

OPTOELECTRONIC AND MORPHOLOGICAL PROPERTIES OF
ZINC OXIDE NANOSTRUCTURES PRODUCED BY
HYDROTHERMAL SYNTHESIS

by

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I. INTRODUCTION

ZnO is an important material that has gained much recognition in the scientific community lately due to its incredible versatility and properties [1]. Physically, the appearance of ZnO is that of a white powder. It is mostly produced synthetically and is used in the manufacturing of many products from rubber to food additives. To the materials science community, however, ZnO is an even more interesting material. ZnO is a wide (~ 3.3 eV), direct bandgap semiconductor that most commonly crystallizes in the hexagonal wurtzite structure. It has very desirable semiconductor characteristics including strong luminescence, high charge carrier mobility, as well as a large piezoelectric effect. ZnO is also easily n-type doped for tunable electronic properties, although p-type doping still remains a problem. One of the biggest advantages of ZnO, however, is its ability to form nanostructures of different morphologies and sizes. Nanoscale materials differ greatly from their macroscopic counterparts in part because of increasing surface to volume ratio. Increasing this ratio to high levels causes the material's properties to be mostly determined by the surface rather than the bulk. This means that surface related defects dominate at the nanoscale which can be used to our advantage. Quantum confinement effects also come into play at the low end of the nanoscale which can greatly impact material properties. Nanoscale materials are becoming more and more popular due to the increasing demand for high-performance materials to be used in electronics, and we study ZnO because it is very promising in this regard. ZnO nanostructures have become a very popular nanomaterial due to its wide range of potential applications in nanoscale electronics and optoelectronics. In order to be useful, however, it is desirable for them to be produced in large quantities, with excellent

crystallinity and reproducible properties. Major challenge in this respect, however, is the difficulty and cost involved in fabricating the nanostructures in any appreciable quantity, as most current methods involve high temperatures or expensive growth equipment. In our project, we aim to develop and refine a low-temperature, inexpensive solution-based method for synthesis of ZnO nanostructures. By developing such a method and expanding the range of morphologies we can create with it, we can effectively lower one of the barriers to using ZnO as a high-performance semiconductor in optoelectronic applications. Additionally, by studying the precursor chemicals used to create the ZnO, we can further the development of other solution based synthesis methods that might appear in the future. We also aim to characterize the optoelectronic properties of different morphologies in order to correlate morphology with changing electronic structure. By doing this, we can truly make ZnO a more versatile material that can be tailored for specific electronic applications.

II. Synthesis

There are several synthesis methods for growing ZnO nanostructures with varying degrees of difficulty and very different final products. Such techniques include chemical vapor deposition (CVD), which is very expensive but produces impressive arrays of highly ordered nanostructures; seeding in conjunction with other methods such as electron beam lithography; or hydrothermal synthesis routes. Our focus is on a hydrothermal synthesis method originally proposed by Lei et al. [2] but greatly refined and developed by ourselves.

A. Technique

Before getting into the specific growth parameters we employ to create ZnO nanostructures, it is important to review hydrothermal synthesis to understand how it is possible that these exotic nanostructures form. Hydrothermal synthesis depends upon the use of an autoclave, which is a chamber usually used to sterilize things such as surgical instruments and glassware. It works by continuously subjecting the objects to be sterilized by hot, pressurized steam that is cycled through the chamber. Although this environment is great for sterilizing instruments, it also has a side effect that makes hydrothermal synthesis possible. By inserting a container filled with growth solution into the autoclave, the steam creates a temperature gradient between different parts of the solution, and the high pressure keeps the solution from boiling. Usually hydrothermal synthesis works by exploiting the temperature gradient to supersaturate the growth solution with the solute and causing it to crystallize when it cools down; our method exploits these environmental conditions in a slightly different manner but achieves similar results.

B. Growth Parameters and Procedure

The growth solution that we employ requires precise amounts of different precursor chemicals. The growth procedure and solution are as follows: 1.26g of Hexamethylenetetramine (HMT, $C_6H_{12}N_4$) and 1.65g of Zinc Acetate Dihydrate ($Zn(C_2H_3O_2)_2 \cdot (H_2O)_2$) of analytical reagent grade are combined with 30mL of deionized water in a 50mL beaker. In some cases, $ZnCl_2$ is substituted for Zinc Acetate Dihydrate in various molar ratios. 2mL of Ammonium Hydroxide (NH_4OH) is then added dropwise under continuous magnetic stirring. After this, a small piece of zinc foil (99.999% pure)

is washed with methanol and put into a plastic bottle along with the solution. The solution is then autoclaved for approximately 10 hours including cool-down time. Finally, the zinc foil is then extracted from the solution, lightly washed with deionized water, and air dried for at least 24 hours in a vent hood. The zinc foil is then characterized with Scanning Electron Microscopy (SEM) to check the morphology and size of the final product. The base product that is produced is shown below.

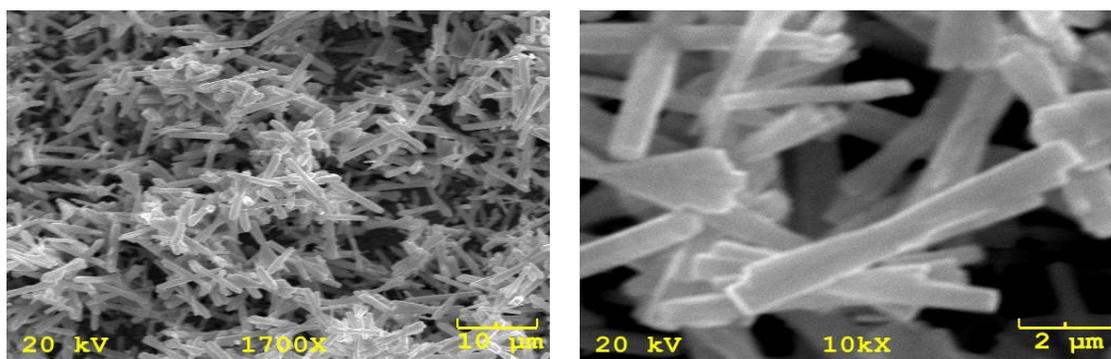


Figure 1

After examining the morphology and considering the growth conditions, a reasonable explanation of the growth process that occurs is evident. First, the autoclave pressurizes the local environment, causing the boiling point of the growth solution to rise and altering the saturation level for the solution. Next, the steam creates a temperature gradient in the solution, causing the top of the solution to become much hotter than the bottom. This results in convective motion inside the solution bringing much of the solute to the top. Additionally, the solution etches and strips some of the zinc from the foil, causing the stripped zinc to rise to the top to participate in the reaction and creating potential seeding sites on the foil itself. Next, the solutes react with each other in the top part of the solution and deposit themselves on the zinc foil at the bottom. Occasionally, if

the reaction is carried out long enough, the ZnO might deposit itself on already formed nanostructures, creating secondary growth structures in the process.

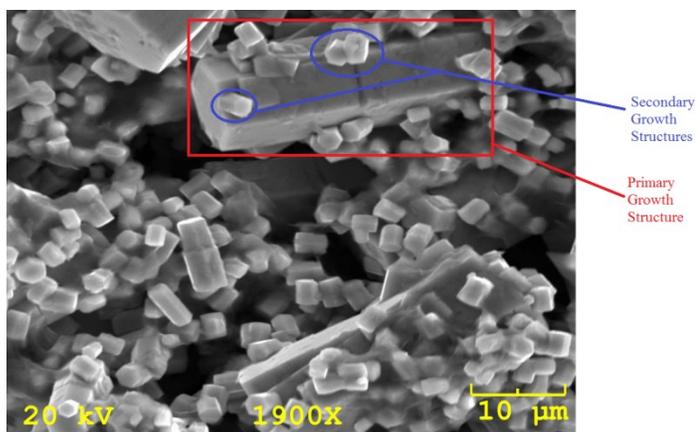


Figure 2

During growth, the ZnO nanostructures seek to minimize surface energy, which generally means that nanostructures will grow axially to maximize energetically favorable nonpolar Zn surfaces rather than grow large polar faces terminated by oxygen. The final structure, however, is difficult to predict due to the complicated reactions happening simultaneously during the growth phase. Additionally, if the lattice is disturbed during growth, crystal twinning may occur which looks like two separate structures grown into each other. The final morphology and size of the ZnO nanostructures can be controlled by changing the growth parameters. In the next few sections, the influence of changing different growth parameters such as concentration of different precursors, growth time, and other factors on morphology will be explored.

