's largest accelerators, causing even more strain on the world's limited supply (Feng).

The lack of helium-3 has spiked market prices for all work needing the material. Though few other materials can provide the neutron versus gamma discrimination found from helium-3, new materials could prove to be viable substitutes. One such detector that could hold promise is ZnO. ZnO is a well-characterized alpha detector and, when doped with a neutron-sensitive material, can perform as a neutron detector. This has been explored in previous work (Burgett). Thin films of ZnO can be grown that exhibit equivalent or superior neutron versus gamma discrimination to conventional neutron detectors. Furthermore, Burgett showed that whether it was doped or coated in ⁶LiF, the ZnO thin film detector's performance was highly efficient. Doped ZnO scintillators can provide neutron spectral data as both the triton and alpha particles can be detected simultaneously in a doped ZnO scintillator.

Using aqueous ZnO growth methods, a cheaper detector system could exist. The aqueous material would need to undergo many forms of testing, including scintillation tests using alpha radiation to prove it was viable. If these tests produced positive results, then a doped aqueous version could be developed to demonstrate its neutron detecting capabilities.

CHAPTER 2. ZnO Growth Techniques

Because of ZnO's exceptional properties, intensive research has been focused on fabricating ZnO nanostructures and on correlating their morphologies to various tasks. Many ZnO nanostructures have been successfully demonstrated including: nanodots, nanorods, nanowires, nanobelts, nanotubes, nanobridges, nanonails, nanowalls, nanohelixes, seamless nanorings, mesoporous single-crystal nanowires, and polyhedral cages (Vasudevan). ZnO nanorods and nanowires have been the most commonly studied because of their easy formation and device applications. The uses for these nanostructures vary widely, allowing for applications in optoelectronics, electrochemical and electromechanical devices (Vasudevan). To facilitate the manufacture of these nanostructures in ZnO, many techniques have been developed, each with their own eccentricities. The simplest of these, an aqueous growth technique, is described herein.

2.1 Aqueous Growth Techniques

There are various aqueous growth methods to grow a variety of ZnO nanostructures. The most common method is growth facilitated by hexamine $((CH_2)_6N_4)$ but that will be discussed in the experimental section as it is the technique favored here. Another aqueous method is the use of alkaline solutions to attain ZnO nanostructures, as normally divalent metal ions do not hydrolyze in acidic environments. This pH correlation was established by Xu. One proposed reaction sequence for aqueous growth is:

$Zn^{2+} + 2OH^{-} \leftrightarrow Zn(OH)_2$	(1)
$Zn(OH)_2 + 2OH^{-} \leftarrow \rightarrow [Zn(OH)_4]^{2-}$	(2)
$[Zn(OH)_4]^{2-} \leftarrow \rightarrow ZnO_2^{2-} + 2H_2O$	(3)
$ZnO_2^{2-} + H_2O \leftarrow \rightarrow ZnO + 2OH^-$	(4)
$ZnO + OH \leftarrow \rightarrow ZnOOH$	(5)

Equations (1) to (5) only describe a theoretical version of the reaction since oxygen molecules in the solution are not factored in and could significantly affect the processes, since removing oxygen from water is easy. The oxygen concentration plays a significant role in the final crystal quality of ZnO formations.

2.2 Metalorganic Chemical Vapor Deposition

Metalorganic chemical vapor deposition (MOCVD) has been used to produce single crystalline material doped with lithium-6 to produce a viable neutron detector (Burgett). This is a highly complex process using ultra-pure gases inside a special reactor vessel. This process utilizes expensive metalorganics which are usually volatile pyrophoric materials typically stored as liquids. Furthermore, the complexity of the process is such that the water-cooled and heated reaction vessel must be modified for different precursors, a time consuming process (Burgett). MOCVD growth, however, does give the user excellent control over structural form, dopants in the material, and the ability to produce a uniform epitaxial layer.

2.3 Electrochemical Deposition

Electrochemical deposition can produce very controlled results since its parameters are tightly controlled but it is not as intensive as the MOCVD technique. Electrochemical deposition is primarily used for creating uniform and large areasynthesis of ZnO nanostructures (Xu), because it exerts a strong external driving force to make the reactions take place. A conductive substrate is required, though it can be curved or flat and the process doesn't need seeds to start the growth. The strong external electric field used for this technique allows for stronger adhesion of the ZnO to the substrate as well as better nanowire alignment (Xu). The typical setup used for this growth method is a three-electrode arrangement using an Ag/AgCl electrode as the reference electrode and Pt as the counter-electrode. The anode, where growth usually occurs, is placed parallel to the cathode in the deposition solution (Xu). The process works by controlling the electrical bias throughout the reaction system. The bias controls the reaction rate by driving voltage or current. $ZnCl_2$ and KCl are typically used for the growth of vertically aligned ZnO nanostructures. The O₂ needed for the reaction is bubbled through the solution to maintain a high level of O₂ for high quality ZnO production.

