

AN ABSTRACT OF THE THESIS OF

Eric B. Hostetler for the degree of Master of Science in Chemical Engineering presented on December 16, 2013.

Title: Processing of Nanoscale Materials.

Abstract approved: _____
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The motivation for undertaking this research was to increase the understanding of processing colloidal semiconductor nanocrystals and thin films metallic glasses to enable their wider application in future devices. This research covered two unique materials, lead selenide (PbSe) nanocrystals and thin film metallic glass alloy of zirconium copper aluminum nickel (ZCAN). Both materials have shown promise in several applications, but have faced barriers that are related to manufacturing.

PbSe nanocrystals have several potential applications including photovoltaics, infrared emitting diodes and lasers, nanoscale electronics and thermoelectric devices. The synthesis of nanocrystals has been historically based on small batch reactions that have been difficult to scale up. The objective of this research was to develop a microwave assisted continuous flow synthesis technique as a potential path for scalable synthesis of high quality colloidal semiconducting nanocrystals. PbSe nanocrystals were chosen as a model system because of the ease of binary nanocrystal synthesis, and the increasing interest in the use of PbSe for photovoltaics and infrared emitters. This research was approached in iterative steps starting with batch microwave synthesis followed by microwave assisted segmented flow synthesis. The synthesized PbSe nanocrystals were analyzed using high resolution transmission electron microscopy, energy dispersive x-ray spectroscopy, and x-ray diffraction to determine their size, composition, and crystal structure.

Metallic glasses alloys, including ZCAN, have potential applications including nanoscale patterning, micro-electro-mechanical systems, electronic devices, protective

coatings, laminates and catalysis. Oxidation is known to affect the physical, electrical, and chemical properties of metallic glasses. Previous research on the oxidation of metallic glasses has focused primarily on long oxidation times for bulk metallic glasses, where oxide growth of a few microns was observed. The objective of this research was to investigate thermal annealing and short oxidation times for thin film metallic glasses, where oxide growth of a few nanometers were studied due to the importance of stable interfaces in electronic devices. For these studies, sputter deposited samples of the thin film metallic glass were oxidized for various lengths of time. Characterization was performed using high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, and secondary ion mass spectrometry in order to examine the initial growth rate of oxide formation and diffusion induced compositional changes through the thickness of the films.

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Processing of Nanoscale Materials.

by
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A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented December 16, 2013
Commencement June 2014

Master of Science thesis of Eric B. Hostetler presented on December 16, 2013.

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ACKNOWLEDGEMENTS

This was only possible due to the support and encouragement of all my family, friends and peers throughout my education. I would like to thank my wife, Lindsay for her patience through several long days and nights of work.

Dr. Herman first allowed opportunity to work in his lab as an undergrad, and allowed me to return as a graduate student. I am appreciative of his trust, and confidence in me through the few years. The members of the Herman lab group have provided a nurturing environment, technical expertise and, an enormous amount of time helping me with this research. In particular, Brendan Flynn, who performed the vacuum annealing and surface XPS of the ZCAN films presented in this thesis, and Richard Oleksak, who spent countless hours to get the beautiful TEM images without which this research would not have been possible. Additionally, I would like to thank Dr. Stickle for his work in performing the XPS depth profiles of the oxidized ZCAN samples, and Ki-Joong Kim for his help in creating, and improving the microwave assisted continuous flow process for synthesis of nanocrystals. The research on lead selenide synthesis was supported by ONAMI-GAP.

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1 PbSe Nanocrystal Synthesis: Introduction

The motivation behind this research was to develop a microwave assisted continuous flow synthesis technique as a potential path for scalable synthesis of high quality colloidal semiconducting nanocrystals. The goals of this research were to synthesize high quality nanocrystals using microwave heating, develop a microwave assisted continuous flow technique for nanocrystal synthesis, and demonstrate control over nanocrystal size in microwave assisted continuous flow synthesis. This research was based on the synthesis and characterization of lead selenide (PbSe) nanocrystals (NCs) as a model material.

The properties of NCs change with size due to quantum confinement and high surface to volume ratios. For this reason, developing methods to synthesize monodisperse NCs of a specific size has been the focus of intense research [1]. Several techniques have been utilized for the synthesis of nanocrystalline materials including non-solution and solution-based techniques [2, 3].

Solution based synthesis of colloidal NCs offer several advantages including inexpensive precursors, high versatility and compatibility with low cost manufacturing techniques such as roll to roll printing, dip coating, and spin coating [4, 5]. In solution-based synthesis, chemical precursors, concentrations, temperatures, and reaction times can be optimized to produce high quality NCs with the desired properties. Formation of colloidal NCs occurs in three main steps: nucleation, growth,

and coarsening. Creation of monodisperse NCs relies on controlling each of these three steps.

In hot injection synthesis, a small distribution of particle sizes is created by a rapid homogenous nucleation event [6]. For this method, small batch sizes are typically used in order to minimize concentration and temperature gradients, which becomes increasingly more difficult to control as the reaction vessel volume is increased. This has made scaling to large quantities of uniform NC for manufacturing difficult. Moving from batch synthesis to continuous flow synthesis represents a path towards scaling up NC synthesis by reducing downtime and improving uniformity. In addition, in-situ process monitoring of continuous flow synthesis methods may allow direct control to synthesize NCs of a desired size, composition, and morphology.

To reduce thermal gradients during NC synthesis microwave-based approaches have been utilized to provide direct volumetric heating of the solution. Microwave heating does not depend on heat transfer, but instead on the interaction between electromagnetic radiation and molecules. This allows more rapid and uniform heating than can be achieved through conduction and convection, which makes microwave based heating attractive for colloidal NC synthesis [7, 8].

Reducing the occurrence of concentration gradients is dependent on short mixing times in both batch and continuous flow synthesis. Micro-mixing techniques utilized in flow chemistry employ extremely short mixing times allowing creation of near homogenous solutions. Additionally, the flowing solution can be segmented

through addition of a nonreactive and immiscible phase. Each segment of the solution works as a small reactor with internal currents mixing the solution throughout the reactor. To further reduce concentration gradients and residence time distributions segmented flow was used to provide narrow size distributions of the synthesized NCs.

PbSe is a IV-VI crystalline semiconductor material with a band gap of 0.278 eV [9], and strong quantum confinement due to the large Bohr exciton radius of 46 nm [10]. The band gap of PbSe can be tuned by adjusting the NC size below the Bohr radius, at which point the exciton experiences quantum confinement, allowing it to absorb and emit light from the mid-infrared to near infrared region. Potential applications of PbSe NCs include solar cells [4, 11], infrared emitters [12, 13], biomarkers [14], thermoelectric devices [15] and nanoelectronics [16].

The research presented here used modified hot injection chemistries to demonstrate synthesis of PbSe NCs using microwave-based heating. Initial experiments were performed using a batch reactor to better understand the process and optimize conditions for synthesizing PbSe NCs. A microwave assisted segmented flow reactor was developed and used to demonstrate the synthesis of high quality PbSe NCs with narrow size distributions and excellent control over NC size through varying the microwave power (i.e., reaction temperature). Characterization was focused on optimizing the colloidal stability, composition, crystal structure, size, and size distribution of the synthesized PbSe NCs.

The research pertaining to PbSe NCs performed for this thesis is presented as follows. Chapter 2 contains a review of PbSe NC literature and discussion of the possible applications of PbSe NCs to establish the technical background for discussion of the experimental results. Chapter 3 provides a detailed description of the microwave reaction systems, the techniques used for synthesis and preparation of PbSe, followed by the techniques used for characterization. Chapter 4 presents the characterization of the PbSe NCs synthesized, and discussion of the results obtained during this work. Finally, Chapter 5 summarizes the research, and conclusions reached in regards to microwave assisted segmented flow synthesis of PbSe NCs.

2 PbSe Nanocrystal Synthesis: Literature Review

This chapter is divided into three main parts: properties, applications, and synthesis of NC semiconductors. Each section will start with the general concepts that apply to a wide range of materials and then focus on the specifics of PbSe.

2.1 Properties

2.1.1 Semiconductors

The energy levels in solids are composed of the energy levels in the constituent atoms. In highly ordered materials such as crystals, this creates bands of possible energy levels. Solid materials can be categorized into insulators, semiconductors, and conductors based on their ability to conduct electricity. The difference between these materials is the energy required for an electron (e^-) to transition from the valence band to the conduction band, which is known as the band gap (E_g). Here it is important to note that all energies within the band gap are forbidden so that these transitions must occur in a single step. In a conductor, the E_g is either zero or smaller than the thermal energy provided at room temperature, where electrons are able to move from the valence band to the conduction band, and therefore conduct electricity. In semiconductors, E_g is larger than the thermal energy provided at room temperature, but generally still small enough that thermal excitation

can occur at temperatures below its melting point. In insulators, E_g is much larger than the thermal energy provided at room temperature or even up to its melting point.

When enough energy is provided to overcome E_g , the e^- becomes excited, moving from the valence band to the conduction band. The empty bonding orbital that the electron left can be thought of as a positively charged particle or hole (h^+). When the e^- and h^+ pair are electrostatically bound to each other they are often referred to as excitons.

An electron in the valence band can absorb a photon with energy larger than E_g , creating an exciton. The attractive forces between the e^- and h^+ can cause them to recombine, losing energy equal to E_g and creating a photon. This process is called photoluminescence. On the other hand, if an electrical potential is applied in order to overcome the attraction between the e^- and h^+ , they can be separated to create a current. If the energy of the photon absorbed is greater than E_g , the excess energy that excites the electron may be converted to phonons, which are optical or acoustic vibrations, in the crystal structure.

In the case of a direct band gap semiconductor, the maximum valence and minimum conduction band line up at the same crystal momentum. This is important since absorption and emission of photons can only occur if the total momentum is preserved, and the momentum of a photon is generally several orders of magnitude less than the crystal momentum of each band. In an indirect semiconductor, the crystal momentum between the valence maximum and conduction minimum is

compensated for by annihilation of phonons, which may have equal energy to the photon. The consequence of this is that direct band-gap semiconductors have much higher band-edge absorption and luminescence. Application of an electric field can also be used to control carrier densities in the conduction and valence band of semiconductors. The electric field allows the conductivity of a semiconductor to be switch on or off, and this property is the basis for transistors.

Crystalline semiconductors can be produced from a wide variety of materials. Some of the more common crystalline semiconductor materials include single element semiconductors (Si, Ge), binary semiconductors of III-V compounds (GaAs, InAs, InP), II-VI compounds (CdS, CdSe, CdTe, ZnSe), IV-VI compounds (PbS, PbSe, PbTe), Ternary compounds (CuInSe_2) and quaternary ($\text{Cu}_2\text{ZnSnS}_4$). This focus of this research was PbSe, a IV-VI semiconductor [1, 4, 6].

Crystalline PbSe has a rock-salt structure with an ideal 1:1 stoichiometric ratio of lead to selenium. PbSe is a direct band gap semiconductor with E_g of 0.278 eV at 300 K [9]. This makes it an excellent absorber and emitter in the mid-wavelength infrared region, which has photon energies between 0.15 eV-0.40 eV. PbSe also has a high thermoelectric figure of merit (ZT) which is defined below (Equation 2-1) due to contributions from the Seebeck coefficient (S), thermal conductivity (σ), and thermal conductivity (k), and T is the absolute temperature [17].

Equation 2-1
$$ZT = \frac{S^2 \sigma T}{k}$$

2.1.2 Semiconductor Nanocrystals

The unique size-related properties exhibited by semiconductor NCs were first observed and explained by Brus and Ekimov in the early 1980s [18, 19]. Crystalline semiconductors start to show unique properties when they are reduced to the nanometer size scale due to quantum confinement. In addition, the high surface to volume ratio of these particles may allow the stabilization of unique crystalline phases and increase reactivity [20]. The size-related properties of semiconductor NCs have resulted in significant interest in their synthesis, as well as their physical, electrical, optical, and chemical properties.