C. Effects of Concentration of Hexamethylenetetramine (HMT)

Although at first glance HMT might appear to be completely unnecessary in the synthesis of ZnO nanostructures, as it is an organic compound $((\text{CH}_2)_6\text{N}_4)$ and is clearly neither a zinc supplier nor an oxygen donor, HMT is actually crucial to the formation of

well-defined nanostructures and plays an important role in the morphology of the final product. The figure below demonstrates the powerful effects changing HMT concentration can have on final morphology. It is clear by these images taken at different concentrations of HMT that it plays a crucial role in determining the thickness of the final product. With increased amounts of HMT, we not only see the thickness of the nanostructures increasing, but also the formation of urchin-type structures. Additionally, it appears as though there is a “sweet spot” in the concentration that produces the highest density of nanostructures. Since HMT concentration affects formation density, it must play a critical role in the chemical reaction; this will be explored later on.

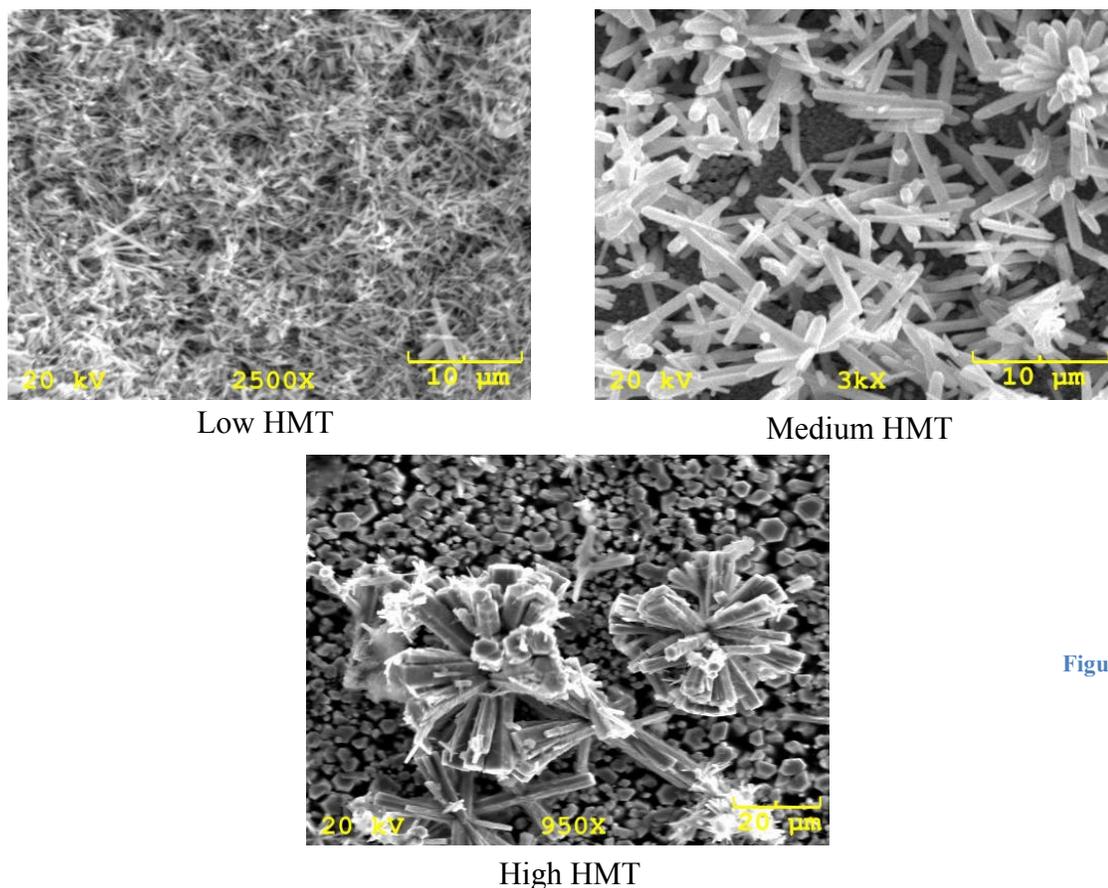


Figure 3

One important thing to note, however, is that HMT affects thickness regardless of what zinc salt is used as a precursor. The images below demonstrate that HMT is also capable

of controlling size when zinc chloride is substituted for zinc acetate. Although ZnO morphologies produced by zinc chloride are different from zinc acetate, HMT is still able to react in a similar manner and is still vital to the growth process.

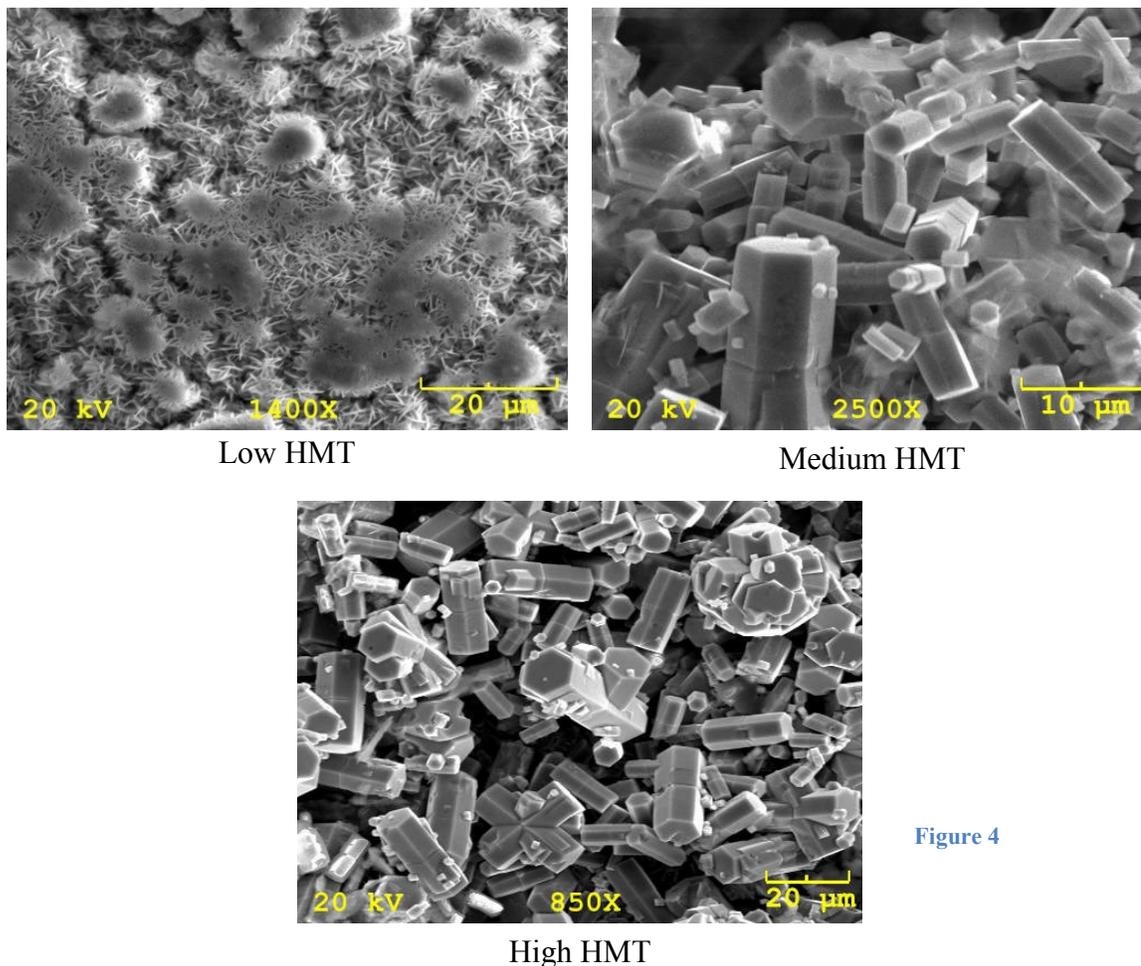


Figure 4

D. Effects of Concentration of Zinc Acetate Dihydrate

Unlike HMT, the effects of Zinc Acetate Dihydrate on the final synthesis product are less pronounced. Zinc acetate acts as a zinc supplying salt as it will dissociate into zinc and acetate ions in water (although not completely). Thus we can predict, at least to a certain extent, that lowering the amount of zinc acetate will reduce the supply of zinc ions available for the reaction and thus limit the growth of the final product. We predicted

that increasing the amount too much might cause excessive deposition, degrading the synthesized product. Zinc acetate lowers the pH of the growth solution as zinc acts as a Lewis acid (electron pair acceptor) which overcomes the effect of acetate acting as a conjugate base (to acetic acid). This causes the solution to become slightly acidic ($5 < \text{pH} < 7$), the effects of which will be discussed later. The images below show the effects of changing the amount of zinc acetate while keeping all other precursors the same.