Each of these techniques has strengths and weaknesses that make the resulting ZnO suitable for specific uses. The all-aqueous processes have the advantage of being relatively inexpensive and less complicated since they can be performed without stringent experimental conditions. They have been extensively studied for factors contributing to the growth of nanostructures (Garcia). Some of these factors include: dopants, seed layers, and alkalinity. In the case of their use for radiation detection work, the ideal condition is theorized to be planar growth on an optically transparent substrate. This gives the largest interaction volume within the ZnO layer and the ZnO layer would ideally be optically transparent as well. This will allow the scintillation light produced to escape the ZnO layer and reach a photomultiplier tube in close proximity. A simple drawing is shown if figure 2. The optical transparencies of samples have been modified

11

in previous work by adjusting the ratios between oxygen and zinc. Excess oxygen will present as white powdery samples and excess zinc will be indicated by black layers and carbon trapping, though this is not possible in aqueous-growth techniques. Either form can lead to optically opaque samples with poor light yields.



Figure 2 - ZnO Scintillator Device

CHAPTER 3. Experimental

3.1 Materials and Methods

In order to match the lattice structure of the ZnO to the surface of a substrate, a material with similar crystal structure was required. Early experiments on sapphire substrates revealed that a lattice mismatch caused random alignment of growth as Figure 4 shows the wildly oriented hexagonal rods on the surface of the sapphire. The substrate used must have geometry similar to the hexagonal wurtzite structure so the strained orientations initially created can be avoided. The lattice of sapphire and that of ZnO have a large mismatch along the a-axis (about 18.4%) (Yang). An additional substrate layer was applied to the sapphire of ZnO as a seed layer. This ability to seed a layer and achieve a wide variety of growth patterns is one of the benefits of wet chemical methods. These seed layers can be applied to any arbitrary substrate and allow for the planar growth that is desired in the case of detectors.

An epitaxial layer of ZnO facilitated as this growth alignment layer for all of the samples. This thin ZnO layer was applied prior to growth by an MOCVD tool. This resulted in a near perfect plane for the growth to originate from. The ZnO could also then align naturally with the substrate to form a more planar surface even when rods were grown in dense packs. This helped to prevent stress points of growth from single crystalline points by not making any area of higher potential to start the growth process. An even potential across the surface allowed for the best possible conditions to achieve planar growth. This is shown in figure 3.

13



Figure 3 - Blank Sapphire with epitaxial ZnO layer



Figure 4 - Early Growth on Sapphire 2475-50 (24 hr, 75°C, 50mM) (not final sample)

3.2 Process

The production of ZnO through aqueous growth was performed using zinc nitrate $(Zn(NO_3)_2)$ and hexamine $((CH_2)_6N_4)$, also called hexamethylenetetramine or methenamine). Hexamine is a nonionic cyclic tertiary amine, as shown below in figure 5. However, the exact process that hexamine undergoes during the chemical reaction with $Zn(NO_3)_2$ is not precisely known. The current theory suggests that it acts as a bidentate Lewis base that coordinates and bridges two Zn^{2+} ions (Xu). In addition to this growth on the polar side of the wurtzite ZnO, hexamine will also attach to the nonpolar facets which facilitates anisotropic growth in the [0001] direction (Xu). In the figure 5 below, hexamine is shown to be a rigid molecule though it readily hydrolyzes in water.



Figure 5 - Hexamine $((CH_2)_6N_4)$ *molecule*

It is important to note that it hydrolyzes in water because it breaks its bonds slowly and produces HCHO and NH₃. This release of the strain energy associated with its initial structure is critical to the synthesis of ZnO. If hexamine hydrolyzed quickly, then a large amount of hydroxide would quickly create a highly basic environment and result in the precipitation of Zn^{2+} ions from the solution. The reaction would take place very rapidly and prevent the growth of oriented nanostructures (Xu). The theoretical chemical process that it undergoes can be seen below.

$(CH_2)_6N_4 + 6 H_2O \longleftrightarrow 4 NH_3 + 6 HCHO$	(1)
$NH_3 + H_2O \longleftrightarrow NH_4^- + OH^-$	(2)
$\operatorname{Zn}^{2^+} + 4 \operatorname{NH}_3 \longleftrightarrow [\operatorname{Z}(\operatorname{NH}_3)_4]^{2^+}$	(3)
$Zn^{2+} + 2 OH^{-} \longleftrightarrow Zn(OH)_2$	(4)
$Zn(OH)_2 \leftrightarrow ZnO + H_2O$	(5)

It should also be noted, that while the counter-ions do not directly affect reactions, they have been shown to affect morphology (Xu).

3.3 Growth Parameters

The concentration of the component chemicals is an important factor in determining various qualities of the ZnO growth. In previous works, 0.1 Molar (M) concentrations of the base chemicals resulted in microrods one to two micrometers wide and up to ten micrometers long and a concentration of 1 milliMolar (mM) resulted in nanowires on the scale of 10-20 nanometers wide (Vayssieres). Since the desired size of the surface structures were to be in the nanometer range, a moderate concentration of 0.01 M was chosen.