The created when a photon with energy greater than E_g is absorbed can be related to the Bohr model of a hydrogen atom containing a single electron and proton [19]. The Bohr radius (a_B) is a convenient scale for defining the critical size of a semiconductor NC for an exciton to be under quantum confinement.

Equation 2-2
$$a_B = \frac{4\pi\epsilon_0\hbar^2}{\mu_{e,h}e^2}$$

Where ϵ is the dielectric constant of the material ($\epsilon_0 \approx 250$ [17] for PbSe), $\hbar$ is the reduced Planck's constant, $\mu_{e,h}$ is the reduced mass of the exciton, and e is the elementary charge. A Bohr radius can be constructed for each of the charged particles in a bulk solid including the e^- , the h^+ and the exciton. When the semiconductor crystal is smaller than the Bohr radius the exciton becomes tightly bound, increasing E_g of the NC. This effect is similar to the classic example of a particle in a sphere, where the energy increases inversely with the radius of the sphere [21].

A second effect of quantum confinement is the formation of more defined energy levels. Bulk materials have energy levels of electrons that are nearly continuous due to the combined states of the constituent atoms. As the total number of atoms is decreased, the density of energy states starts to show peaks related to energies of higher probability [20]. The peaks become more defined with decreasing size, moving from the near continuous energy levels of the bulk material to the discrete energy levels of individual atoms.

The final aspect of the unique properties of nanocrystals is due to their large surface to volume ratio. A higher relative percentage of atoms exist at the surface compared to the bulk for NCs [20]. These surface atoms also have dangling bonds that lower the overall cohesion energy of the atoms in the NC. Surface sites also are important due to their potential as recombination centers and as heterogeneous catalytic sites.

2.1.3 Unique Properties of PbSe Nanocrystals

Crystalline PbSe has a large exciton Bohr radius of 46 nm, meaning that the exciton becomes quantum confined when one or more dimensions of the crystal become smaller than 46 nm [10]. In comparison, CdSe, a widely studied II-VI direct band gap material, has a Bohr exciton radius of approximately 10 nm. This is approximately 5 times smaller than that of PbSe, so charge carriers in CdSe begin to experience quantum confinement at much smaller particle sizes than charge carriers in PbSe. The large exciton Bohr radius of PbSe NCs makes them an ideal system for studying strong confinement in three dimensions.

Since PbSe nanocrystals experience quantum confinement at a larger size, a smaller percentage of the total atoms are at the surface when the particle is under quantum confinement. The smaller percentage of atoms present at the surface has been shown to improve stability, and may allow better control of the size related properties [10]. The high number of surface sites in NCs and the absorption properties of PbSe NCs have attracted increasing interest for their use as photocatalysts [22].

The band gap energy of the PbSe can be tuned using quantum confinement from the bulk 0.278 eV to 1.76 eV [12, 23, 24, 25]. This energy covers mid infrared to the near infrared region, which includes wavelengths important for communication and biological imaging [26]. The ability to control the band gap in semiconductor NCs makes them important in optoelectronic devices [5]. The band gap determines the minimum energy of a photon that can be absorbed, and the energy of a photon

emitted during luminescence. PbSe is also a material of interest in thermoelectric devices [27] including Peltier cooling, and thermoelectric power generation. PbSe has a large ZT due to the mix of large S , large σ , and low k .

2.2 Applications

The unique electronic, optoelectronic and thermoelectric properties of PbSe nanocrystals have made them a material of interest for several applications [21]. This section will discuss the use of PbSe NCs in several applications including photodiodes [28, 29, 30, 31, 32], solar cells [33, 34, 35, 36, 37, 25, 38, 39], optical sensors [40], light emitting diodes [41, 42, 43], lasers [24], biological labels [14], field effect transistors [44], and thermoelectric devices [17, 45]. The sections will be divided into three sections based on the principles on which the applications are based: photon absorption, photon emission, and electronic properties.

2.2.1 Absorbers: Solar Cells and Photodetectors

As a bulk material, PbSe has a band gap of 0.278 eV which corresponds to the energy of a photon with a wavelength 4593 nm. Using Wein's law we find that the temperature that gives a maximum intensity for this wavelength is approximately 631 K. This makes PbSe important for thermal imaging at moderate to high temperatures, and PbSe is widely used in infrared detectors for applications including hot spot detection, infrared spectroscopy, high speed imaging, and flame analysis.

As a direct band gap material, the conduction band minimum and the valence band maximum have the same lattice momentum, allowing efficient band edge absorption. Efficient band edge absorption allows thinner absorption layers when compared to devices based on indirect band gap semiconductors such as Si, which results in the use of less material to obtain a similar amount of light absorbance, and may potentially decreased production costs [4].

When PbSe becomes smaller than the Bohr radius, charge carriers become confined and are more strongly bound, causing an increase in the band gap. This effect allows the band gap of PbSe to be engineering for specific applications. Literature shows that the band gap can be tuned from the bulk 0.278 eV to 1.76 eV [12, 23, 24, 25], allowing the tuning of E_g , and, hence, the photovoltage that can be extracted. In photodiodes and photovoltaics, an internal potential may be introduced through a p-n junction. Allowing charge carriers to be effectively separated and collected to create a current based on the number of photons absorbed, called a photocurrent.

In conventional devices, the e^- and h^+ are created in the bulk material and then drift in opposite directions because of the potential in the material. The most common example of these devices is a P-I-N junction cell, which is used in amorphous silicon solar cells. In comparison, devices where the e^- and h^+ are created and then immediately split across an interface of two materials are termed excitonic solar cells [46]. Examples of excitonic solar cells include organic, dye sensitized, and quantum

dot solar cells. The most interesting aspect of excitonic devices is that it is possible to create a voltage greater than potential due to band bending. The increased photovoltage due to the excitonic effect has been demonstrated in PbSe based solar cells [39].

Any photon with greater energy than the E_g can be absorbed. If the photon absorbed has greater energy than the E_g , the excess energy is imparted to the charge carriers, e^- and h^+ , as kinetic energy. The energy imparted to each depends on the effective mass of the carriers. The particle with the lower effective mass, the e^- in most cases, will generally have higher kinetic energy. This kinetic energy moves the e^- to a higher energy state in the conduction band and the h^+ lower in the valence band. When the e^- is above the conduction band minimum, it is termed a hot electron.

In most cases the excess energy of a hot electron is lost as the electron relaxes to the conduction band minimum. This generally occurs through creation of phonons. The energy of a single phonon is much smaller than that of a photon or E_g , so energy loss through phonon creation can occur at energy levels inside an energy band, which are nearly continuous, but not over the forbidden energy levels between the valence band maximum and the conduction band minimum [11].

An alternative route for the relaxation of hot electrons may occur when the excess energy exceeds twice the band gap of the material. This route, termed impact ionization, involves the creation of a second exciton [47]. Impact ionization has been observed in bulk semiconductors when a photon with a large excess of energy

compared to E_g is absorbed, but is extremely rare due to the competition with phonon relaxation which generally occurs on a much quicker time scale.

Increasing the phonon relaxation time of hot electrons may allow collection of the hot electrons that increases photovoltage, or impact ionization that increases photocurrent [11]. In 2002, Nozik first proposed that quantum dots hold particular interest in photovoltaics due to these two mechanisms [11]. Carrier relaxation times may be increased by quantum confinement in nanocrystalline semiconductors allowing for either increased likelihood of impact ionization or easier collection of hot electrons.

Here it is good to note that hot carrier collection and impact ionization are mutually exclusive. Impact ionization in nanoparticle based devices has been termed multiple exciton generation (MEG). Increased quantum efficiency due to MEG has been demonstrated in several devices under artificial light. Currently, there is no known maximum to the number of excitons created by impact ionization. Schaller et al. observed the generation of seven excitons in PbSe NCs from the absorption of a single photon with energy of $7.8 \times E_g$ [48]. Theoretically MEG can increase single junction cell efficiency above the theoretical Shockley–Queisser limit of 35 % [49] to a maximum of 66 % [11].

Colloidal nanocrystals have been used to inexpensively deposit absorber layers for thin film solar cells [33, 34]. In addition, several schemes have been investigated to exploit the unique properties of quantum dots [11, 50]. The three main

ideas to improve cell efficiency involve the excitonic mechanism, where charge carriers are separated over an interface increasing photovoltage, MEG, where an inverse Auger process can create multiple excitons as a hot carrier relaxes thereby increasing photocurrent, and hot carrier collection, where carriers are collected before they relax increasing photovoltage.

Several different devices have been proposed to take advantage of these effects in NCs under quantum confinement, which are also termed quantum dots. PbSe NCs have been used in quantum dot organic polymer hybrid cells [39, 35], quantum dot array cells [51], and quantum dot sensitized cells in order to exploit these mechanisms. One version of the quantum dot organic polymer hybrid involves NCs dispersed at the interface between an h^+ conducting polymer and an e^- conductor. When an exciton is created the h^+ is injected into the h^+ conducting polymer, often MEH-PPV, and the e^- into the other phase, often TiO_2 or an e^- conduction polymer. This approach takes advantage of both the excitonic and MEG mechanisms. Quantum dot array cells consist of a thin layer of NCs that are used as the absorber layer, and an internal potential created by a Schottky junction, p-n junction between two NC layers or a P-I-N junction with the NC layer as the intrinsic absorber. Quantum dot sensitized cells are analogous to dye sensitized cells with the NCs in place of the sensitizing dye. Currently reported efficiencies for PbSe quantum dot solar cells are around 3.5 % and the record efficiency in 2011 of 4.57 % [25]. The record quantum dot solar cell has an efficiency of 8.6 % [52].

2.2.2 Emitters: Light Sources, Convertors and Lasers

Luminescence occurs when excited carriers recombine and a photon with energy equal to the band gap is emitted. As discussed previously, luminescence in direct band gap semiconductors can have high efficiencies at the band edges. In NCs, the size tunable band gap enables tuning the energy of the emitted photons. A single material can be used as emitters over a range of wavelengths. PbSe NCs have been used to create emitters with wavelengths between 800-4100 nm [26, 28, 42]. In addition, amplified spontaneous emission has been observed in PbSe NC devices making them a potential material for infrared lasers [13]. Emitters in the infrared region are important as biological markers since wavelengths of 700-1400 nm give the best light penetration through tissue [26], communications where the telecom range is between 1300-1550 nm [12], and chemical spectroscopy and sensing where bond stretching and bending occurs from 400-4000 nm [43].

Luminescence can occur through electroluminescence or photoluminescence. Luminescence in devices such as light emitting diodes (LEDs) occurs when a current is applied. This is termed electroluminescence. Luminescence that occurs after absorption of a photon is photoluminescence. Photoluminescence is often used for biological labeling but may also be used for photon down conversion. Photons emitted from a single semiconductor NC is equal to the band gap and therefore monochromatic (i.e., emits at a single wavelength). Monochromatic light sources are important since many applications including communication, chemical spectroscopy,

and sensing require clear separation of wavelengths. It is important to note that since E_g is strongly dependent on size, small size distributions are needed to create small distributions of photon wavelengths. Emission efficiencies for multiple NC may diminish due to higher energy photons emitted from smaller NCs being absorbed by larger NCs due to the differences in E_g .

Traditional near infrared emitters consist of organic dyes and rare earth doped semiconductors. Near infrared organic dyes for biological imaging show very low quantum yield (< 10 %), can have broad emission spectra, and are limited to wavelengths below 950 nm. Rare earth doped semiconductors are expensive and offer limited emission wavelengths. In contrast, PbSe nanocrystals can be tuned throughout the near infrared and mid infrared wavelengths, can obtain photoluminescence emission efficiencies around 89 %, and can be produced using abundant inexpensive precursors. It is important to note that the reported photoluminescence emission efficiencies for PbSe in solution ranges from 6-80 % [43].