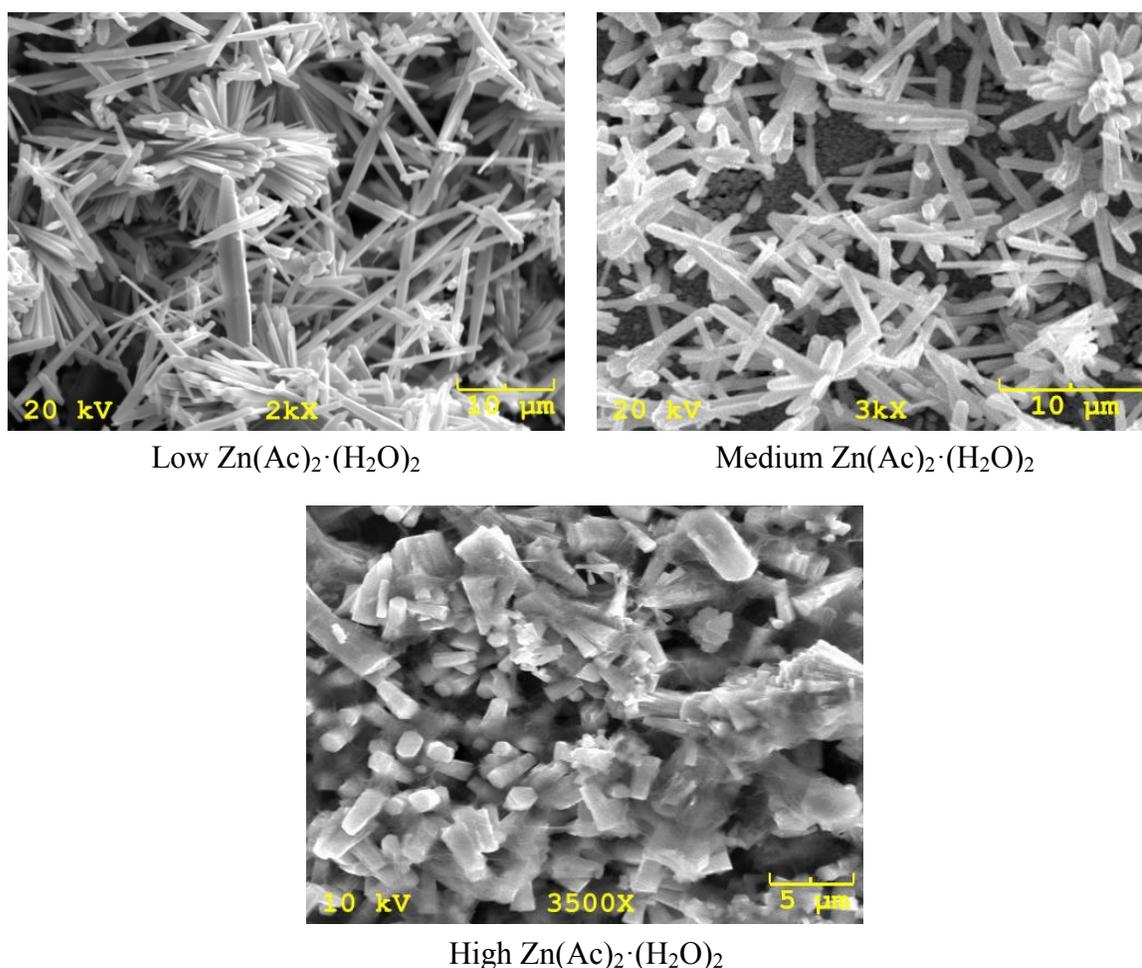


Figure 5

As it can be seen above, intermediate amounts of zinc acetate dihydrate produce normal ZnO nanorods, whereas lower amounts produce thinner rods and higher amounts begin to form plates. Clearly the predictions for medium and high amounts of zinc acetate

dihydrate proved true, but the product obtained for lower amounts was unexpected. There are two possible explanations. It is possible that the amount of zinc acetate dihydrate was not reduced enough to cause a shortage of zinc ions. It is likely that less zinc acetate dihydrate is available to neutralize the hydroxide and so the pH of the solution increases. In a similar fashion, the product obtained from high amounts of zinc acetate dihydrate cannot be completely attributed to excessive deposition as there are significant contributions from the pH of the solution as well to the final morphology. It is not necessary to use zinc acetate as the zinc supplying salt; in theory, it is possible for several different zinc salts to work in synthesis as well, as long as any secondary reactions caused by the anion do not affect the primary reaction. An example of a zinc salt that can be used in place of zinc acetate is zinc chloride, which will be explored in the next section.

E. Effects of Substituting in Zinc Chloride

Zinc chloride (ZnCl_2) is an interesting zinc salt to use in hydrothermal synthesis of ZnO and has profound effects on the final morphology that is not seen in most other growth methods. ZnCl_2 readily dissociates in water to supply both zinc and chlorine ions. Zinc chloride is reasonably acidic as zinc is a Lewis acid, while chlorine is the conjugate base to a strong acid (HCl) and is therefore pH neutral. As zinc chloride is more acidic, it has an easier time removing the passive layer of zinc carbonate from the zinc foil, allowing the foil to react more readily with the growth solution. The SEM images below demonstrate the exotic structures that are formed with zinc chloride.