The synthesis of ZnO was accomplished using a hydrothermal aqueous growth technique. This is a simple process that works by adding heat to the solution to cause crystalline ZnO to form on a substrate suspended by the surface tension of the solution. A total of one hundred fifty samples were prepared for the experiment. They were prepared in 10 mM steps ranging from 50 mM down to 10 mM. The zinc nitrate and hexamine were measured out on a lab scale to the accuracy of hundredths of a gram and then added to their respective solutions at a molar ratio of one to one. The solutions were initially mixed with 400 mL of deionized water in a separate 600 mL beaker. Due to the

need to reduce chemical waste, this was later reduced to 80 mL of deionized water in 100 mL beakers.

After each solution was prepared in a separate beaker, the sapphire pieces coated with epitaxial ZnO were carefully suspended on top of the surface of each solution. They were suspended using the surface tension of the water and thus required careful placement so as not to break the surface of the water. Then each beaker was sealed with aluminum foil to prevent evaporation of the solution in the oven. Evaporation would cause increased concentrations of the base chemicals though it would not affect the ratio of molar concentrations. An image of the beakers is shown below following a 24-hour bake.

The temperature was set in intervals of 5°C ranging from 50°C to 95°C. The samples were allowed to bake for a period of 12, 24, or 36 hours. The ovens used for the experiment were a Thermolyne Oven Series 9000 model 47510 and a GCA Corporation Precision Scientific Group Oven model 124. They have tightly controlled temperature tolerances to maintain a precise temperature with only 0.1°C variation. The ovens were turned on early to allow for temperature stabilization before the samples were introduced. The time was manually controlled by removal of the samples from the ovens.

CHAPTER 4. Results and Discussion

The quality of the crystalline material produced needed to be at least as high as the quality of the ZnO demonstrated in previous detector work. In order to demonstrate this, x-ray diffraction measurements were performed on the complete sample set produced using the hydrothermal growth method and compared against high quality ZnO thin film samples manufactured using MOCVD techniques. The samples' defects and impurities were studied using PhotoLuminescence (PL) measurements. The peaks found during PL measurements allow a better understanding of the wavelength emission shift from other elements present during the sample's formation. Samples were also analyzed using a Focused Ion Beam (FIB) microscope, which allowed for additional surface information to be attained. The samples were named with a numerical designation denoting time grown, temperature for growth, and mM concentration of the base chemicals. Thus sample 1255-10 would be a 12-hour growth cycle at 55°C with a molar concentration of 10 mM.

4.1 Powder X-Ray Diffraction Analysis

Powder X-ray Diffraction (XRD) is used primarily in crystallographic work to determine the quality and lattice characteristics of various crystalline materials. By measuring the angles and intensities of diffracted beams by the crystal, the mean position of atoms in the crystal can be determined, as well as their chemical bonds. Disorder, as well as a three-dimensional representation of the density of electrons, can also be obtained (Harp). A Bruker D-8 Discover was used to collect XRD data on the samples. Two samples from previous work (Burgett) were used as a baseline against which to judge the success of ZnO as a detector material. They were analyzed using XRD to quantify the crystalline quality of the samples relating directly to its alpha detection capabilities. From the data the Full Width Half Maximum (FWHM) could be determined. This metric directly correlates to the crystal quality of the sample. These results showed that the samples had a FWHM of 763.200±0.001 arcseconds for the undoped ZnO prepared using MOCVD techniques and 576.000±0.001 arcseconds for the undoped Cermet prepared ZnO. These samples also demonstrate very high relative intensities of x-rays compared to the aqueous samples analyzed.

A sample diffractogram is shown below in Figure 6. The graph shows the characteristic peak for ZnO at 34.6 degrees for the 002 crystal orientation. All samples peaks were found at 34.6 degrees; however, their relative intensities were lower than that of the baseline samples. The decrease in relative intensity indicates that the alignment of the rods or planar surface produced from aqueous growth, deviates from vertical orientation and thus are misaligned from optimal crystal orientation. Previous work (Vasudevan) discusses the relative intensity changes that are seen due to crystal orientation with relation to the 002 plane peak and the 100 plane peak. This study also concluded that decreasing molar concentration in sample growth resulted in decreased peak intensity for the 002 plane. In the present study, the concentrations were very similar to Vasudevan though the time duration and temperatures used were varied a great deal.



Figure 6 - Diffractogram Example Peak 002 (24 hr, 70°C, 50mM)

Using these two samples as a baseline for working ZnO detectors, each sample could be assessed for quality against proven samples. Below is a chart of the samples and their FWHM for all samples grown.