2.2.3 Nanoelectronic and Thermoelectric Applications

Colloidal semiconductor NCs are compatible with low cost manufacturing methods such as reel-to-reel printing, and are used to create polycrystalline thin films for traditional devices or as part of a nanoscale device which takes advantage of their unique properties. Colloidal NCs have been used in a variety of electronic devices

including: field effect transistors (FETs), flash memory devices, memristors, and thermoelectric devices [5].

Semiconductor NCs possess unique electrical properties. Quantum confinement causes more defined energy levels to become apparent versus the continuous bands of bulk semiconductors. No current flows in a semiconductor NC placed between a source and drain until the bias voltage exceeds the energy needed to add or remove a charge carrier, creating a Coulombic step. Note that charge carriers are strongly bound due to quantum confinement. Addition of a gate electrode allows the Coulombic staircase to be shifted producing Coulombic oscillations that creates a device called a single electron transistor [20]. Solution processed FETs fabricated at room temperature have been prepared using colloidal PbSe NCs [44, 53]. Single PbSe nanocrystals have also been used to make single electron transistors. PbSe NCs have been shown to be a potential material for random-access memory (RAM), and read-only memory (ROM) applications [16].

It has been observed that the ZT of PbSe may be increased up to 10 times by quantum confinement in PbSe NCs [15]. Studies have shown that σ of semiconductor NCs generally decreases with size, but this may be offset by increases in S . In one study, S was observed to increase from 700 $\mu\text{V/K}$ to 1150 $\mu\text{V/K}$ as PbSe particle size was decreased from 8.6 nm to 4.8 nm [17].

2.3 Synthesis

Nanoparticle synthesis has been, and still is the focus of intense research. The applications of NCs are dependent on the ability to produce materials with a specific size, uniformity, shape, composition, crystal structure, and surface functionalization. The use of nanocrystalline semiconductors in commercial devices also depends on the development of low cost, high throughput methods for synthesizing high quality NCs with the desired properties. Many approaches for the synthesis of nanocrystalline semiconductors have been presented [3, 54, 55, 56, 57, 58]. A summary of solution based and non-solution based synthesis will be given, followed by an in depth analysis of the hot injection technique, and a review of microwave-based methods for nanocrystal synthesis.

2.3.1 Summary of Non-Solution Based Techniques

In 1981, Ekimov and Onushchenko first observed that the colors in stained glass were due to quantum size effects [59]. Nanocrystalline materials have been synthesized and used for centuries to create beautiful colors. It is now clear that the colors are produced by the absorption of light by the particles produced by these ancient craftsmen. Today, the techniques for synthesizing high quality nanoparticles have become much more complex. Several techniques have been used to create PbSe NCs including precipitation in a glassy matrix [54, 55], the Stranski-Krastanov method [60, 61], ion beam implantation and electron beam annealing [62], and

molecular beam epitaxy. The most commonly reported of these is the Stranski-Krastanov method.

The Stranski-Krastanov method involves growing a film via chemical or physical vapor deposition, usually involving decomposition of a single precursor at high temperatures, on a substrate with a large lattice mismatch to that of the NC. Stress in the film caused by this mismatch causes island formation to minimize the Gibbs energy. The islands eventually grow into a single NC, which can be detached from the substrate.

2.3.2 Summary of Solution Based Techniques

Brus first explained the effect of quantum confinement in colloidal semiconductor NCs in 1984, and soon published some of the first work dealing with the synthesis of colloidal nanocrystals [19]. Since this time, colloidal quantum dots have been the focus of over 14,000 journal publications [1]. The intense interest in colloidal semiconductor NCs may be due to the advantages of solution-based synthesis including: ability to use a wider range of less expensive precursors, compatibility with low-cost additive manufacturing, ability to functionalize the particles for several different chemical environments, lower cost reactors, and the ability to control particle properties through a small number of process conditions. The goal of solution based synthesis is to create stable dispersions of a desired size of NCs, with a small size distribution.

A wide variety of solution-based approaches have been used to synthesize various semiconductor NCs. PbSe NCs have been synthesized by sol-gel [63], solvothermal/hydrothermal [64, 65], precipitation through pH changes [66, 67], precipitation by reduction [56, 68, 69], hot-injection [57, 70, 71, 72, 73, 74, 75, 58], quasi-seeded synthesis [77], photochemical [78, 79], sonochemical [80, 81], and microwave based synthesis [82, 83, 84, 85, 86].

The sol-gel process involves mixing the metal precursors with a cross-linking agent, commonly tetraethylorthosilicate (TEOS), to form a gel. Particles can be grown in the cross-linked matrix or gel, which controls the growth of nanoparticles. The gel is then dried and calcined, forming a metal oxide powder. Sol-gel synthesis is commonly used to create metal oxides, but has been applied to PbSe by creating PbO/SiO₂ hybrid NCs in an aero-gel containing Se⁴⁺ ions, after the calcination process. The oxides are then reduced in hydrogen to form PbSe/SiO₂ [63]. In addition, the Sol-Gel process has been used to form a PbSe NC TiO₂ shell structure [24].

Solvothermal and hydrothermal synthesis use high pressure and temperature to drive the reaction and precipitate NCs. The difference between solvothermal and hydrothermal processes is the choice of solvent. Hydrothermal processes use water, while solvothermal processes may use a wide variety of solvents besides water. Synthesis is commonly performed in sealed stainless-steel vessels heated in an autoclave. Solvothermal synthesis of PbSe has been performed at 200°C by reacting

elemental Se with lead stearate in 1,2,3,4-tetrahydronaphthalene for 12 hours [64] or lead acetate in octadecylamine for 4 hours [65]. Use of octadecylamine as both a solvent and coordinating ligand was found to yield NCs with narrow size distributions where the variation in particle size ($V_{ps} = 100 \% \times \sigma / \mu$) was 5.5 %, where the mean particle diameter (μ) and standard deviation (σ) were used for the calculation. This was the lowest variation in particle size reported for PbSe synthesized by solvothermal methods. It was also found that particle size could be controlled between 11 nm to 50 nm when the Pb to Se ratio of the precursors was varied from 1:0.33 to 1:1, respectively [65].

Chemical precipitation takes advantage of chemical changes to control the solubility of the nanocrystalline phase. PbSe NCs have been synthesized at temperatures as low as 40 °C, by precipitation through the addition of NaOH, which increases the pH to 8, and results in PbSe becoming insoluble [66, 67]. It was found that the PbSe NCs synthesized by this method required HCl treatments to remove impurities, were agglomerated, and had large variation in particle size. PbSe has also been produced by reduction of Se compounds in solution, but the synthesized NCs were lead rich and had large variation in particle size [68].

Hot injection methods have been used in the majority of the studies that synthesized PbSe NCs in literature. This method demonstrated the widest range in average PbSe NC diameter synthesized (3-25 nm), and low variation in particle size ($V_{ps} = 5-10 \%$) [57, 87]. In hot injection methods, a precursor is injected into a

rapidly stirred hot solution, causing a burst nucleation event. The solution is then cooled to a growth temperature. This effectively separates the nucleation and growth phases in NC synthesis, leading to good nanocrystal size uniformity. Particle nucleation and growth will be discussed in more detail later on with the in-depth discussion of hot injection.

The methods presented so far have all largely depended on traditional heating to overcome activation energies, and depend on heat transfer and mixing to reduce thermal gradients. Several unique schemes utilizing other methods to overcome process limitations include sonochemical, electrochemical, photochemical and microwave assisted techniques. Electrochemistry can be used to deposit PbSe NC films through reduction of metal precursors [88]. Sonochemical methods use ultrasonic baths or probes to transfer energy to the solution, which can cause bubbles in the solution to implosively collapse. The energy of these collapsing bubbles can be extremely high, equivalent to 5000 K, and dissipates very quickly [80]. Photochemical synthesis generally uses high power ultraviolet or near ultraviolet lamps to impart energy to the solution [79]. PbSe NC synthesis employing microwave based heating depends on reduction at high temperature. A review of microwave based methods is found after the in-depth discussion of hot injection.

2.3.3 Hot Injection: Separation of Nucleation and Growth

In 1993, Murray first described the hot injection process for the synthesis of CdSe NCs with small size distributions [89]. Since then, hot injection has become one of the most common NC synthesis methods, and been applied to several different NC systems including PbSe [57]. In this section, the important concepts involved in hot injection synthesis of NCs will be discussed, as well as the different chemistries used in the hot injection synthesis of PbSe.

The NC growth process can be divided into stages: nucleation, growth, and coarsening. Synthesis of high-quality monodisperse NCs via hot injection relies on separation of the nucleation and growth phases. Small NC size distributions are created through a single spontaneous nucleation event followed by homogenous growth, and stabilization. The nucleation process may consist of several steps including reduction of precursors, formation of monomers, and finally precipitation of nuclei [3]. The process can be thought of thermodynamically through the minimization of Gibbs energy. The Gibbs energy (ΔG) of the system can be represented as shown (Equation 2-3).

$$\text{Equation 2-3 } \Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \frac{-RT \ln\left(\frac{C}{C_{eq}}\right)}{V_m}$$

Where r is the radius of the solid particle or nuclei, γ is the surface energy, V_m is the molar volume of the solid phase, C is the concentration of the monomer in solution and C_{eq} is the equilibrium concentration of the monomer [6]. A maximum in ΔG occurs representing the critical Gibbs energy (ΔG_c) for spontaneous nucleation is shown (Equation 2-4), and can be used to find the critical radius (r_c) of the nuclei formed as shown (Equation 2-5).

$$\text{Equation 2-4 } \Delta G_c = \frac{16\pi\gamma^3 V_m^2}{3 \left[RT \ln \left(\frac{C}{C_{eq}} \right) \right]} \text{ at } \frac{\partial \Delta G}{\partial r} = 0$$

$$\text{Equation 2-5 } r_c = \frac{2\gamma V_m}{RT \ln \left(\frac{C}{C_{eq}} \right)}$$

The nucleation event continues until the rate of monomer creation is less than the rate of nucleation [6, 3]. Equation 2-3 assumes that particles are spherical in order to minimize the surface area and energy [20]. Several papers show HRTEM of small, 1-5 nm, spherical shaped PbSe NCs which transition to cubic or octahedron morphology upon further growth [58, 75, 87]. The transition is expected to occur when the energy of the volume becomes greater than that of the surface, and has been found to be strongly affected by ligand coordination with surface atoms [87, 90, 91].

Particle growth begins as soon as a solid phase is nucleated, and will continue until the addition of monomer to the solid phase NC no longer decreases ΔG , or the

kinetic energy required is no longer available. Growth is also dependent on the kinetic barrier and diffusion of monomer species to the surface of the solid phase [6]. As a result, the growth rate of the NC can be controlled through temperature and diffusion. Ligands with bulky organic groups are often used to slow or block the diffusion of monomers to the particle surface through steric hindrance. Coarsening generally occurs as the monomers are depleted to a point where ΔG of the system is decreased by dissolving small NCs with higher surface energy to continue the growth of larger NCs. In addition NCs may attach and grow together to reduce their surface energy.

Hot injection creates the nucleation event by preheating the reactants, and then rapidly injecting them while mixing. Monomer creation occurs extremely rapidly after the injection, creating a burst nucleation event. The system cools quickly due to the injection of cold precursors, which reduces the rate of monomer creation. Further nucleation of NCs is prevented through the reduction of available monomers due to the reduced rate of monomer creation, and use of monomers for continued growth of previously nucleated NCs. The solution is held at a growth temperature until NCs of the desired size and morphology are formed. The growth of the NCs can be quickly quenched through addition of cold solvent, which cools the system, lowering the rate of monomer creation and diffusion, and reducing monomer concentration in the solution [57]. Additionally, this may prevent further growth since the activation energy for further reactions may no longer be available.