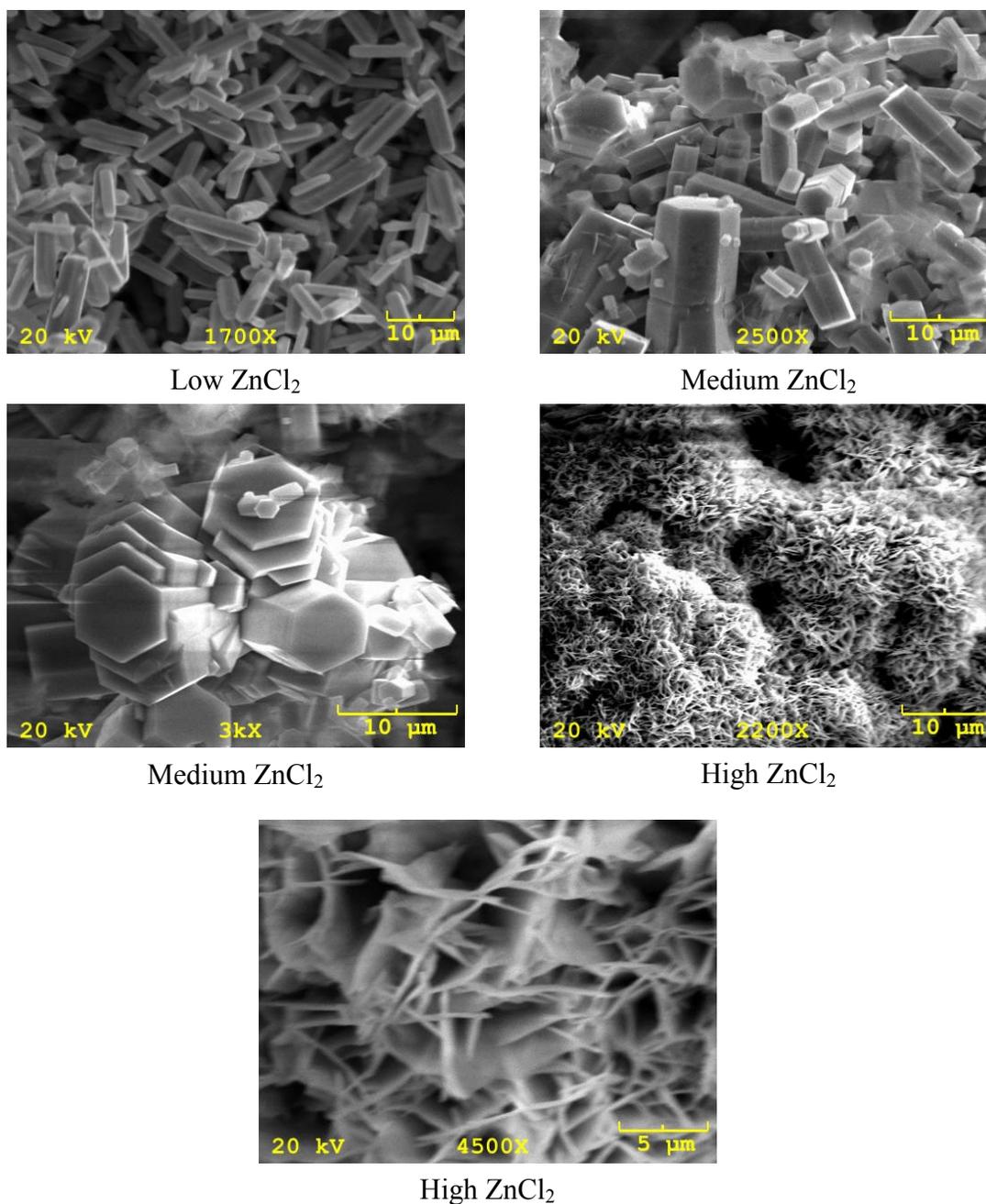


Figure 6

The difference in morphology when compared to zinc acetate is quite pronounced. At low amounts of zinc chloride, mostly normal nanorods are produced. This is not surprising because the low amount of zinc chloride that was used is 1.65g, which is the same mass as that used for the medium amount of zinc acetate dihydrate. The key difference, however, is that zinc chloride has almost half the molar mass of zinc acetate

dihydrate, so we are supplying twice as much zinc with the same mass of salt. This suggests that excess zinc ions might not necessarily cause excessive deposition and pH might have a larger role to play in the reaction than previously thought. The amount of zinc ions supplied by the zinc foil could be different with each zinc salt. At medium amounts of zinc chloride (3g), we see a very interesting shift in growth preference for polar surfaces over nonpolar. We also see a drastic increase in the amount of twinning near the top surface, which is greatly increasing the polar surface area. This is both surprising and possibly advantageous as nonpolar surfaces are usually energetically favorable and very few synthesis methods have been able to produce large polar surfaces. Many of these crystals are also extremely well-defined and almost perfectly hexagonal. The implications of having such large polar surfaces will be explored later on as large oxygen terminated surfaces generally have interesting optoelectronic features. At high amounts of zinc chloride (4.5g), we see an almost complete shift into two dimensional sheet-like structures that look like leaves of a bush. Whether the large surfaces are zinc terminated or oxygen terminated is currently unknown but warrants further investigation. It is interesting to note that even at extremely high molar amounts of zinc chloride, it has still not shown signs of structure degradation unlike zinc acetate dihydrate, which at 1.95g (which is still a very low molar amount compared to zinc chloride) starts to form a film rather than separate nanostructures. In the next section, the effects of various other factors on the morphology of the product will be explored, as precursors are only part of the puzzle surrounding the growth mechanism.

F. The Effects of Changing Multiple Concentrations

Although the effect of changing only one precursor concentration generally has a clear-cut trend, the effects of changing multiple concentrations introduce strange effects and variations on the morphology. When both HMT and zinc acetate are increased, the most visible change to the morphology happens to the urchin and bushel type structures. In particular, they appear to fan out more into a common plane making the structures “flatter”. These effects can be seen below.

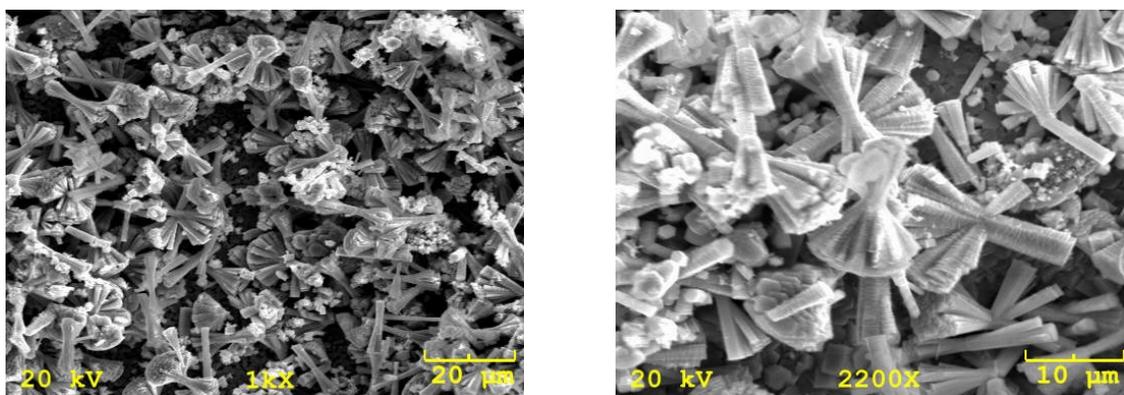


Figure 7

G. The Effects of Various Other Growth Factors

Hydrothermal synthesis is a very complex process that is sensitive to a wide range of growth conditions. Although precursor concentrations are generally considered to be the most important factor influencing the final morphology, there are other factors that must also be considered. In particular, factors such as pH, directly result from concentration but have their own effect on the growth process. In the next few sections, the effects of growth time, pH, growth temperature, and purity of zinc foil will be explored.

1. Growth Time

The effects of growth time are probably the easiest to determine and quantify. Under normal circumstances, the growth time is 8 hours of autoclaving (~10 if including warm-up and cool down). This time period is when the critical chemical reactions take place and crystallization sets in. It can reasonably be assumed that a negligible amount of the reaction takes place at any other time as room temperature is nowhere near the optimal reaction temperature and the pressure is not conducive to crystallization. Since crystal growth takes quite a bit of time, we can assume that less growth time will lead to smaller ZnO nanostructures, and indeed this is the case. When growth time was reduced to half of the base amount, we observed much smaller structures. Although there is some variability in the sizes of the structures grown with each precursor concentration (some concentrations produce uniform sized structures, while others had very inconsistent sizes), the samples with half the growth time had half as big of structures on average. We did not perform many growth time dependent studies as they had been done multiple times before [3], but this is clearly not a linear relationship despite the fact that we obtained roughly twice as large of nanostructures with twice the growth time because you will get diminishing returns with longer growth times as you will eventually run out of reactants.

2. Growth Temperature

We did not run any temperature-dependent growth experiments, but according to literature, higher temperatures support the growth of films, while lower temperatures produce shorter, less hexagonal rods [2]. This is most likely due to changing reaction rates, as rod formation requires slow reaction times due to the lengthy amount of time it

takes to arrange and form the long bond chains. As temperature would speed up the reaction rate, it is expected that films would be grown and nanorod formation would be suppressed.

3. Purity of Zinc Foil

To study the effect of zinc foil purity, we used the following grades: 99.9% and 99.999%. In most cases, less pure zinc foil resulted in a smaller density of nanostructures and less uniformity. In one case, growth was severely impacted and very few ZnO structures were grown at all. This is due to the reactive properties of zinc. When zinc is present in a highly pure form, it actually reacts more slowly, which is preferential for growing nanostructures. If the zinc used in the reaction is too impure, the reaction will proceed too rapidly for any nanostructures to form. We observed the best results using 99.999% pure zinc foil, which is the purity used in nearly every synthesis performed. Depending on the particular growth solution, however, 99.9% pure foil was found to be adequate, which is good news for potential industrial application, as commercially used Special High Grade Zinc is 99.995% pure, which would be more than adequate for our growth method.

4. pH

Probably the most influential of all the miscellaneous factors is pH. Although the pH is determined by the relative concentrations of the precursor chemicals, changing the pH is a side effect of the precursors and not the main focus, and the effect of pH is large enough to warrant a separate discussion. Synthesis techniques that rely on growth solutions are very sensitive to the precursors that are used. One main reason for this is that nanostructure growth is extremely sensitive to pH. Both acids and bases have

important effects on the growth process and the pH of the growth solution must be tailored to the application that is desired. For our synthesis technique, a pH neutral solution cannot be used because a passivating layer of zinc carbonate forms on the surface of zinc foil that will keep it from reacting with the growth solution and prevents the formation of seeding sites. Acids are able to neutralize this passivating layer, freeing up the zinc foil to react with the solution. This is not the only function of acids in nanostructure growth, however, as they are effective etching agents. The important crystal growth pH, region, however, is that above a pH level of approximately 8 or 9. This pH region is ideal for crystal growth and is what facilitates the creation of these exotic structures. OH^- ions are strongly attracted to the positively charged zinc ions and surfaces, which causes the zinc to form ZnO bonds in a long chain rather than into a plate. If pH is too low, there will not be enough OH^- ions to force the zinc into intermolecular bonds, which will cause it to form plates or film. If pH is too high, intermolecular bonding can grow out of control and cause bond formation to become unselective in preferential orientation, which would cause undesired nanostructure growth and decrease in uniformity. The importance of pH on the final product is so important that many systematic studies have been done on the subject [4,5]. Therefore, when high amounts of zinc acetate dihydrate were added to the solution, the film that was developed was partially from the lowering of the pH level as zinc acetate acts as a mild acid. We can also see the opposite effect when very little is added and nanowires are created, because preference has shifted to long chains of ZnO due to the alkalinity of the growth solution.