12 hr FWHM (arcseconds) ±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	640	597	576	633	586
55°C	554	579	676	597	525
60°C	619	597	586	576	568
65°C	547	651	576	597	597
70°C	680	640	666	604	680
75°C	680	619	644	637	554
80°C	536	601	576	619	576
85°C	568	615	676	561	536
90°C	550	576	698	597	658
95°C	601	658	576	585	694

24 hr FWHM (arcseconds) ±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	586	698	597	547	676
55°C	687	637	838	655	554
60°C	534	586	619	576	565
65°C	626	655	1130	662	586
70°C	615	558	637	536	514
75°C	619	597	673	637	669
80°C	608	615	554	54	676
85°C	658	608	651	597	558
90°C	608	637	658	558	547
95°C	597	676	608	536	554
36 hr FWHM (arcseconds) ±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	648	550	604	554	586
55°C	633	658	658	561	637
60°C	630	536	547	543	597
65°C	550	597	547	637	637
70°C	568	594	619	597	576
75°C	781	658	586	594	597
80°C	565	669	622	547	594
85°C	608	619	576	637	597
90°C	694	644	615	576	576
95°C	597	626	597	576	615

Table 1: XRD FWHM (arcseconds) for all samples

From Table 1 above, the values of the FWHM of the samples are all lower than that of the MOCVD grown sample. Recall from page 11, the FWHM for the MOCVD grown baseline sample was 763.200±0.001 arcseconds. The MOCVD sample was successfully demonstrated as a viable detector material in previous work (Burgett). The excellent crystalline quality determined via XRD shows that these samples should be exceptional detector material with respect to crystalline quality alone. While they are lower than that

of the MOCVD sample, no discernable differences can be established when only considering single sets of data. Statistical analysis using a t-test between grouped sets of samples was used to determine that neither the baking temperature nor the amount of time the sample baked caused meaningful differences in their FWHMs. From the FWHM of the samples, many other patterns can be seen and analyzed when the data is put into various sets. For example, the t-test shows that across all time and temperature groups the 10 mM concentration compared to the 40 mM concentration is significantly different. The confidence interval demonstrates that 96% of the time the average FWHM of 40 mM solution grown ZnO is smaller than that of the 10 mM grown ZnO. This comparison is made against each group and found to be significant. This allows for the conclusion that a 40 mM solution results in a better crystalline quality as the FWHM is on average lower across all samples.

4.1.1 t-Test Analysis

First the average and variance for each group must be found:

Average =
$$\frac{\left(\sum_{i=1}^{n} FWHM_{n}\right)}{n}$$
$$\sqrt{\frac{\left(\sum_{i=1}^{n} \left(FWHM_{n} - Average\right)^{2}\right)}{n-1}}$$
Variance = $\sqrt{\frac{n-1}{n-1}}$

Then the t-value can be calculated between any two of the data sets.

$$t = \frac{\left(Average_1 - Average_2\right)}{\sqrt{\frac{Var_1^2}{n_1} + \frac{Var_2^2}{n_2}}}$$

From this value the significance can be determined by looking the t-value up in a table.

<u>T-test</u>	10 and 20	10 and 30	10 and 40	10 and 50	20 and 30	20 and 40	20 and 50	30 and 40	30 and 50	40 and 50
Average 1st	615.36	615.36	615.36	615.36	618.84	618.84	618.84	639.96	639.96	589.68
Average 2nd	618.84	639.96	589.68	596.64	639.96	589.68	596.64	589.68	596.64	596.64
Variance	46.8920	86.1919	46.1622	51.5566	82.0818	37.9387	44.3449	81.6671	84.8331	43.5725
t differenc e	-0.2874	-0.1564	-2.0639	1.4063	0.9965	-2.9768	-1.9389	2.3845	1.9777	-0.6186
Confiden ce Interval	22.42%	12.31%	95.20%	83.41%	67.28%	99.42%	93.77%	97.61%	94.25%	45.90%

Table 2: Statistical Analysis of XRD Data for All Samples at Given Concentrations

This also means that, with respect to XRD results, no other parameter besides concentration has a meaningful impact on the FWHM of the samples. Whether this is due to not enough variation in temperature across the phase space investigated or that temperature has little impact upon the relative crystalline quality is unknown. The time parameter is also void in this analysis since it also only yielded nonsignificant results (shown below). Again variations for this phase space may not have been large enough to show significant impact on sample quality.

<u>T-test</u>	12 and 24	12 and 36	24 and 36
Average 1st	607.25	607.25	624.02
Average 2nd	624.02	605.02	605.02
Variance	72.9435	45.3414	45.1073
t difference	1.1499	-0.2461	1.3055
Confidence Interval	74.42%	19.34%	80.22%

Table 3: Statistical Analysis of XRD Data for All Samples at Times

In Burgett, an established FWHM for high quality samples was 390 arcseconds. Wider FWHM could indicate broadening. This broadening is a well-known feature of polycrystalline samples. A prime example is on sample 2465-30. See figure 9.

4.2 FIB Microscope Analysis

The FIB microscope allows for an in-depth analysis using its beam to both image and selectively mill areas of interest. This allows for minimal damage to the sample while still allowing one to obtain information on subsurface composition and surface structures. The surface structures of the samples varied widely depending upon the parameters used to make the samples. The model used to perform the analysis was a FIB 800 built by FEI. The system uses a liquid-metal ion source, in this case gallium, and accelerates the ions through a 30 kV potential. These ions then impact the sample with either enough energy to mill or image the desired area, based on the current. The imaging capabilities of a FIB offer a few advantages over traditional Scanning Electron Microscopes (SEM). FIBs utilize either secondary electron or secondary ion detection to produce the image. Looking at the secondary charge particles from samples allow the operator to see intense grain orientation contrast.