A common method first described by Murray and coworkers [57] for synthesis of monodisperse PbSe NCs involves rapid injection of room temperature lead oleate (Pb(OA)_2) and trioctylphosphine-selenium (TOPSe) into rapidly stirred diphenylether at 150 °C. The temperature drops due to injection of the cool reagents, but is then adjusted to a growth temperature between 90-220 °C. The growth temperature is held for up to 15 minutes, and then cooled when the PbSe NCs reach the desired size. The NCs can then be isolated by addition of a short chain alcohol followed by centrifugation. NC sizes can be tuned between 3.5-15 nm with a V_{ps} around 10 % by varying the reaction time and temperature. The V_{ps} of the NC can be further reduced by size-selective precipitation from 10 % to 5 %. The use of 1-octadecene (ODE), a non-coordinating solvent, in place of diphenylether was first described by Yu et al. [58]. The non-coordinating ODE allows synthesis of larger PbSe NCs up to 25 nm, while still producing a small $V_{\text{ps}} = 5\text{-}10\%$. Additionally, the higher boiling point of ODE when compared to diphenylether may allow better removal of impurities such as water and acetate during preparation of the precursors, leading to more consistent size control [73].

In this study both oleic acid (OA), which preferentially ligates the Pb atoms at the surface, and TOP, which can ligate either Se or Pb atoms at the surface, were used. The OA and TOP ligands are thought to adsorb and desorb from the surface of the PbSe NC during the growth process. The TOP is expected to be much more weakly coordinating than OA for the reaction conditions used for these studies.

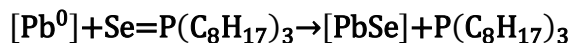
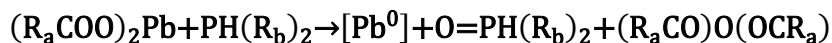
Oleylamine has also been successfully used as an alternative to the OA/TOP ligand combination giving a small V_{ps} of 5-10 % [76].

It is widely expected that the impurities in technical grade TOP such as diphenylphosphine (DPP) may play important roles in NC synthesis as reducing agents. Two possible growth mechanisms are shown below [73, 92, 93] (Equations 2-6 and 2-7).

Equation 2-6



Equation 2-7



Where $R_a = (CH_2)_7CH=CH(CH_2)_7CH_3$, $R_b = \text{Phenyl}$, $(R_aCO)O(OCR_a)$ is oleic anhydride. In the first mechanism, PbSe nucleates are directly created in the reaction of $Pb(OA)_2$ with TOPSe. In the second mechanism, $Pb(OA)_2$ is initially reduced to Pb^0 by DPP/TOP, creating a Pb^0 monomer that further reacts with TOPSe to create PbSe. NMR has shown DPP concentrations in as-received technical grade TOP of approximately 1 molar percent [73, 75]. Additionally, complete oxidation of the DPP

impurity during synthesis in an oxygen free environment was seen with the partial oxidation of TOP, indicating that both mechanisms are present.

HRTEM images of PbSe NCs generally show both the (100) and (111) planes. The surface of the (111) planes consists of either all Pb or all Se atoms. When (111) planes on opposite sides of the particle have different elements at the surface, a dipole is created due to the difference in the electronegativity of Pb and Se [91]. This dipole may play a key role in oriented attachment on PbSe NCs. Long reaction times using OA/TOP have generally led to cubic NCs, but recently amine co-ligands have been shown to lower the (111) surface energy leading to octahedral NCs [87].

PbO, PbCl₂ or Pb(OAc)₂, where OAc is acetate, can be reacted with oleic acid to form Pb(OA)₂ which is a precursor in synthesis of PbSe NCs. The counter ion, O²⁻ Cl⁻ or OAc, is removed by heating under vacuum during the reaction. In some cases, the OAc may not be completely removed before the reaction and competes with OA to ligate the Pb atoms at the surface, creating larger star-like NCs [94]. Addition of shorter chain ligands, such as hexanoic acid and acetic acid as co-ligands leads to increasing particle size with decreasing chain length, and creates larger NCs with irregular morphologies and larger size distributions [90, 95]. Increasing the excess of OA causes the particle shape to transform from round to cubic to polyhedral [87]. The cubic shape is created by a fast growth rate in the <111> direction, while the polyhedral shape comes from passivation of the (111) surface with higher ligand concentrations.

Additional phosphines, such as tributylphosphine (TBP) or diphenylphosphine (DPP) can be added to or substituted for TOP in the precursor during the synthesis [71]. Shorter chain phosphines increase growth rate and reduce the temperature at which growth can be controlled [89]. DPP addition produces an increased nucleation rate and yield, which is attributed to an increase in the mechanism shown in equation 2.1.G. Addition of excess phosphines has been shown to increase photoluminescence up to a critical concentration. This effect may be due to passivation of Se atoms on the surface, while too high of a phosphine concentration may lead to cleaving of the OA-Pb bond on the PbSe NC [96].

2.3.4 Microwave Heating in Nanocrystal Synthesis

Microwaves represent wavelengths from 1 mm to 1 m. Microwave heating generally uses a frequency of 2.45 GHz. A photon at this frequency has a wavelength of 12.236 cm and an energy of approximately 0.01 meV. This energy is much smaller than bond energy between atoms. Microwave heating occurs via two main mechanisms: dipolar polarization, and ionic conduction. In dipolar polarization, polar molecules try to align with the oscillating electromagnetic field. Energy is lost as rotating molecules lag behind the alignment of the electric field, resulting in dielectric loss (ϵ'') that transforms electromagnetic energy into thermal energy. The ability of a substance to convert the electromagnetic energy into thermal energy may be characterized by the loss tangent ($\tan\delta$) defined below (Equation 2.1.H).

Equation 2-8 $\tan \delta = \frac{\epsilon''}{\epsilon'}$

Where ϵ' is the dielectric constant. The second method, ionic conduction, occurs as ions oscillate in the electric field colliding with other species and creates thermal energy. The oscillating electric field can also create eddy currents in solid conductors causing resistive heating. Finally, heating may also occur due to the magnetic field through hysteresis, domain-wall resonance, and electron spin resonance mechanisms [7, 8].

Microwave based heating can be used to provide rapid volumetric heating. Heating of a 20 mL sample by microwave irradiation has been shown to have no observable temperature gradient [7]. In contrast traditional heating relies on conductive heating from the vessel walls, and forced convection in the solution to reduce thermal gradients. A consequence of traditional heating is that the rate of heating is limited by heat transfer, which is driven by a temperature difference. This causes a conflict between having fast heating rates, and small thermal gradients. The electromagnetic energy in microwave heating is directly converted to thermal energy inside the entire volume allowing increased heating rates.

Other unique aspects of microwave heating that may benefit NC synthesis include the lack of wall effects, selective heating, and instantaneous temperatures. Wall effects occur in conductive heating due to the temperature gradient that drives

heat transfer, where the walls of the vessel must be hotter than the solution for heating. Selective heating may occur between phases, when one phase is better at converting microwave irradiation to thermal energy than the other. This effect has been exploited in microwave catalysis where selective heating of the catalyst may explain the increases in catalytic activity, reaction rates, and product selectivity [97, 98, 99]. It may also be possible that selective species in solution experience a similar effect, although little evidence exists to support this in a homogenous solution. Molecules may experience high instantaneous temperatures above the temperature of the solution due to absorption of microwave energy, which is quickly dissipated to the bulk solution. This instantaneous temperature effect has been theorized as a possible reason for the increased reaction rates seen in microwave chemistry.

Bulk PbSe synthesis using microwave irradiation was first carried out in 1994, where rapid microwave heating was used to accelerate the slow solid state reaction [100]. PbSe QDs synthesis using microwave irradiation was first reported in 2000 by Zhu et al. where $\text{Pb}(\text{OAc})_2$ was reacted with Na_2SeSO_3 in a mixture of water and chelating agents [83]. This reaction produced 30-40 nm sized agglomerations of irregular PbSe NCs. Kerner et al. used $\text{Pb}(\text{OAc})_2$ and elemental Se in ethylene glycol to produce large agglomerations of 15-25 nm PbSe NCs [81]. Two different groups used this same chemistry in 2010, Xiaofeng et al. produced 50-100 nm PbSe NCs [84], where Lv and Weng used ultrasonic-microwave co-irradiation to produce 30-50 nm PbSe NCs [86].

Sliem et al. demonstrated microwave assisted growth of PbSe hierarchical dendrites in 2007 [82], and then PbS and PbSe nanocrystals in 2011 [82]. The synthesis of PbSe NCs utilized $\text{Pb}(\text{OAc})_2$ and OA in diphenylether with selenourea in N,N-dimethylformamide (DMF) at 3 Bar and 100 °C for 1 minute to obtain semi-spherical PbSe NCs with a size of 5.8 ± 2.2 nm. An additional growth stage at 160 °C at 3 Bar for 2 and 5 minutes was used to produce cubic PbSe NCs with sizes of 7.3 ± 1.2 nm and 14.4 ± 1.6 nm, respectively.

3 PbSe Nanocrystal Synthesis: Materials and Methods

This chapter covers the microwave reaction systems used during this research, the chemistry and techniques used for synthesis of PbSe NCs, and the tools and techniques used for characterization of PbSe.

Samples using five different reaction conditions were shown to be stable with minimal precipitation, and these samples were chosen for full characterization and are presented in the results section. HRTEM, XRD and EDX was performed on one sample from the batch microwave synthesis produced at 140 °C, three samples from the segmented flow microwave synthesis produced with average microwave nucleation temperatures of 124 °C, 142 °C and 159 °C and a growth temperature of 140 °C, and one sample produced with an average microwave nucleation temperature of 160 °C without the growth zone

3.1 Preparation of Colloidal PbSe Nanocrystals

Lead(II) oxide (PbO powder, >90 %), tri-n-octylphosphine (TOP, 90 %) and selenium powder (Se, -325 mesh, 99.5 %) were obtained from Alfa Aesar. Oleic Acid (OA, 90 %), toluene, and 1-octadecene (ODE, 90 %) were obtained from Aldrich. Acetone and methanol were obtained from Marcon, and acetonitrile was obtained from JT Baker. All chemicals were used as purchased with no further purification.

All precursor preparation for both batch microwave and microwave assisted segmented flow synthesis was performed in a nitrogen filled glovebox to prevent oxidation of the TOP and limit exposure to atmospheric moisture. For batch microwave synthesis, 1.000 g (0.150 M) of PbO was added 3.535 mL (0.375 M) of OA and 11.295 mL of ODE in a 40 mL glass beaker. In a second 40mL beaker, 0.708 g (0.300 M) of Se powder was added to 5.995 mL (0.450 M) of TOP and 8.778 mL ODE. An auto pipette with a range of 1 μ L to 1 mL was used to get accurate volumes. This gave a concentration ratio of 2:5:4:6 of Pb:OA:Se:TOP with a 0.15 M concentration of Pb. A Teflon coated magnetic stir bar was added to each beaker and the beakers were covered with watch glasses. The solutions were heated on a hotplate to 150 °C with continuous stirring for 2 hours. After preparation both solutions were clear liquids.

For microwave assisted segmented flow synthesis, 10.000 g PbO (0.10 M) was added to 35.4 mL of OA (0.25 M) and 187.6 mL ODE in a 250 mL beaker. In a second 250 mL beaker, 7.075 g Se (0.20 M) was added to 60.0 mL TOP (0.30 M) and 162.5 mL ODE. In this case a graduated cylinder was used to get volumes accurate to 0.1 mL. This gave a concentration ratio of 2:5:4:6 of Pb:OA:Se:TOP with a 0.10 M concentration of Pb. The solutions were heated on a hotplate to 150 °C with continuous stirring for 2 hours. After being prepared the solutions were clear liquids. The concentrations for the segmented flow reactions was reduced to prevent the

Pb(OA)_2 from condensing into a waxy solid in the reactor prior to reaching the microwave zone due to cooling.