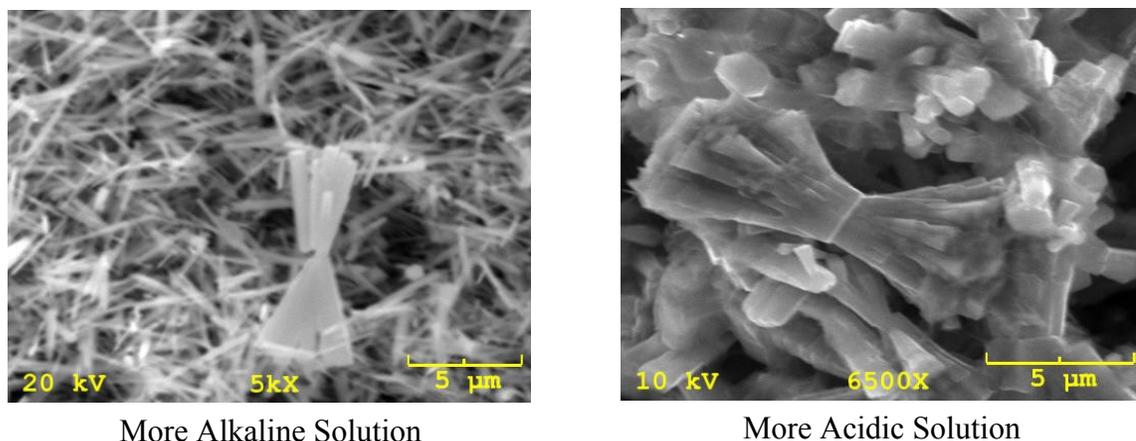
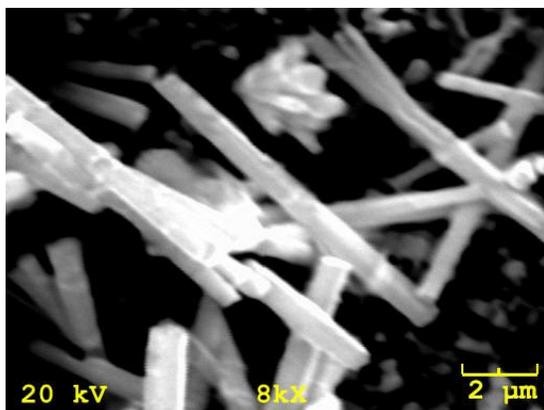


Figure 8

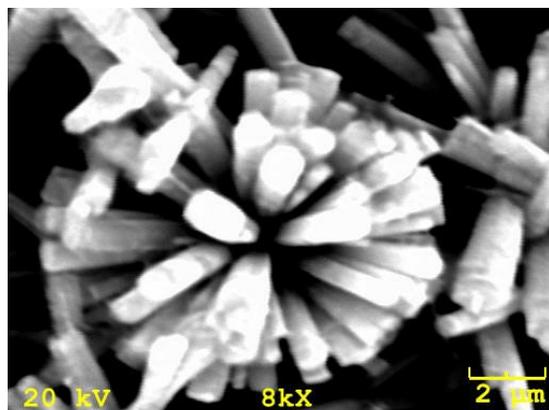
This is also the reason why ammonium hydroxide is added to the growth solution, as we want to push the pH of the solution into the crystal growth region. Therefore, when choosing the concentrations of precursors, it is important to note each precursor's effect on the pH of the solution and calculate the final pH before synthesis. If it is desired to add a large concentration of an acid such as the zinc salt, it may be possible to add a strong or a weak base that is relatively strong in order to balance out the pH and make the final growth solution alkaline. This cannot be done in all cases, however, and the solubility of the added base at elevated temperatures must be taken into account.

H. Morphologies Capable of Being Produced

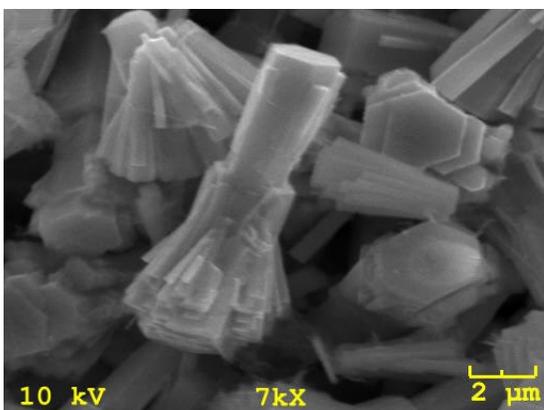
The reason that this synthesis technique is so powerful, aside from the obvious benefits of it being inexpensive and easy to perform, is the variety of morphologies it is able to produce. By simply changing the growth parameters slightly, we are able to obtain a completely different set of nanostructures with different optoelectronic properties. The morphologies that we have been able to obtain so far include urchins, rods, wires, leaves, plates, brooms, bushels, and a few others. The SEM images below showcase a few of these obtained morphologies.