Many different images were taken of the samples to help collect an accurate representation of the surface growths. A program was written to allow the FIB to take a series of images sequentially from top to bottom of a wide field of view. This allowed the compiling of mosaic images that give a greater qualitative understanding of each sample's individual structural traits. An example of a mosaic image of a sample can be seen below (Figure 7).

24



Figure 7 - The image was stitched together using open-source image analysis software, ImageJ. Sample ZnO 2475-40 (24 hr, 75°C, 40mM)

All of these images were taken using a moderate beam (~66 pA). This allowed for less destructive imaging of the structures found and clear imaging of the sample. It also helped to reduce charging effects on the surface since ZnO's electrical conductivity has been shown to vary from being resistive $[(5x10^4) - (3x10^5) \text{ Ohm cm}]$ or low n-type conductivity with mobilities of 130-150 cm²/V sec (Polyakov). This can clearly be seen in the areas of contrasting brightness. The localized surface charging effects can make imaging very difficult without a conductive path for charged particles that become embedded in the sample. To mitigate this, grounding points can be made using the deposition of metal with the FIB or the sample can be tilted to allow the incident electron beam to spread its charge density over a larger area. In our case, a conductive layer was not added to samples because of the need for laser light interaction with the surface of the sample. Intensity of the light would also have been reduced during PL measurements if the emission light was only seen through sapphire, which is 90% transparent at these wavelengths, or through a thin conductive coating.

4.3 Qualitative Analysis

A perfunctory examination of the images reveals that the majority of the samples show rod structure growth. Many of these are well-aligned with the surface forming a near planar layer of ZnO with very small gaps between rods. However, on some samples a lattice mismatch is clearly visible. The figures below (Figure 8 and 9) demonstrate this respectively. From the XRD analysis, broadened diffractograms indicate strain and lattice defects. Figure 9 shows an area of the sample 2465-30 demonstrating seemingly randomly oriented growths emerging from a semi-planar ZnO layer. This sample's XRD FWHM of 1130.400±0.001 arcseconds was exceptionally high and this correlates with what is seen on the surface of this sample.



Figure 8 - Well aligned planar surface (24 hr, 50°C, 30 mM)



Figure 9 - Mismatched lattice surface (24 hr, 65°C, 30mM)

Another characteristic that correlates to the XRD data is the growth of nanopetal structures on many of the samples. When micro-area analysis of the sample is conducted on formations, they show an increase in crystalline quality from EDS analysis, this is discussed in detail later. The best (smallest) FWHM values (indicating high crystalline quality and/or lack of strain and lattice defects) were always found to have this structure present. Figure 10 below shows the structure of the nanopetals covering the entirety of the sample.



Figure 10 - 1280-10 (12hr, 80°C, 10mM)

Cross-sections were also milled on several samples to measure the approximate thickness of the ZnO layer. This was performed using the FIB to mill away small sections of the sample. These differences in material density are displayed as gray scale differences due to their individual electron backscatter. The growth pattern for ZnO is also clearly visible in Figure 11 which shows an image of the cross section taken at 45 degrees from sample and Figure 12 showing the same mill at 0 degrees. The thickness was approximately 5 micrometers across all samples.



Figure 11 - ZnO 2475-50 (24 hr, 75 °C, 50mM) Cross Section at 45 ° tilt



Figure 12 - ZnO 2475-50 (24 hr, 75 °C, 50mM) Cross Section at 0 ° tilt

4.4 Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy Analysis

Using an FEI XL30 Environmental Scanning Electron Microscope (ESEM), an elemental analysis was made using Energy-Dispersive X-ray Spectroscopy (EDS). It works by looking at the x-rays produced by excitation of the elements in the sample from either an electron beam or an x-ray beam. Since each element has a unique atomic structure, they each produce a unique set of x-ray emissions. To stimulate these characteristic spectra, a high-energy beam of electrons is directed at the area of interest. When the incident electrons interact with the atom, it will cause it to become excited. It will then give off this excess energy in the form of an x-ray. The incident charged particle may also eject an electron from the inner shell of the atom and create an electron hole. This hole is then filled by a higher shell electron which must give off energy to reach its new lower energy state. This energy is emitted in the form of an x-ray as well. Using an energy-dispersive spectrometer, the energy of the x-rays and the number of them can be determined.



Figure 13 - EDS Data for 2485-50 (24hr, 85 °C, 50mM)



Figure 14 - EDS DATA FOR 3685-50 (36hr, 85 ℃, 50mM)

Figure 13 (above) shows the elemental composition of a rod found on the surface of sample 2485-50. This clearly shows that it is primarily composed of zinc and oxygen. The aluminum present is due to the sapphire upon which the ZnO was grown. The other contaminates are likely a result of impurities introduced in the growth process.