3.1.1 Batch Microwave Synthesis

Batch synthesis of colloidal PbSe was performed using a CEM Mars V microwave system with CEM green-synth vessels as shown (Figure 3-1).



Figure 3-1 CEM Mars V microwave used for batch synthesis.

The CEM Mars V system is a multimode microwave with an output of up to 1800 W at a frequency of 2.45 GHz. Temperature can be monitored using either an infrared or a fiber optic probe, and controlled by varying the microwave power. In

this synthesis procedure, the fiber optic probe was used to monitor temperature, and provide temperature control in the reaction vessel.

The green synth vessels are thick walled glass that hold up to 15 mL of solution. A two piece polytetrafluoroethylene (PTFE) cap is used to allow pressure to be released from the vessel during the reaction. An additional PTFE cap with a glass sleeve was used for monitoring the temperature of a single vessel using the fiber optic probe. The vessels were placed in a rotating carousel inside the microwave in order to ensure even irradiation. Stirring during the reactions was performed using a small magnetic stir bar in the reaction vessel.

For the batch PbSe nanocrystal synthesis the precursors were stored in the nitrogen filled glovebox at 40 °C with constant stirring. In the glovebox, 6.5 mL of each precursor was loaded into a CEM green-synth vessel using an auto pipette. A small stir bar was added, and the vessel was capped with the temperature monitoring cap. The capped mixture was quickly (< 5 minutes) transferred from the glovebox to the microwave, and the reaction was started.

A maximum power of 800 W was used due to the use of weakly absorbing solutions of $\text{Pb}(\text{OA})_2/\text{OA}$, TOPSe/TOP and ODE. In addition to the reaction vessel containing the mixed precursors, four vessels with 13 mL of OA were also added to the carousel to produce a minimum of 50 mL of solution in the microwave to prevent damage to the magnetron. All vessels were evenly spaced in the carousel, with the precursor solution in position 1, during heating.

The CEM Mars V system was programmed to ramp up to 140 °C at the maximum power for 4 minutes, hold the temperature at 140 °C for 9 minutes, and then cool down. It was observed that 140 °C was achieved after approximately 3.5 minutes, so the total reaction time was 9.5 minutes. The reaction vessel was allowed to cool to 80 °C in the microwave before being removed and cooled under running water to room temperature. During the reactions the vessels were constantly stirred with the magnetic stir bar. The cooled solution was then pipetted to polyethylene centrifuge tubes for cleaning.

3.1.2 Microwave Assisted Segmented Flow Synthesis

The microwave assisted segmented flow synthesis was carried out using the setup shown (Figure 3-2). This reactor may be broken up into four unique zones: mixing zone, microwave nucleation zone, growth zone, and quench zone. A photograph of the reactor is also shown (Figure 3-3)

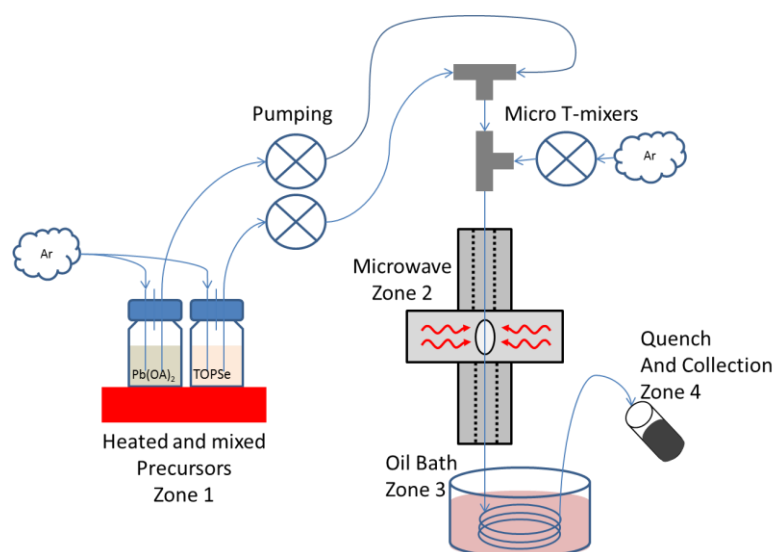


Figure 3-2 Diagram of the microwave assisted segmented flow



Figure 3-3 CEM Mars V microwave used for batch synthesis.

The precursors were prepared either the night before or day of synthesis as stated and stored at 40 °C with constant stirring in the nitrogen filled glovebox. The precursors were transferred to glass sample bottles (Kimax, 250 mL) in the glovebox. While in the glovebox, a large PTFE stir magnetic stir bar was added to each sample

bottle, and the bottles were capped. The samples were removed from the glovebox, and transported to the reactor. The solid caps were replaced with modified caps (Figure 3-4) before running the microwave assisted segmented flow synthesis, and the precursors were pretreated.

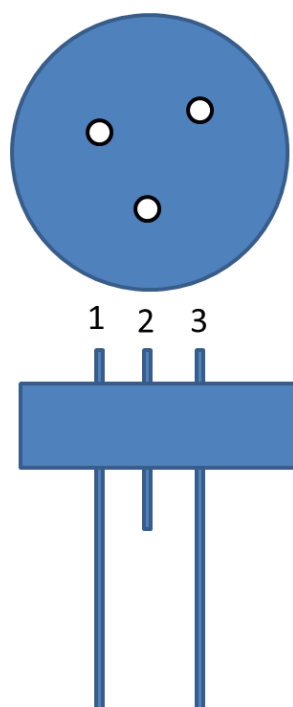


Figure 3-4 Modified cap showing (1) argon gas input tube, (2) pressure release tube (3) solution out tube.

For the purpose of discussion the three ports are labeled Ar in, solution out, and pressure release. The Ar in and solution out ports had 1/16" inner diameter high temperature PTFE tubing attached which reach the bottom of the solution vessel, and all three ports had a PTFE through fitting that allowed them to be connected to the various lines. Hot glue was used to seal the fittings to the cap, and 3 cm long pieces of

3 mm inner diameter Tygon tubing with clamps was used to seal ports when they were not in use.

The precursors were pretreated to remove any water or air that might have been present. The pretreatment consisted of heating the solutions under vacuum followed by purging the solutions with argon gas. The house vacuum line was connected to the pressure release port and vacuum line valve fully opened. The solution was held at 150 °C for 20 minutes under the house vacuum after which both precursors would be a clear liquid. It is important to note that the $\text{Pb}(\text{OA})_2$ solution often condensed in transport from the glovebox to the microwave assisted segmented flow reactor. The vacuum was removed, leaving the pressure out port open, and Ar gas was connected to the Ar in port. The Ar gas pressure was slowly increased until a slow steady stream of bubbles was seen flowing through the precursor solutions. Solution temperature was reduced to 90 °C, and Ar gas was bubbled through the solution for an additional 20 minutes. During the pretreatment and synthesis process, the temperature of the precursors was checked using a fine gauge thermocouple, which was inserted through an unconnected port. Immediately before the synthesis, the two precursor vessels were connected to 1.52 mm inner diameter 3-stopper Tygon peristaltic pump tubing (IDEX Health & Science).

The two precursor vessels were heated on a hotplate to 90 °C for the duration of the synthesis. Each precursor was pumped by a peristaltic pump (REGLO digital) at 0.30 mL per minute using the 1.52 mm inner diameter 3-stopper Tygon tubing which

was connected to 1/16" inner diameter Tygon tubing by a PTFE straight thru connector. The 1/16" inner diameter Tygon tubing was connected to the first of two polyether ether ketone (PEEK) micro T-mixers with a 0.5 mm through hole (IDEX Health & Science) where the two precursors mixed. The first PEEK micro T- mixer was connected to a second mixer by a 4 cm long piece of 1/16" inner diameter high temperature PTFE tubing (McMaster-Carr). Ar gas is injected at the second PEEK micro T-Mixer with a constant flow rate of 0.15 mL per minute using a second peristaltic pump to segment the mixed solution. The segmented solution was flowed through the 1/16" inner diameter high temperature PTFE at a rate of 0.75 mL per minute, where the solution entered the top aluminum chimney on the microwave, moving from the mixing zone to the microwave nucleation zone. It is important to note that the flowrate in this system was not constant through the entire volume since the Ar gas expands with decreased pressure and increased temperature.

The microwave unit (Sairem) used in this reactor has a maximum output of 3 kW of microwave radiation at 2.45GHz. The microwave was adjusted using three waveguide cylinders and a reflector panel in order to achieve a maximum temperature at in the solution before running the synthesis process. The solution is irradiated in an approximately 4 cm long length in the center of the microwave. Aluminum chimneys with a ¼ inch through hole were connected above and below the microwave region to prevent microwave leakage and provide cooling. A Pyrex tube with PTFE tape was used to help center the top and bottom of the 1/16" inner diameter high temperature

PTFE tube in the top and bottom chimneys. Additionally a fiber optic probe (Neoptix) was attached to the outside of the tubing wall using PTFE tape. The tip of the fiber optic probe was positioned in the center of the microwave region using a viewing window in the side of the microwave region. The temperature in the microwave zone was controlled by changing the microwave power and then adjusting the reflector to achieve a maximum temperature.

A PTFE pressure tight fitting to luer-lock connection was located 5 cm after the tubing exited the bottom chimney, and was used to allow quick replacement of the tubing in the microwave region. The tubing exiting the microwave region was connected to a 350 cm of coiled 1/16" inner diameter high temperature PTFE tubing submerged in an oil bath. The oil bath was held at a constant 140 °C during the synthesis process. The submerged coil was used as a growth zone.

The quench zone started when the solution exited the oil bath. The air surrounding the 1/16" inner diameter high temperature PTFE tubing quickly cooled the solution in the last 10 cm of 1/16" inner diameter high temperature PTFE tubing. The product solution dripped from the end of the tubing into a glass vial for collection.

During microwave assisted continuous flow synthesis the microwave temperature was adjusted to determine the effect of the microwave nucleation temperature on the synthesized NCs. The microwave temperature was controlled by adjusting the microwave forward power between 270 W and 360 W followed by

adjusting the reflector to obtain the minimum reflected power and highest solution temperature. Temperatures measured by the fiber optic probe on the outside of the 1/8" outer diameter, 1/16" inner diameter high temperature PTFE tubing were between 120-165 °C. During the synthesis, the reactor was run constantly for 3.5-6 hours at a time, either until the precursors were consumed or until the reactor clogged.

3.1.3 Cleaning

After 10 minutes of collection, the particles were cleaned by multiple precipitation steps and suspend in toluene for storage. First the collected product solution was pipetted into polyethylene centrifuge vials. With 7 mL of product solution per vial, 1-2 mL of methanol was added. The solution was centrifuged at 7000 RPM for 10 minutes. Visual inspection was performed after centrifugation, and 1-2 mL of acetonitrile was added and the solution was centrifuged at 7000 RPM for an additional 10 minutes if the solution wasn't clear. In most cases, the solution was clear after centrifugation and the supernatant was pipetted off into a waste container. 6 mL of toluene was added to the black precipitate. Rapid shaking followed by 5 minutes in an ultrasonic bath was used to resuspend the particles in solution. This cleaning process was repeated a minimum of three times to remove unused precursors. After cleaning, the suspended NCs were stored at room temperature, and visually monitored for stability.

Samples that were synthesized using only the microwave nucleation zone and no growth zone were much more difficult to clean. These samples did not precipitate with addition of methanol or acetonitrile and required a new cleaning technique. For these samples, 2 mL acetone was gently added to the top of the solution, and the glass vial was gently swirled. After swirling, the acetone on top of the solution turned a cloudy white opaque color. This cloudy solution was pipetted off the top of the solution, and the process was repeated until the acetone no longer became cloudy. Then 2 mL of methanol was added, and the solution was centrifuged at 7000 RPM for 20 minutes. The solution was pipetted off the precipitated NCs, and then the particles were suspended in 6 mL of toluene.