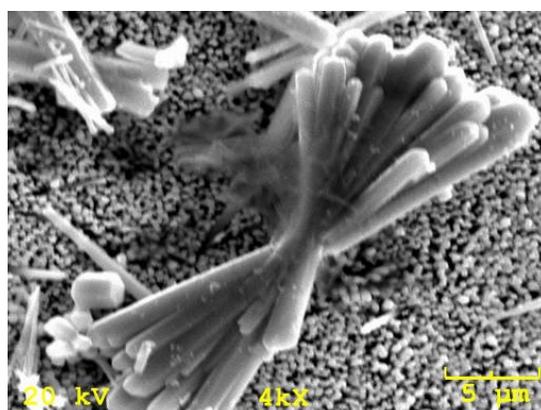
Rods



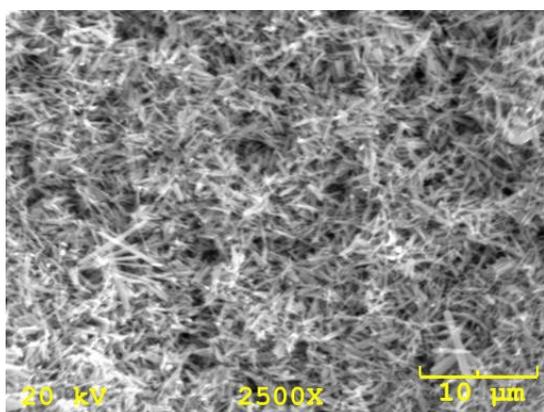
Urchins



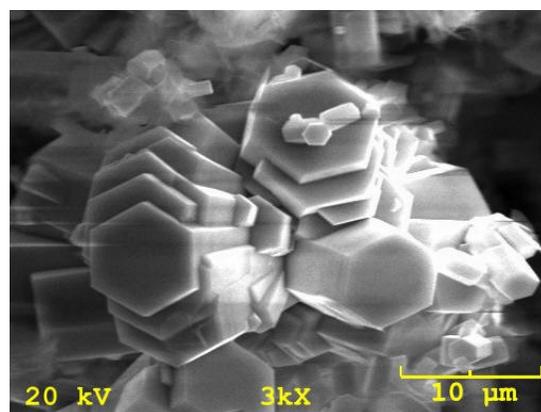
Brooms



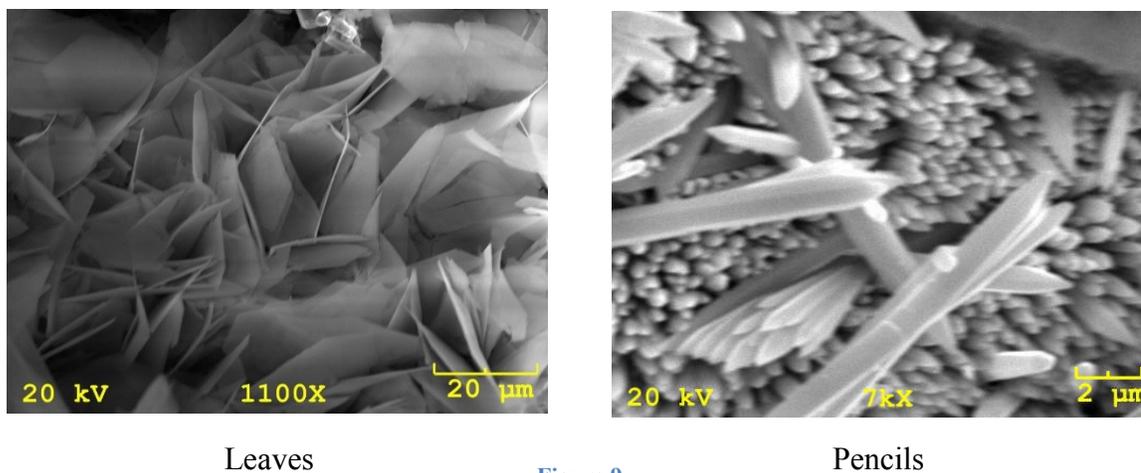
Bushels



Wires



Massive Polar Faces



By using different zinc salts, we can also obtain different variants of the same morphology. Substituting in zinc chloride instead of zinc acetate yields “fatter” versions of the same morphologies. These variations can be seen below.

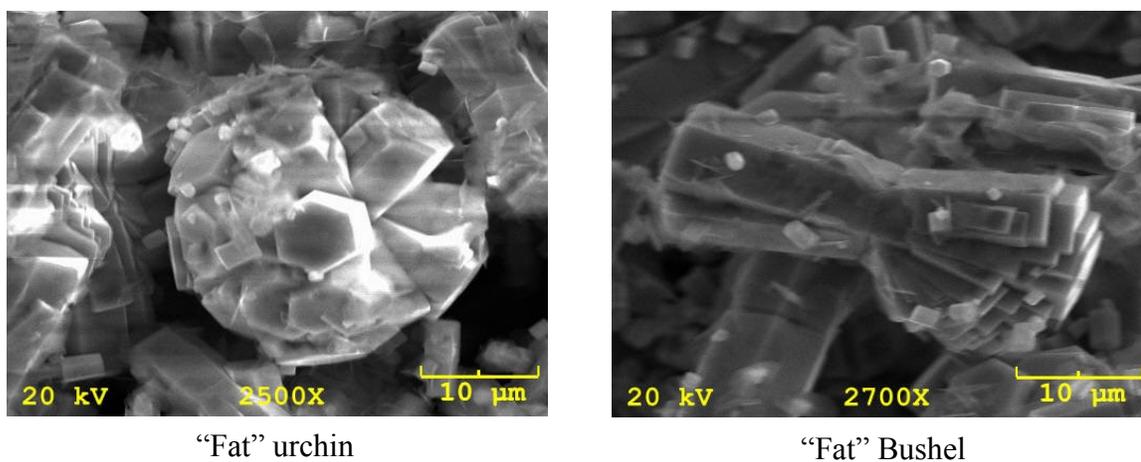


Figure 10

Clearly the synthesis method we employ is extremely versatile and capable of producing a wide variety of different sizes and morphologies. This is extremely advantageous, as the next section will demonstrate that certain optoelectronic properties depend heavily on the morphology of the material.

III. CHARACTERIZATION

Now that we have been over how these exotic nanostructures are produced and what the effects of changing different growth parameters are, we must now characterize them so that we may know how the final optoelectronic properties are affected by their morphology. We will determine the purity of the synthesized products as well as the degree of crystallinity. In order to do this, we will deploy several characterization techniques: photoluminescence spectroscopy (PL), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

A. Experimental

The results obtained from PL, EDS, and XRD studies will be presented here. These techniques will allow us to learn how morphology affects certain electronic defect levels and provide insight into how these defects impact charge transport. In this section, I will go over details of the experimental methods that were employed.

1. X-ray Diffraction

XRD is an extremely useful tool for determining the structure of the crystals present in a sample. It works by bombarding the sample with X-rays from an X-ray generator. X-rays are generated by applying a large voltage to a stream of electrons which accelerate to high speeds and smash into a metal plate. This excites the inner shell electrons of the metal and causes it to emit monochromatic X-rays corresponding to its $K\alpha$ and $K\beta$ lines (these lines are explained in figure 11 below.) The X-rays scatter off the atoms that make up the crystal and undergo either destructive or constructive interference as described by Bragg's Law. The sample is rotated with a goniometer so a detector can measure the intensity of the diffracted X-ray at different angles, and a plot of intensity

versus angle is produced. Different elements have unique diffraction patterns (diffraction peaks for different Miller indices) which can help in analysis of the results. In our case, we use it to confirm that our synthesized samples have good crystallinity and to some extent, correct composition.

2. Energy-Dispersive X-ray Spectroscopy

EDS is a powerful technique for determining the composition and purity of a wide variety of sample types. EDS works by exploiting the uniqueness of electron shells to specific elements. By using an excitation source such as an electron or X-ray beam, electrons in the sample's inner shells are ejected and electrons from higher energy shells fill the empty spot (electron hole). The difference in energy between the inner and outer shells is then released through an X-ray, which can be detected by a spectrometer. The number of X-rays emitted are also counted so that a near exact composition percentage can be determined.