The zinc to oxygen ratio could prove important. The ratio of zinc to oxygen will cause noticeable coloration of the sample. Additional oxygen content should yield an opaquer and whiter coloration of the sample surface and decrease photoluminescence detection through the sample which is not optimal for detector applications. Figures 15 and 16 below are images of the surface of the same sample and 3685-50 using an optical microscope. The surfaces of the samples each display some amount of opaque white material. This demonstrates the unbalanced zinc to oxygen ratio. The more transparent areas illustrate a more balanced stoichiometry. The second figure is of sample 3685-50 and clearly shows a larger area of transparency in the center of the sample which is the area being surveyed using EDS. The EDS data can be seen above in Figures 13 and 14.



Figure 15 - Optical Image of 2485-50 (24hr, 85°C, 50mM) Area of analysis highlighted



Figure 16 - Optical Images of 3685-50 (36hr, 85°C, 50mM) Area of analysis highlighted

4.5 Photoluminescence Measurements

Another analysis technique was PhotoLuminescence (PL) spectroscopy. This is a non-destructive probing of the sample with a very narrow wavelength of light, which causes electron excitation, resulting in the emission of light in a very narrow band of wavelengths. The PL measurements were performed using a Melles Griot Series 56X Omnichrome helium-cadmium laser. It lased at 325 nm using a pulsed beam with an intensity of 35 mW maximum. The emission peak wavelength can be used to determine the impurities in the sample since they can extend the de-excitation time and cause a shift in wavelength. The intensity of the emission also yields information about the stoichiometric properties of the sample since, in previous works (Wu), oxygen imbalance has been tied to lower intensity peaks.



Figure 17 - PL Measurement Experimental Setup

A diagram of the setup is shown above (Figure 17). The laser light is projected directly onto the sample with a diameter of approximately 1.1 mm. The sample's light emissions are then recorded using a Lambda LEOI-100 Experimental CCD

12 hr PL Data (unitless)±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	318	363	333	283	348
55°C	185	212	157	210	685
60°C	219	244	254	257	237
65°C	361	264	267	351	228
70°C	379	297	257	259	221
75°C	376	273	224	376	178
80°C	235	332	371	272	265
85°C	251	408	351	363	235
90°C	318	228	240	194	154
95°C	243	255	280	199	229
24 hr PL Data (unitless)±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	232	470	504	339	253
55°C	431	350	260	218	692
60°C	217	214	201	263	317
65°C	188	222	338	241	249
70°C	206	345	323	355	121
75°C	554	470	546	549	330
80°C	300	259	240	252	256
85°C	269	255	265	229	220
90°C	373	332	274	235	190
95°C	307	461	600	321	281
36 hr PL Data (unitless)±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	233	222	747	210	448
55°C	453	386	320	267	499
60°C	414	319	740	299	873
65°C	318	260	431	449	321
70°C	596	366	325	364	217
75°C	506	420	366	342	229
80°C	244	828	424	664	532
85°C	495	195	587	616	381
90°C	286	239	276	231	253
95°C	466	388	179	248	340

Spectrophotometer.

Table 4: PL Intensity Data.

As stated previously, a perfect balance between Zn and O should result in the best PL measurements, *i.e.* both a high relative intensity and very little wavelength shift

between samples. The PL data above (Table 4) shows that the samples all photoluminesce at or near 380 to 400 nm. The variation seen in the samples can most likely be attributed to defects present in the crystal structure, though the defect related green PL band would have to be compared to confirm this. The relative intensities of the samples also give insight into the stoichiometry of the samples. These samples demonstrate a fairly wide range of relative intensities, most likely due to an imbalance of zinc relative to oxygen. This is significant since this behavior will translate to low intensities under alpha irradiation. This is due to both radioluminescence and photoluminescence exciting electrons that follow the same transitions. Table 5 below shows the wavelength peak in nm for each of the samples.

12 hr PL Data (nm)±1	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	391	391	391	383	391
55°C	393	392	393	393	392
60°C	393	392	390	392	392
65°C	398	392	391	398	393
70°C	391	391	391	393	393
75°C	391	393	391	389	391
80°C	393	392	392	392	392
85°C	391	382	391	393	382
90°C	393	391	393	391	390
95°C	393	391	391	391	393
24 hr PL Data (nm)±0.4	10 mM	20 mM	30 mM	40 mM	50 mM
24 hr PL Data (nm)±0.4 50°C	10 mM 388	20 mM 398	30 mM 398	40 mM 392	50 mM 393
24 hr PL Data (nm)±0.4 50°C 55°C	10 mM 388 391	20 mM 398 391	30 mM 398 383	40 mM 392 391	50 mM 393 393
24 hr PL Data (nm)±0.4 50°C 55°C 60°C	10 mM 388 391 392	20 mM 398 391 391	30 mM 398 383 393	40 mM 392 391 391	50 mM 393 393 393 391
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C	10 mM 388 391 392 391	20 mM 398 391 391 391	30 mM 398 383 393 391	40 mM 392 391 391 391	50 mM 393 393 391 391
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C 70°C	10 mM 388 391 392 391 383	20 mM 398 391 391 391 391 391	30 mM 398 383 393 391 391	40 mM 392 391 391 391 391 391	50 mM 393 393 391 391 390
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C 70°C 75°C	10 mM 388 391 392 391 383 393	20 mM 398 391 391 391 391 391 392	30 mM 398 383 393 391 391 393	40 mM 392 391 391 391 391 391 393	50 mM 393 393 391 391 390 391
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C 70°C 75°C 80°C	10 mM 388 391 392 391 383 393 393 391	20 mM 398 391 391 391 391 391 392 382	30 mM 398 383 393 391 391 393 393 391	40 mM 392 391 391 391 391 391 393 393 391	50 mM 393 393 391 391 390 391 393
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C 70°C 75°C 80°C 85°C	10 mM 388 391 392 391 383 393 391 393	20 mM 398 391 391 391 391 392 382 391	30 mM 398 383 393 391 391 393 391 391	40 mM 392 391 391 391 391 393 391 392	50 mM 393 393 391 391 390 391 393 382
24 hr PL Data (nm)±0.4 50°C 55°C 60°C 65°C 70°C 75°C 80°C 80°C 85°C 90°C	10 mM 388 391 392 391 383 393 393 393 393	20 mM 398 391 391 391 391 392 382 391 392	30 mM 398 383 393 391 391 393 391 391 391 393	40 mM 392 391 391 391 391 393 393 391 392 392	50 mM 393 393 391 391 390 391 393 382 391