3.2 Characterization of PbSe Nanocrystals

Samples were characterized using high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and visual inspection.

To prepare samples for the HR-TEM measurements the PbSe NC toluene solutions were resuspended using an ultrasonic probe to ensure breakup of agglomerations and good suspension. The solution was diluted until the solution showed only a slight transparent brown color, and a single drop of solution was placed on a TEM grid. The TEM grid consisted coated with Formvar and carbon. Samples dried for 3 hours before being placed into the grid box. High-resolution

images were difficult to obtain in these samples due to carbon contamination from the samples. In order to obtain HR-TEM images the samples were cleaned using an oxygen plasma for 10-40 seconds to remove excess organics in samples after medium resolution images were obtained. The particle size before and after cleaning was examined and showed no significant change in size for all samples except the microwave only sample.

XRD and EDX samples were prepared by drop casting the solution onto a glass slide cover which was cleaned using acetone, isopropyl alcohol, and deionized water (AMD wash), dried with nitrogen, and then placed on a clean hotplate held at 50 °C. A disposable pipette was used to place 2-3 drops of the PbSe NC solution onto the heated glass slide, and allowed to dry. This process was repeated several times to form a thick film of PbSe NCs.

3.2.1 Size

NC size was determined using the free ImageJ program from the National Institute of Health (<http://rsb.info.nih.gov/ij/>) to analyze images taken with a FEI Titan 80-200 TEM/STEM. In ImageJ, single particles were outlined using the freehand selection tool, and added to the overlay by pressing Ctrl+B. During this process, single particles showing clear outlines and approximately cubic, octahedral or spherical shapes were counted. Particles were added to the ROI manager and area of each of the outlined NCs was measured using the ImageJ software. Data was then

exported to Excel and an approximate diameter was calculated assuming the NCs were spherical (Equation 3-1).

$$\text{Equation 3-1} \quad d = 2 \times \sqrt{A/\pi}$$

Where d is the particle diameter, and A is the particle area measure by ImageJ. The mean particle diameter (μ), standard deviation (σ) and variation in particle size, V_{sp} (Equation 3-2) were calculated for each sample.

$$\text{Equation 3-2} \quad V_{sp} = \frac{\sigma}{\mu} \times 100\%$$

A two tailed t-test was used to test if the particle sizes were significantly different (Equations 3-3, 3-4 and 3-5).

$$\text{Equation 3-3} \quad S_{1,2} = \left(\frac{(n_1-1) \cdot \sigma_1^2 + (n_2-1) \cdot \sigma_2^2}{n_1+n_2-2} \right)^{1/2}$$

$$\text{Equation 3-4} \quad t_{1,2} = \frac{\mu_1 - \mu_2}{S_{1,2} \cdot \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

Equation 3-5

$$\mathbf{H_a: \mu_1 - \mu_2 > 0, reject H_0: \mu_1 - \mu_2 = 0 \text{ if } |t_{1,2}| > t_{\text{critical}}}$$

Where the subscripts 1 and 2 refer to the different samples, $S_{1,2}$ is the estimated standard error for the two samples, n is the number of particles measured in the sample, $t_{1,2}$ is test statistic calculated from the data and t_{critical} is approximately 2.812 for a 99 % confidence interval. H_a is the hypothesis that the sample 1 is significantly different from sample 2, and H_0 is the null hypothesis that the two samples are not significantly different.

3.2.2 Crystal Structure

The crystal structure was determined using XRD on drop cast films of PbSe NCs, and HR-TEM images of single NCs. A Bruker D-8 Discover tool was used to take XRD spectra of the drop-cast PbSe NC films at angles of two theta between 20-80 °. Due to the variable thickness of the drop-cast films, the scan rate was adjusted for each sample in order to get well defined peaks in each sample. The XRD peaks were then compared to the position and intensity of references in the tool library.

High-resolution images of plasma cleaned samples were taken using an FEI Titan 80-200 TEM/STEM. ImageJ was used to measure the average lattice spacing in the HR-TEM images by creating a line perpendicular to the plane and dividing the length of the line by the number of planes it crossed. For accurate results the line

distance crossed 25-30 planes for each sample that was measured. In the HR-TEM images the resolution was approximately 0.01 nm per pixel and values are reported to the nearest 0.1 Å.

3.2.3 Composition

The composition of the synthesized NCs was determined using an FEI QUANTA 600F environmental SEM equipped with an energy dispersive X-ray spectrometer (EDX) for the drop-cast PbSe NC films. The PbSe films were broken up and an approximately 1 cm × 1 cm piece of each sample was secured to an aluminum SEM stud with conductive carbon tape. During the EDX analysis of the films the $L\alpha_1$ emission for Se at 1379.1 eV, and the $M\alpha_1$ emission for Pb at 2345 eV were used to determine the relative amounts of Pb and Se. The quantification was done using the EDX software with the internal library values for Z, A, F and K provided with the instrument. Where Z is the atomic number effect, A is the X-ray absorption effect, F is the x-ray fluorescence effect, and K is the intensity ratio. EDX analysis was performed in three different regions on each of the drop-cast PbSe films.

3.2.4 Stability

Stability of the cleaned particles was confirmed by visual inspection of the particles in solution. Color change and visible precipitation was observed hourly for 2 hours after cleaning, daily for the first two weeks, and then biweekly for the next two

months. As NCs precipitated the solution color was observed to change from opaque black to slightly transparent brown to transparent light brown to clear. The precipitated particles were a black oily solid. Some precipitation was observed in all samples after two months, but many samples remained brown indicating at least some of the particles were stable.

4 PbSe Nanocrystal Synthesis: Results and Discussion

PbSe NCs were synthesized using both the batch microwave method, and the microwave assisted segmented flow method. This section will present the characterization of the resulting material, followed by discussion of the results.

4.1 Characterization of Products

Samples of cleaned PbSe NCs in toluene were checked routinely for color and precipitation. The solution was black and opaque after resuspending the particles. A color change was observed as the nanocrystals precipitated from the solution. The color of the solution went from opaque black to slightly transparent dark grey to dark brown to light brown, and finally to clear. In addition, a layer of black precipitation was observed at the bottom of the glass vial. All samples showed some change in color, but once the samples were dark brown most of them were stable over a period of weeks.

All samples showed some black precipitant in a matter of hours, and generally went from opaque black solution to dark brown solution in 2-3 days at room temperature. After this, several samples were stored for two months with no visible change in the color or amount of precipitation. The five samples that were fully characterized and are shown here remained dark brown over the two months of observation.

The relative composition of the PbSe NCs was analyzed using EDX (Table 4-1). The average of the three regions that were analyzed on each sample showed a relative composition close to the ideal 1:1 atomic ratio of Pb to Se. The deviation from the 1:1 ratio was within the expected error in the measurement, which was 5-10 atomic percent on a rough film with no standard. Samples produced using the microwave assisted segmented flow reactor showed an increasing ratio of Pb to Se with increasing temperature, with all samples being slightly Se rich. The relative atomic percent of Se was found to be 56.21, 53.81 and 52.73 for samples synthesized with microwave nucleation temperatures of 124 ± 2 °C, 142 ± 3 °C and 159 ± 3 °C, respectively.

Table 4-1 Relative atomic concentrations of Pb and Se obtained via EDX.

140 °C Batch		124 °C Flow		142 °C Flow		159 °C Flow	
PbSe		PbSe		PbSe		PbSe	
Pb	Se	Pb	Se	Pb	Se	Pb	Se
M α_1	L α_1	M α_1	L α_1	M α_1	L α_1	M α_1	L α_1
(At %)	(At %)	(At %)	(At %)	(At %)	(At %)	(At %)	(At %)
50.69	49.46	46.22	53.78	49.74	50.26	52.37	47.63
50.54	49.31	45.58	54.42	48.75	51.25	48.70	51.30
48.70	51.30	39.56	60.44	40.07	59.93	40.74	59.26

PbSe NCs were synthesized in the batch microwave was heated from room temperature, $\sim 21\text{ }^{\circ}\text{C}$, up to $140\text{ }^{\circ}\text{C}$ in 3.5 minutes followed by a holding period at $140 \pm 1.7\text{ }^{\circ}\text{C}$ for 9.5 minutes. During experiments to determine the minimum nucleation temperature, a color change in the solution from clear to opaque black was observed as low as $110\text{ }^{\circ}\text{C}$. At $100\text{ }^{\circ}\text{C}$, the solution was light brown and turned dark brown after being left at room temperature overnight. When the solutions were mixed at room temperature and allowed to sit overnight a yellowish color was observed.

TEM examination of PbSe NCs synthesized using the batch microwave showed a square shape with planes parallel to the sides indicating a cubic shape with the (100) planes exposed, and a octahedron shape indicated truncated octahedral shape with the (100), (110) and (111) planes exposed (Figure 4-1). The PbSe NCs were measured using ImageJ, and an average diameter of $17.4 \pm 5.2\text{ nm}$ was observed, giving a $V_{ps} = 30\%$ (Figure 4-2). HR-TEM of a cubic particle showed that the atomic spacing was $3.1\text{ \AA}$, which matches the $3.1\text{ \AA}$ spacing for the (200) planes of PbSe (Figure 4-1). The EDX results (Table 4-1) for the $140\text{ }^{\circ}\text{C}$ PbSe NCs synthesized using the batch microwave showed an average composition of 50.00 atomic percent of Pb and 50.00 atomic percent of Se with a standard deviation of 1.34 atomic percent. The EDX results are consistent with the idea 1:1 composition ratio of Pb to Se.

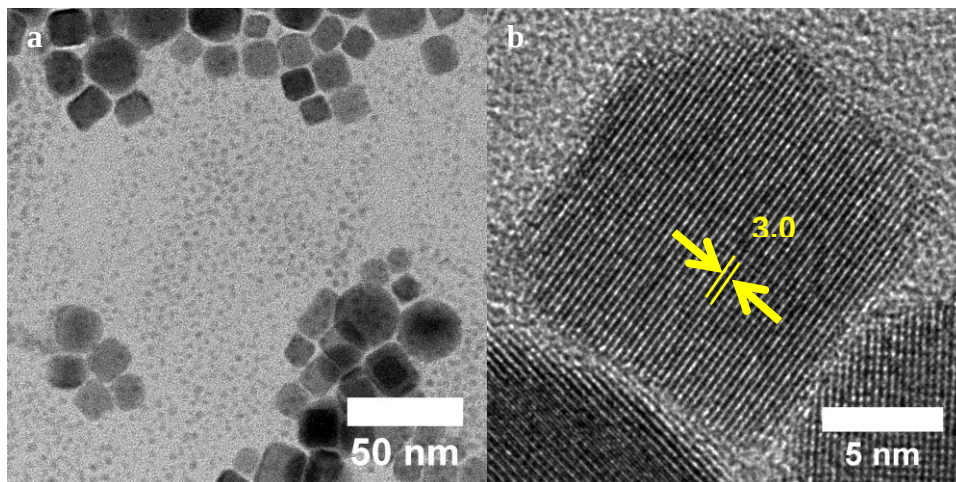


Figure 4-1 TEM images of PbSe synthesized at 140 °C in the CEM Mars V microwave at (a) low and (b) high magnification.