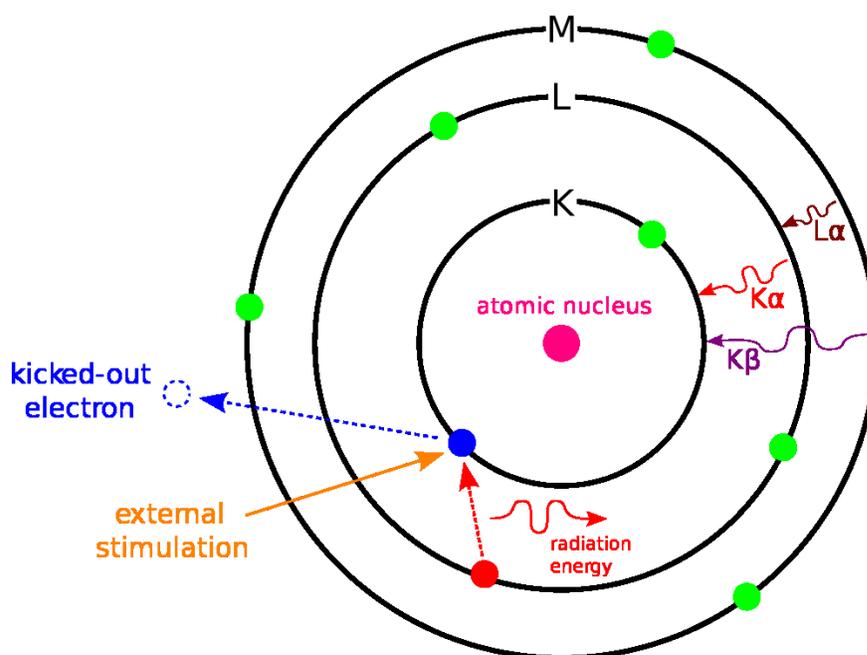


Figure 11

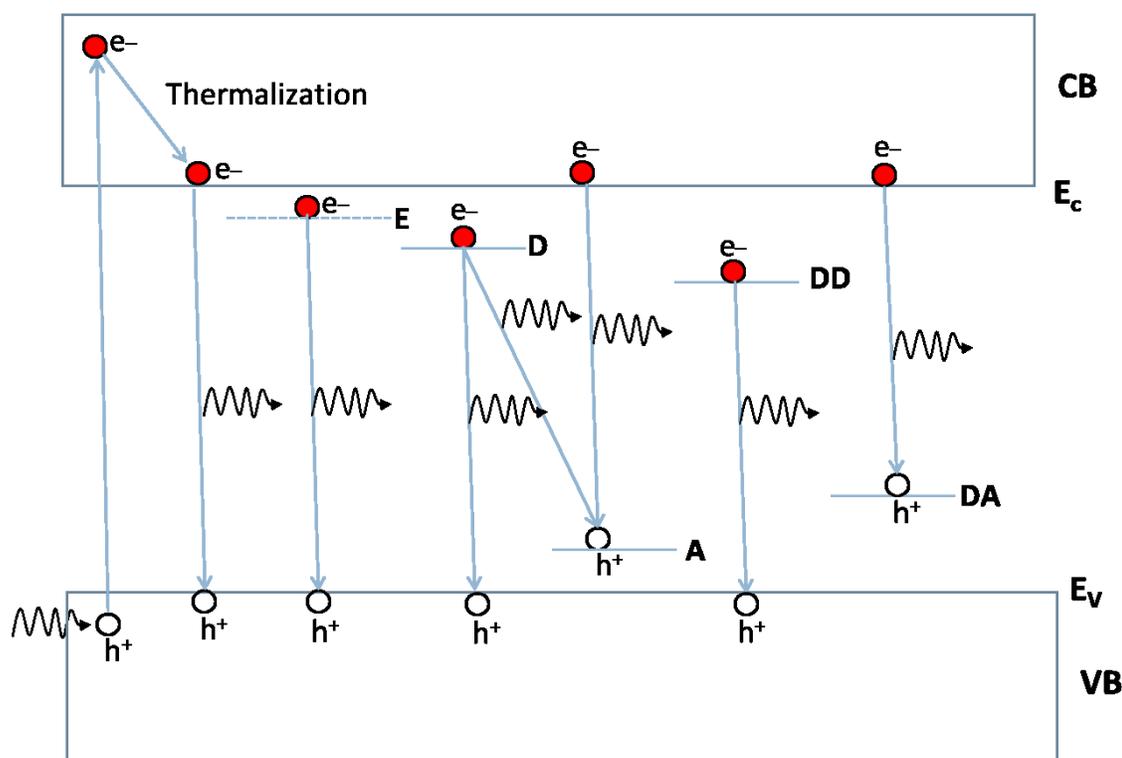
In this graphic, the blue electron is ejected by external stimulation and replaced by the red electron, thus emitting energy $K\alpha$. $K\alpha$, $L\alpha$, and $K\beta$ refer to energy differences between electron shells, which are unique to each element and can be used to determine composition.

This technique is extremely powerful for analyzing unknown samples and elucidating the purity of a specimen. Although this technique is good for quick analysis, it can be inaccurate for inhomogeneous samples and for samples that contain elements with similar electron shell energies. In our study, we use it to ensure that our samples are not contaminated with other zinc species such as zinc hydroxide or zincates.

3. Photoluminescence Spectroscopy

Unlike the other two experimental techniques, which are focused on the quality of our synthesized products, PL focuses on the optoelectronic properties of the material. PL is a popular nondestructive technique for probing the electronic structure of a material. PL works by using an excitation source such as a laser or a lamp with an energy higher than the material's band gap energy to excite electrons from the valence band to states inside the conduction band. After a period of both energy and momentum relaxation (thermalization), the electron occupies an energy state either near the band gap minimum or a defect state that can be from multiple sources such as vacancies or interstitials inside the lattice. The electron then transitions back down to the valence band or an acceptor state, emitting a photon with the energy difference which can then be detected by an optical spectrometer. A range of energies are scanned to identify the energy of the band gap and defect states through measurement of the photon's energy. An optical chopper and lock-in amplifier are generally used in tandem to filter out noise and improve the

signal-to-noise ratio. PL can also be performed at lower temperatures (<100 K) to improve resolution by minimizing the amount of thermal energy the electrons have available to jump to other energy states. Low-temperature PL is also useful for investigating exciton (electron-electron hole pairs bound by Coulomb force) behavior in semiconductors as most light emission at lower temperatures from semiconductors is from excitonic recombination due to the thermal energy being lower than the exciton binding energy.



In this graphic, the electrons in the valence band (VB) are excited up to available energy states in the conduction band (CB) or donor states (shallow or deep donors; D and DD). The material wants to minimize energy so the electrons transition back to the valence band or acceptor states (shallow or deep acceptors; A and DA) and emit a photon to conserve energy with energy equal to the difference between the states.

Figure 12

We will be using PL on our synthesized ZnO to correlate changing morphology with shifting electronic structure. In particular, this study will provide insight into the origins

of ZnO defects and how to control them. By learning how to control the relative size and location of defect states in our synthesized ZnO, we will be able to tailor a semiconductor material with specific electronic properties for industrial applications.

B. Results

The PL results showcase the electronic structure of the ZnO nanostructures, but through XRD and EDS data we may demonstrate that ZnO has been synthesized and that it is relatively high quality. First of all, the XRD data below taken of a synthesized ZnO sample illustrates several key concepts.

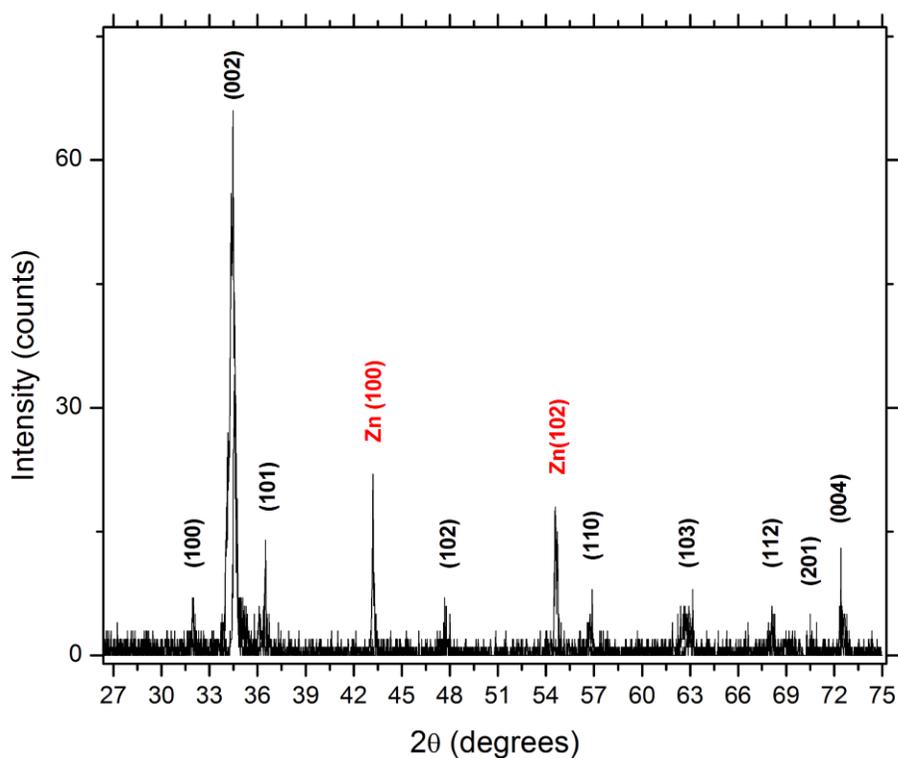


Figure 13

As it can be seen, there are several diffraction peaks, each belonging to a different crystal face designated by its Miller index in parenthesis. Clearly there is no definite preferred orientation, indicating that the nanostructures are randomly aligned. Most crystal face diffraction peaks for ZnO are present and are quite narrow, confirming good crystallinity. There are also no discernible diffraction peaks belonging to any

contaminating zinc species, which confirms the purity of the ZnO. The peaks in red indicate diffraction peaks belonging to the zinc foil, which is to be expected and is not indicative of any contamination. The next set of data is from energy-dispersive X-ray spectroscopy. Although the XRD data indicates that the sample is pure, EDS data is a bit more sensitive and is capable of picking up contaminants that the XRD data might miss. Below is the EDS spectrum of a representative sample of synthesized ZnO nanostructures.