36 hr PL Data (nm)±0.4	10 mM	20 mM	30 mM	40 mM	50 mM
50°C	398	393	394	392	392
55°C	398	398	391	398	393
60°C	398	398	391	398	398
65°C	393	391	391	382	382
70°C	392	393	392	393	392
75°C	393	391	391	389	391
80°C	398	393	398	398	398
85°C	392	398	383	391	398
90°C	392	391	391	391	391
95°C	398	392	392	393	393

Table 5: Peak Wavelength on all samples

A statistical analysis of the peak intensity data (Table 4) shows that very few samples demonstrate significant changes between parameter variations. The analysis was performed using a t-test to compare each sample set to one another. Due to the small sample set sizes, they were grouped according to the fields being compared. For example, to compare time variation between growths, the set of five data points was chosen that varied concentration with constant time and temperature being average across the other two sets. This set was then compared against another that had different time but the same concentration and temperature averaging across the set.

Concentrations vs Time	<u>12hr vs 36hr</u>	<u>12hr vs 24hr</u>	<u>24hr vs 36hr</u>	
All Samples at Time	100.00%	92.14%	99.06%	
50 mM	79.18%	14.78%	72.07%	
40 mM	97.21%	45.83%	93.73%	
30 mM	82.83%	87.86%	7.76%	
20 mM	97.78%	79.80%	77.27%	
10 mM	90.64%	33.96%	82.05%	
Table 6: t-Test Analysis of PL Intensity Data				

The table above is one example of the t-tests performed between sample sets. The significant results occur above 95%. When all of a time groups samples are compared, as in the first line, the 36 hour samples have a significantly higher intensity return than the

other two time groups. This doesn't translate to each concentration subgroup. The other data sets did not show any other distinct patterns in the PL intensity data.

4.6 Alpha Spectroscopy

The alpha radiation response of the sample yielded valuable insight into the properties of these aqueously grown samples. Alpha spectroscopy was performed on a select few scintillators due to time constrains with the experiment. The primary PMT used was the Thorn EMI 9956KB PMT. The alpha source selected was plutonium-239 because of its well-characterized alpha spectrum. Table 7, shown below, details the energies of alpha particles emitted by Pu-239.

Energy (keV)	Probability (%)						
4117	9.30E-10	4392	2.46E-09	4392	2.46E-09	4934	6.00E-05
4181	5.60E-10	4400.3	1.03E-07	4400.3	1.03E-07	4960	7.00E-05
4187	7.40E-10	4408	1.00E-09	4408	1.00E-09	4987	1.30E-04
4202	4.00E-10	4419	3.30E-09	4419	3.30E-09	5006	1.70E-04
4204.5	6.10E-10	4448.5	2.00E-08	4448.5	2.00E-08	5028	9.00E-05
4280	1.90E-09	4464.7	1.15E-07	4464.7	1.15E-07	5054	4.70E-04
4306	1.00E-09	4467.4	6.90E-08	4467.4	6.90E-08	5076	7.80E-04
4326	4.20E-10	4497	1.50E-10	4497	1.50E-10	5105.5	1.19E-01
4327	2.30E-09	4503	5.38E-08	4503	5.38E-08	5111	1.00E-04
4349	3.00E-09	4510	8.00E-07	4510	8.00E-07	5144.3	1.71E-01
4364.5	8.40E-10	4529.6	3.19E-08	4529.6	3.19E-08	5156.59	7.08E-01
4380	2.50E-07	4534	2.84E-08	4534	2.84E-08	5156.7	3.00E-04
4390	1.00E-08	4559	1.20E-07	4559	1.20E-07		10000000

Table 7: Table of alpha particle energies and corresponding probabilities for Pu-239

The spectroscopy was conducted in a light-tight box inside a dark room. The box was constructed from yellow pine and then painted a flat black. The top of the box was covered in felt to reduce any additional light introduction to the system. The PMT and a holder for the alpha source were placed in the box. They were placed very close to one another to minimize the impact of air between the sample and the source. Air can affect the spectrum by broadening the expected peaks of the alpha spectrum and making the scintillator's performance appear worse. Additional felt was used to wrap the source

housing and the PMT directly to further reduce outside light interference. The ZnO sample was placed directly onto the glass of the PMT using optical grease to adhere it to the surface. The PMT used a Digibase to provide power and directly output its readings to Maestro, which can precisely control the power and gain for the PMT. A picture of the setup is detailed below.