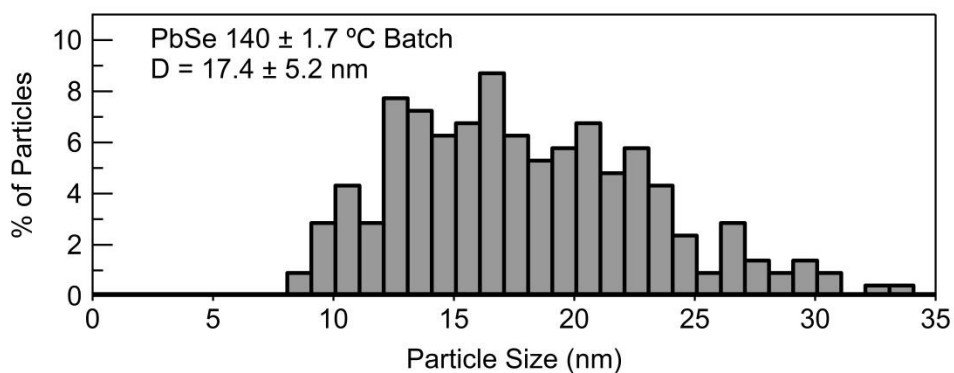


Figure 4-2 Histogram showing the distribution of particle sizes produced at 140 °C in the CEM Mars V microwave.

PbSe nanocrystals were produced using the microwave assisted segmented flow method with nucleation temperatures between 120-165 °C and a growth temperature of 140 °C. The precursor concentrations were reduced from 0.15 M Pb in

the batch microwave method to 0.10 M Pb in the microwave assisted segmented flow method, while keeping a molar ratio of 2:5:4:6 of Pb:OA:Se:TOP. This change was made because the Pb(OA)_2 precursor would condense into a white waxy precipitant, and clog the reactor before the microwave zone.

The temperature profile in the microwave region was adjusted between 120-165 °C with flow rates of 0.30, 0.30 and 0.15 mL per minute for the Pb precursor, Se precursor and Ar gas, respectively. Four stable samples produced using the microwave assisted segmented flow method were fully characterized using TEM, XRD, and EDX. Three samples were synthesized with nucleation temperatures of 124 ± 2 °C, 142 ± 3 °C and 159 ± 3 °C in the microwave and a growth temperature of 140 ± 2 °C in the oil bath. The fourth sample was synthesized using a nucleation temperature of 160 ± 2 °C in the microwave without the oil bath. The temperature was recorded every second for the 10 minute synthesis using the fiber optic probe (Figure 4-3). During the synthesis a noticeable temperature increase was observed in the waveguide after running the reactor for approximately 1 hour and the reflector had to be adjusted between each sample. The variation of temperature may be due to heating of the waveguide and reflector, uneven absorption of microwave energy in the gas and solution segments, and deposition of material on the inside wall of the reactor.

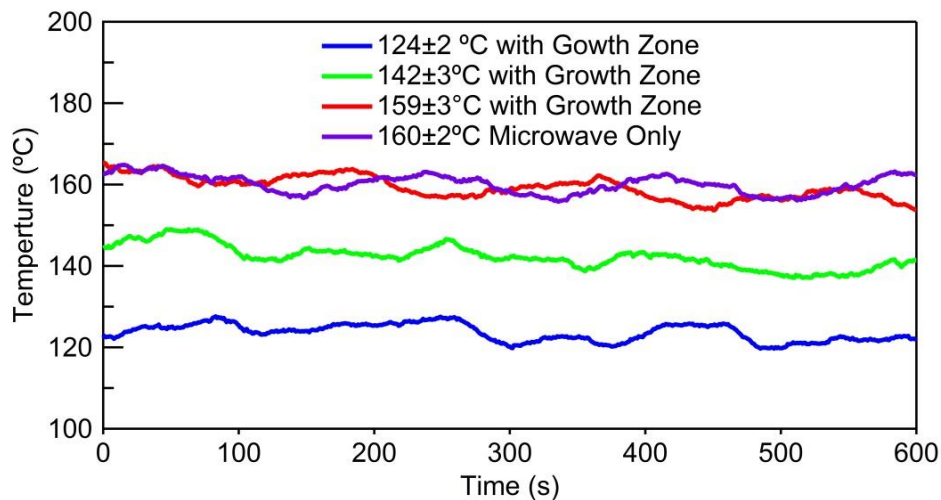


Figure 4-3 Temperature in the microwave nucleation zone during microwave assisted segmented flow synthesis.

The XRD of the three samples (Figure 4-4) synthesized using the microwave assisted segmented flow reactor showed that all three can be indexed to the synthesized rock salt structure of PbSe (JCPDS 00-006-0354). In the range from 20-80 ° match the position and relative intensity of the reference spectra.

The EDX results from PbSe NCs produced using a nucleation temperature of 124 ± 2 °C in the microwave showed an average composition of 43.79 atomic percent of Pb, and 56.21 atomic percent of Se with a standard deviation of 3.00 atomic percent (Table 4-1). This result indicates that the PbSe NCs are slightly Se rich compared to the ideal 1:1 atomic ratio of Pb to Se. Analysis of the TEM images of the 124 ± 2 °C PbSe NCs showed an average particle diameter of 13.9 ± 2.1 nm and a

$V_{sp} = 15\%$ (Figure 4-7). HR-TEM images of a single NC showed atomic spacing of 3.1 Å between planes, which matches the expected spacing for the (200) planes of PbSe (Figure 4-5). The planes are oriented at a 45 ° angle from the sides indicating a [110] projection of an octahedral shaped PbSe NC. Indents or fringes are observed in the particle which may be caused by rearrangement to the lower energy (200) surface [101].

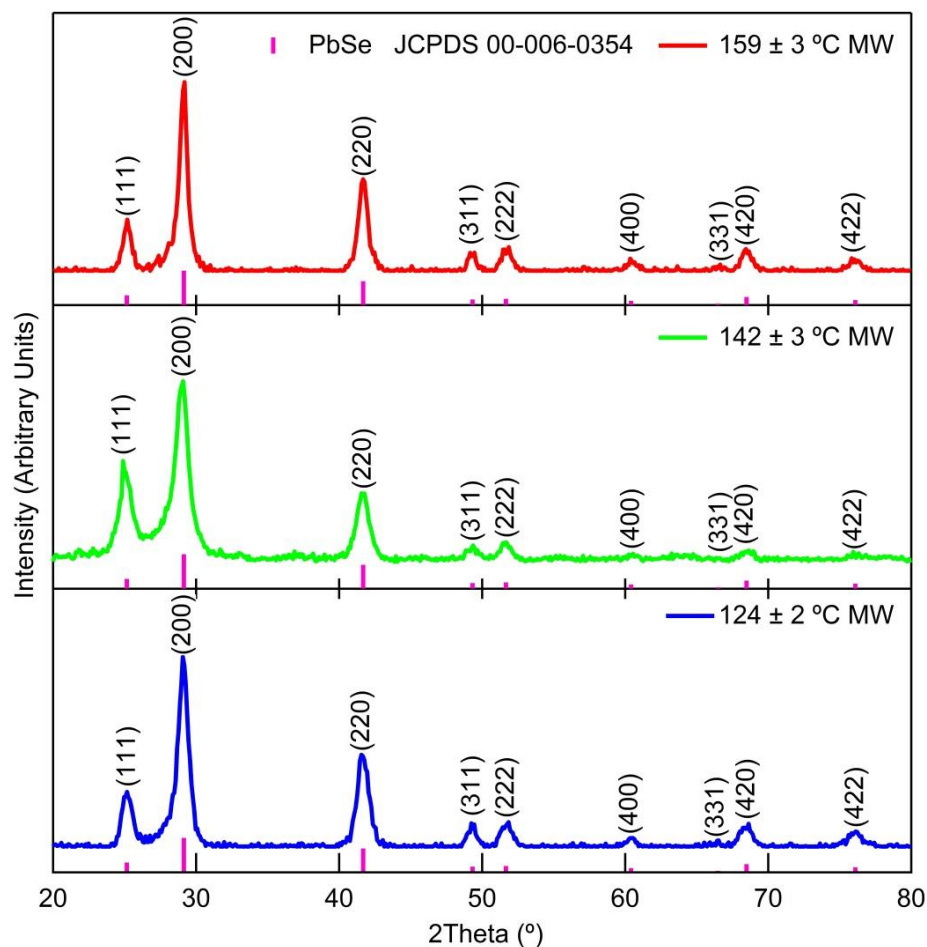


Figure 4-4 XRD spectra of drop-cast PbSe NCs synthesized in the microwave assisted segmented flow reactor.

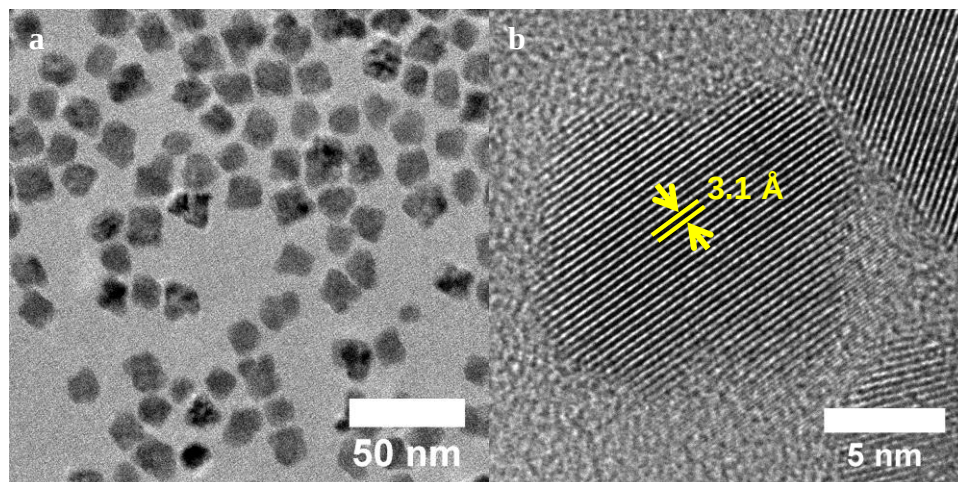


Figure 4-5 TEM images of PbSe NCs produced using 124 °C in the microwave nucleation zone at (a) low and (b) high magnification.

The EDX of PbSe NCs synthesized using a nucleation temperature of 142 ± 3 °C in the microwave nucleation zone showed an average composition of 46.19 atomic percent Pb, and 53.81 atomic percent Se and a standard deviation of 4.3 atomic percent (Table 4-1). The sample may be slightly Se rich but results are within one standard deviation of the ideal 1:1 atomic ratio of Pb to Se. The TEM examination of the PbSe NCs synthesized with a nucleation temperature of 142 ± 3 °C showed an average particle diameter of 12.5 ± 2.0 nm with a $V_{ps} = 16$ % (Figure 4-8). High resolution TEM observation of a single particle showed an atomic spacing of $2.2 \text{ \AA}$ between planes, which matched the expected $2.2 \text{ \AA}$ spacing for the (220) planes of PbSe (Figure 4-6). Since the (220) planes are parallel to the sides this is expected to be the [110] projection.

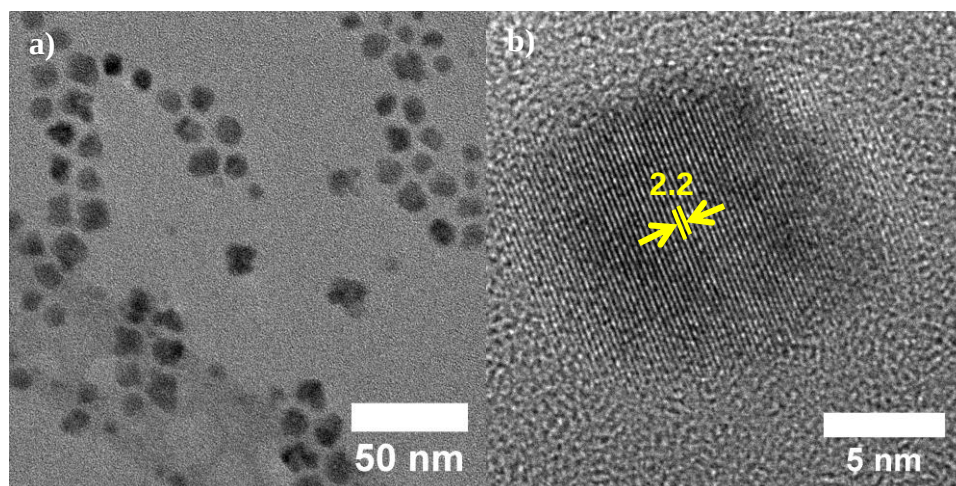


Figure 4-6 TEM images of PbSe NCs produced using 142 °C in the microwave nucleation zone at (a) low and (b) high magnification.