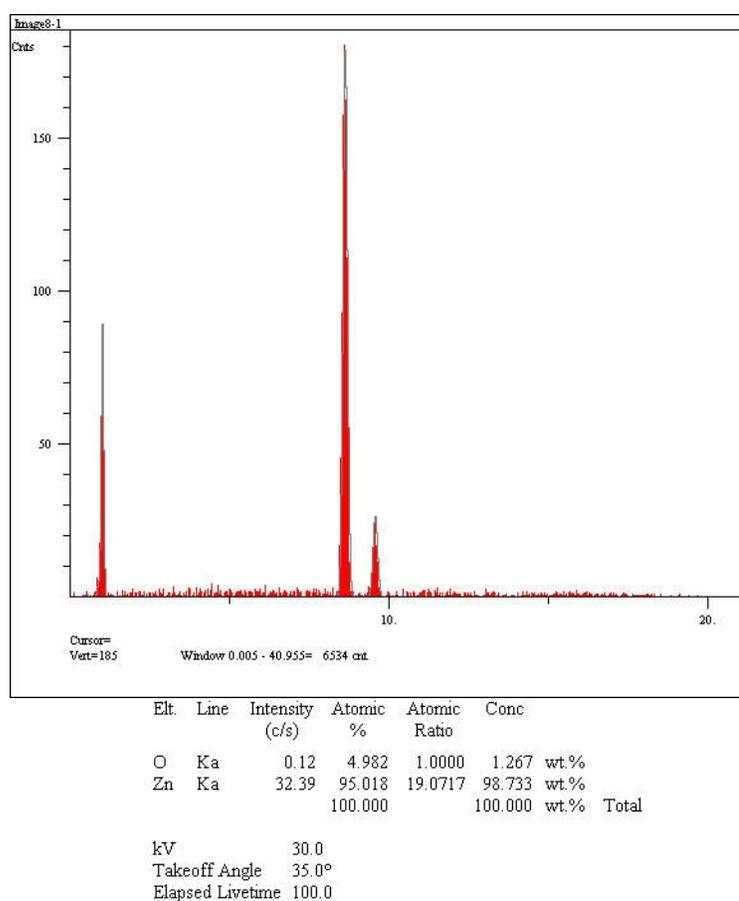


Figure 14

The EDS spectrum has negligible counts for any emission peak belonging to contaminating species. This is clear evidence that our synthesized ZnO is pure and that

any PL results are from ZnO alone. The low counts for oxygen are expected as the $K\alpha$ line for oxygen is weak and our EDS setup is not very sensitive to oxygen.

It is important to go in depth on the PL results and analyze what they mean. During the course of this project, a massive amount of samples were synthesized (>30), however only certain ones were analyzed with PL. The reason behind this, besides time considerations, is that not every sample can guarantee quality results. This is because not all samples have a uniform distribution of morphologies. Samples that had highly variable morphologies could not be accurately characterized because it would be difficult to ascertain which morphologies were contributing to the PL spectrum. This does not mean that these samples are useless, however, because filtering techniques or micro-PL could be effectively used on them. The room-temperature PL results that we obtained for each morphology are shown below.

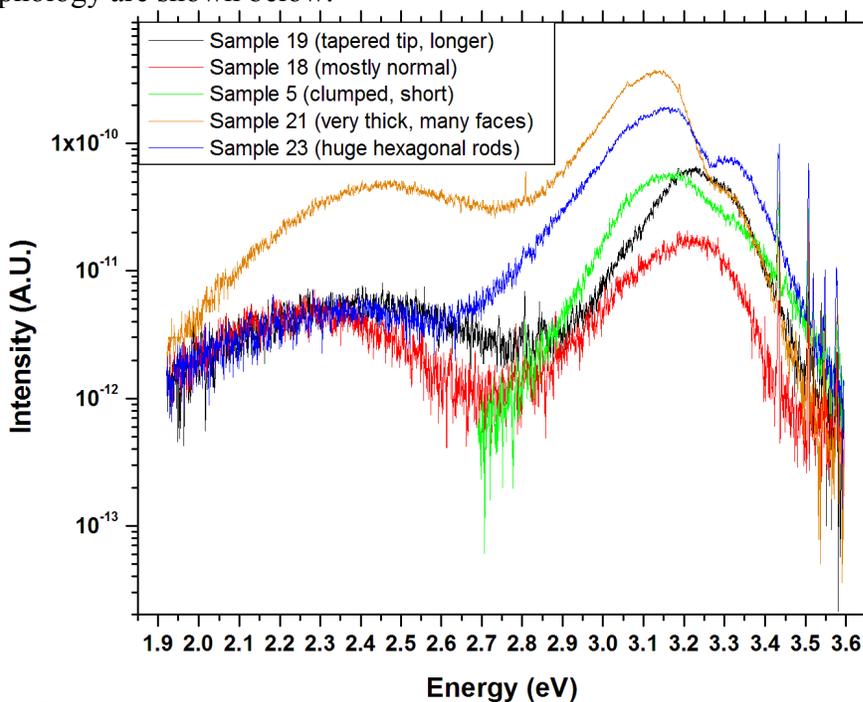


Figure 15

The first thing to note here is that there are four main spectral features that we can see here. The first would be the band gap which is ~ 3.3 eV. Another near band-edge defect is present in all samples at various locations. The final two are deep defects present

in all samples except sample 21 (thick polar faces) and possibly sample 23 (huge hexagonal rods), which only appear to have one deep defect. There are several things that we can garner from this information. First of all, by combining the fact that samples 21 and 23 are missing a deep defect with the fact that the samples are by far the largest size-wise, we can conclude that the defect is most likely surface related. This is because the sample has a low surface-to-volume ratio, and surface defects are passivated with larger surface-to-volume ratios. It is possible that this state is from oxygen interstitials at the surface, in which case the passivation of this defect in sample 21 and 23 would make sense. Another thing to note is that sample 21 has by far the most green luminescence. This is not surprising because the green luminescence in ZnO is usually attributed to oxygen vacancies [6] and sample 21 has a larger ratio of oxygen-terminated polar surfaces (hexagonal faces) to nonpolar surfaces (side, rectangular surfaces). Probably the most interesting part, however, is the near band-edge emission. The location and relative intensity of the near band-edge emission in each sample is quite different.

Conventionally, this defect has been attributed to recombination of free excitons, but a study done by one group gives evidence that it could actually be from a band of donor states [7]. Even more interesting, is the fact that this emission is also heavily influenced by the ratio of zinc-terminated surfaces to oxygen-terminated surfaces [8]. Whatever the case may be, it is clearly influenced by the morphology of the ZnO. Low-temperature PL might be able to tell us more about these samples, but unfortunately the size disparity is too high and many of the excitonic features overlap and distort themselves in these samples.

IV. CONCLUSION

We have demonstrated the feasibility of using our synthesis method for manufacturing a wide variety of morphologies of nanoscale ZnO. This method is scalable and would be adequate for industry-scale synthesis and application. The ZnO synthesized with this method was experimentally shown to be pure with excellent crystallinity. We also were able to gain insight into the growth processes used in ZnO nanostructure synthesis, which will be useful for other groups attempting to create synthesis techniques, as well as helping fundamental understanding of the underlying synthesis mechanisms. Additionally, it was shown that the electronic structure of the synthesized ZnO is heavily dependent on morphology. This means that specific morphologies of ZnO can be grown to fit a needed application. For example, if more green luminescence is needed relative to the band gap emission, then normal nanorods might be more useful. This greatly extends the versatility of ZnO, which is already considered to be a fantastic candidate for many electronics applications.

V. Future Work

There are several things that can be done to extend the life of this project beyond what has been presented here. For one thing, if the samples can be separated by size or morphology, it will open up several other samples to PL analysis as well as the already studied samples to low-temperature PL. Other experiments that could be performed include surface sensitive experimental techniques such as surface photovoltage spectroscopy. Finally, there are many combinations of precursor concentrations that have not been tried yet that may produce unseen morphologies. Other zinc salts could also be used to produce new and interesting ZnO specimens for study. In closing, although much

has been done on this project, there is still plenty of work left for anyone willing to pick it back up.

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ABSTRACT

ZnO nanostructures with controlled morphology have a very wide range of potential applications in UV photodetectors, sensors, field effect transistors, Shottky diodes, etc. In many instances it is desirable for ZnO nanostructures of a specific geometry to be produced in large quantities, with excellent crystallinity and reproducible properties. Major challenge in this respect, however, is the low yield of most current synthesis methods. In our work, we successfully applied a low-temperature inexpensive method for synthesis of ZnO nanostructures. This approach involves hydrothermal synthesis and subsequent deposition of nanostructures on the surface of a zinc foil by immersing it in a solution of hexamethylenetetramine (HMT), zinc acetate dihydrate, ammonium hydroxide, as well as deionized water, and autoclaving for several hours. By modifying the synthesis parameters we succeeded in creating a variety of ZnO nanostructures, such as nanorods, nano-“urchins”, nano-“bushels”, nano-“brooms”, and nanoplates. In particular, it was found that the morphology and size distribution of the synthesized product was extremely sensitive to the precursor concentrations. Autoclaving time appears to most strongly affect the final size of the obtained nanostructures. X-ray diffraction and energy-dispersive X-ray spectroscopy confirm that the products are pure and of excellent crystallinity. Photoluminescence spectroscopy measurements reveal a strong dependence of the spectral shapes on the morphology of the synthesized nanocrystals. We discuss the influence of the precursors on the growth dynamics of ZnO surfaces with different polarities as well as their implications for the electronic structure of ZnO.