Figure 18 - Alpha Detection Setup

The experiment for alpha spectroscopy yielded relatively poor results. The spectrum was generated by subtracting background contributions from the source spectrum itself. This showed a spectrum that doesn't show the three characteristic peaks expected for Pu-239: 5156.59 keV with a probability 70.77%, 5144.3 keV with a probability of 17.11%, and 5105.5 keV with a probability of 11.94%. If these peaks are not readily apparent, appearing as a bulge in the spectra, then the discrimination of this material as a detector is very poor.



Figure 19 - Original ZnO Alpha Spectra

Figure 19 displays the results of alpha radiation on one of the aqueously grown ZnO detectors. The spectra does not show obvious alpha interaction. This spectrum includes potential sources in the background that could be obscuring the results. Therefore, a background is taken, which includes all non-alpha contributions to the spectra, and subtracted from the source spectra.



Figure 20 - Pu-239 Alpha Spectrum Composite from Detection Experiment Sample 2475-50 (24 hr, 75 °C, 50mM)

Figure 20 displays the results of alpha radiation on one of the aqueously grown ZnO detectors with the background subtracted. The spectrum is not well defined. A characteristic bulge is expected but instead only an indistinct energy distribution shown. We could even expect to see one a slight rise of increased counts that could be energies but the spread of energy across the entire spectra yields little discrimination. This detector did not perform on par with the baseline material using the similar tests (Burgett). The spectrum shows some degree of alpha detection though there is definitely not a distinct area from alpha contributions as would be expected given the spectra described above. Below is shown MOCVD-grown samples at various temperatures responding to alpha radiation from Thorium-230 (Figure 21).



Figure 21 - Burgett Alpha Spectra using Th-230

If all counts above channel 1000 are assumed alpha radiation, then a rough efficiency calculation can be made. Using the solid angle formula (Knoll), the detectors intrinsic effectiveness can be found. The plutonium used was a 0.1-microCurie (μ Ci) alpha source. From this the total number of alphas emitted over the time, can be found. Approximately 3.3E8 alpha particles were emitted in the 9057 second run. The detector only saw 1762 alpha particles in this time. From the solid angle formula the detectors efficiency is 0.00000358%. This is extremely low.

From the PL data we can conclude that the ZnO was behaving similarly under alpha irradiation and thus produced low intensity scintillation. This could be the reason why the spectrum appears so poor. This low intensity return is most likely due to excess oxygen present in the samples causing a lack of transparency. The low intensity returns could also be attributed to a quenching effect. Quenching occurs when dopants trap the scintillator material, preventing it from scintillating. This only occurs when there is an excess of dopants in the lattice. Excess oxygen could be acting as acceptors in the scintillator and passivating the PL centers by trapping excited electrons. Oxygen has been shown to act as an acceptor in semiconductors (Akimoto). More likely, there is hydrogen entrapment as it has been shown to completely prevent scintillation in ZnO detectors at high enough concentrations (Burgett). This could have resulted from the hydrogen ions present in the water.

CHAPTER 5. Conclusion

The data shows that the aqueously-grown samples demonstrate comparable crystalline quality to previous attempts but fail to compare favorably with other techniques when analyzed as a detector material. The variation of growth factors showed very little correlation to significant sample improvement between parameters. The only parameter of note is the variation in concentration relating to FWHM in the XRD measurements, suggesting that the best crystalline quality is at 40 mM concentration regardless of the other two phase spaces. The PL measurements also showed that intensity was greater for samples with longer bake times, the 36-hour data being the most ideal. The FIB analysis shows a great deal of variation in the surface structures observed across all growth parameters. EDS analysis shows several features. The low-level silicon contamination may have come from the beaker in which the sample was baked. The beakers were thoroughly cleaned after each bake though the zinc oxide growth on the side walls proved difficult to removed and required a great deal of scrubbing. This could have caused small amounts of silicon from the glassware to come free and contaminate samples. The low level chlorine contamination is most likely from salt introduced during handling of the samples, as salt is present on our skin and is easily transferred. The sodium is not visible due to the strength of the zinc peak which overlaps around 1 keV. EDS analysis also shows that there is likely excess oxygen relative to zinc. This resulted in very low PL emission from the surface of the material compared to MOCVD-grown samples. This is very significant for alpha spectroscopy results. With the low light emission observed in PL measurements, it can be postulated that the samples are behaving similarly under alpha radiation and giving off very little light. Thus, the

43

spectrum observed is very poor. With this data, we conclude that aqueously-grown ZnO under these temperatures and times produces material ill-suited for detector applications.

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