The EDX of PbSe NCs synthesized using a nucleation temperature of 159 ± 3 °C in the microwave nucleation zone showed an average composition of 47.27 atomic percent Pb, and 52.73 atomic percent Se with a standard deviation of 4.85 atomic percent (Table 4-1). This is very close to the ideal 1:1 atomic ratio of Pb to Se. TEM examination of the 159 ± 3 °C PbSe NCs showed an average particle diameter of 11.2 ± 1.7 nm with a $V_{ps} = 15$ % (Figure 4-8). High resolution TEM of a single NC showed atomic spacing of 3.1 Å between planes, which matches the expected 3.1 Å spacing for the (200) planes of PbSe (Figure 4-7). This is expected to be the [110] projection of an octahedral PbSe NC since the (200) planes are at a 45 ° angle to the sides. A

small indent is seen on one of the sides of the particle which is expected to be from the rearrangement to the (200) surface.

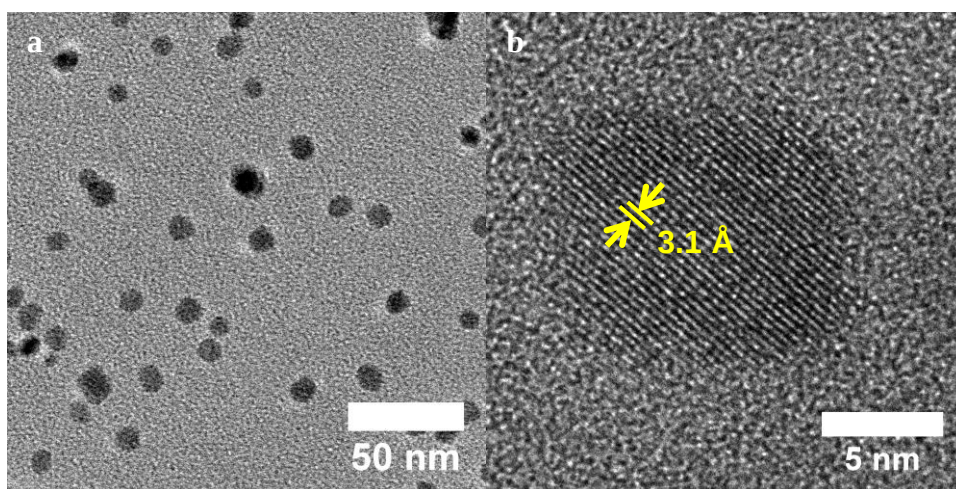


Figure 4-7 TEM images of PbSe NCs produced using 159 °C in the microwave nucleation zone at (a) low and (b) high magnification.

The three samples produced with the oil bath had average particle diameters of 13.9 ± 2.1 nm at 124 ± 2 °C, 12.5 ± 2.0 nm at 142 ± 3 °C, and 11.2 ± 1.7 nm at 159 ± 3 °C (Figure 4-8). The mean NC diameters of the samples were found to be significantly different with ($t_{124^{\circ}\text{C},142^{\circ}\text{C}} = 12.26$, $t_{142^{\circ}\text{C},159^{\circ}\text{C}} = 25.52$, and $t_{124^{\circ}\text{C},159^{\circ}\text{C}} = 25.52$ all of which are greater than $t_{\text{critical}} \sim 2.814$). Samples showed a variation in particle size of 15-16 %. Average PbSe NC size was observed to decrease with increasing nucleation temperature.

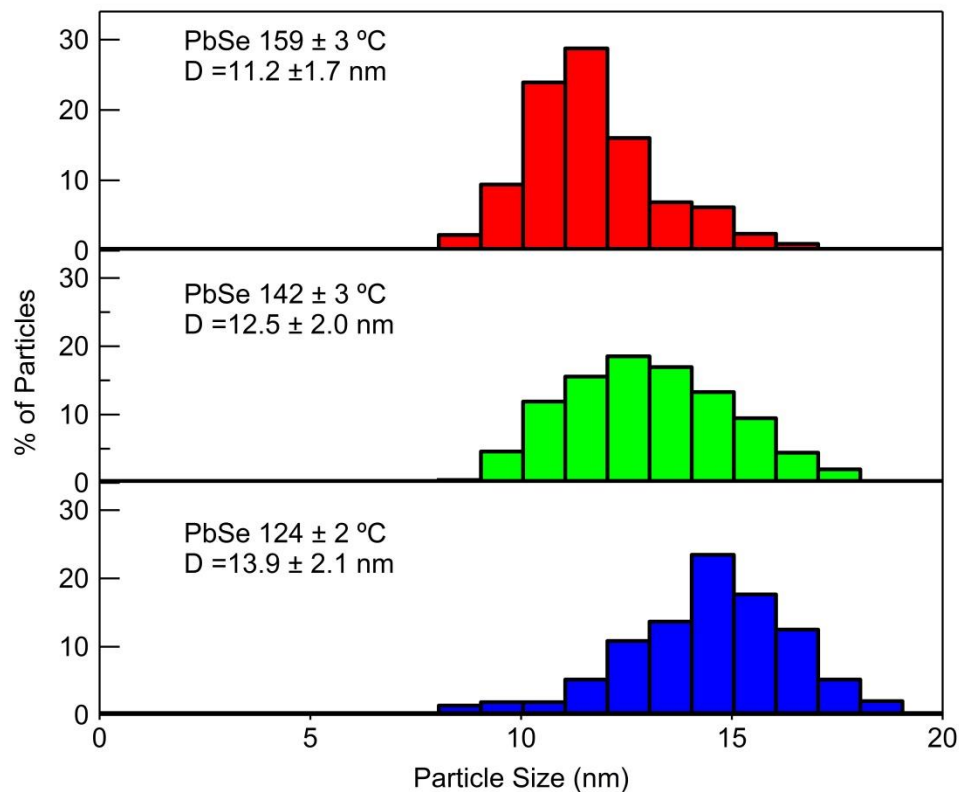


Figure 4-8 Histograms showing the particle size distributions of PbSe NCs synthesized using the microwave assisted segmented flow reactor.

Particles synthesized using a $160 \pm 2 \text{ }^{\circ}\text{C}$ nucleation temperature in the microwave without the oil bath was characterized by EDX, XRD and TEM. EDX showed that the particles were extremely Pb rich, with an average 93.4 atomic percent Pb and 6.2 atomic percent Se with a standard deviation of 1.0 atomic percent (Table 4-2).

Table 4-2 Relative atomic percent of Pb and Se from EDX.

160°C MW Only	
Pb $M\alpha_1$	Se $L\alpha_1$
(At %)	(At %)
91.95	8.05
94.37	5.63
93.38	6.17

XRD spectrum of the particles showed a maximum intensity at 28.2 °, but no other peaks were distinguishable. The closest match found was lead oxide (PbO) (JCPDS 00-038-1477), which has its most intense peak at 29.1 ° representing (111) planes (Figure 4-9). The one broad peak found even on a thick film may indicate that the particles were amorphous or nanocrystalline agglomerates. 5 of 250 particles measured in the TEM images for sizing showed what looked like atomic planes, but it was not possible to obtain accurate enough measurements to match the atomic spacing to a crystal structure.

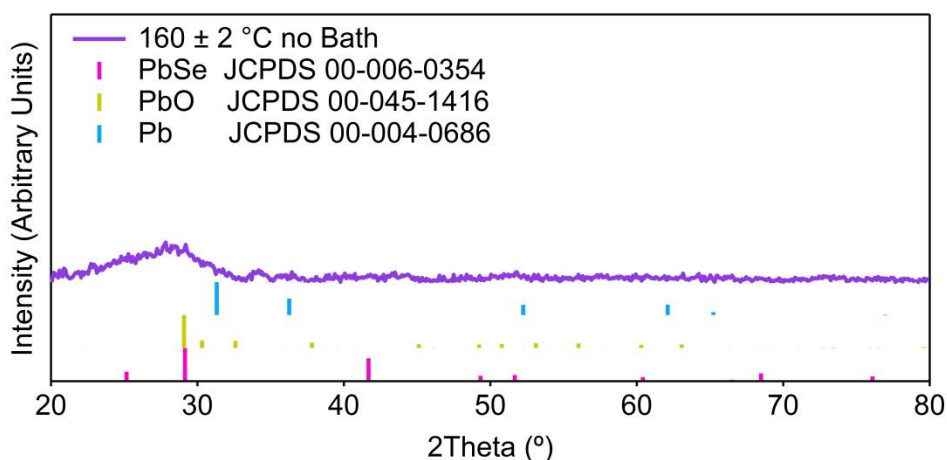


Figure 4-9 XRD spectra of particles synthesized at 160 °C in the microwave nucleation zone without the growth zone.

HR-TEM was attempted on the particles but when they were exposed to the electron beam the images became blurry due to carbon contamination. Carbon contamination could be from the amorphous particles being damaged by the electron beam and thereby releasing hydrocarbon from left over ligands. Plasma cleaning was attempted on the sample, but the carbon contamination persisted and a large decrease in particle size was observed (Figure 4-10). TEM images showed an average particle diameter of 11.0 ± 1.2 nm with a $V_{sp} = 11$ % in the sample prior to plasma cleaning (Figure 4-11). The particle size present after the microwave nucleation zone at 160 ± 2 °C was found to be close to the particle size of the PbSe NCs synthesized using a 159 ± 3 °C nucleation temperature with the 140 ± 2 °C growth temperature.

However, after plasma cleaning the TEM images showed an average particle diameter of 3.9 ± 0.4 nm with a $V_{sp} = 10$ %

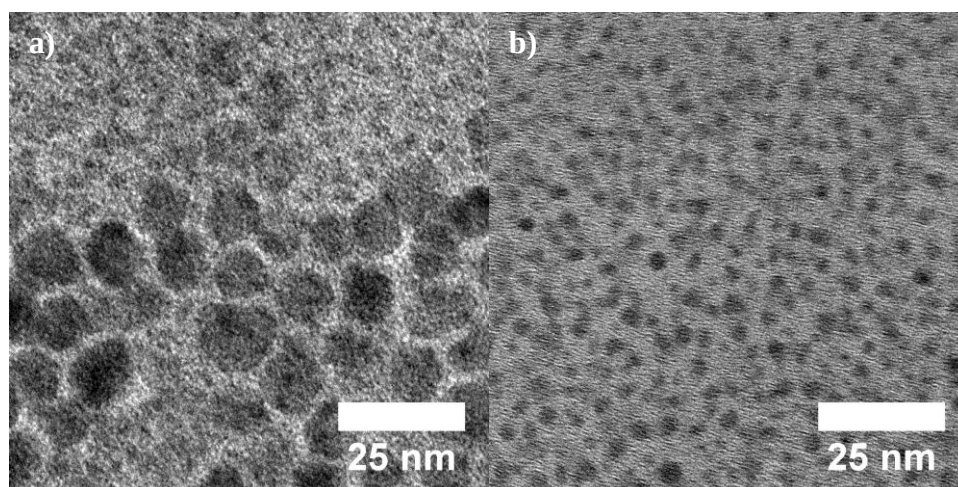


Figure 4-10 TEM images a) before and b) after plasma cleaning of samples synthesized at 160 °C in the microwave nucleation zone without the growth zone.

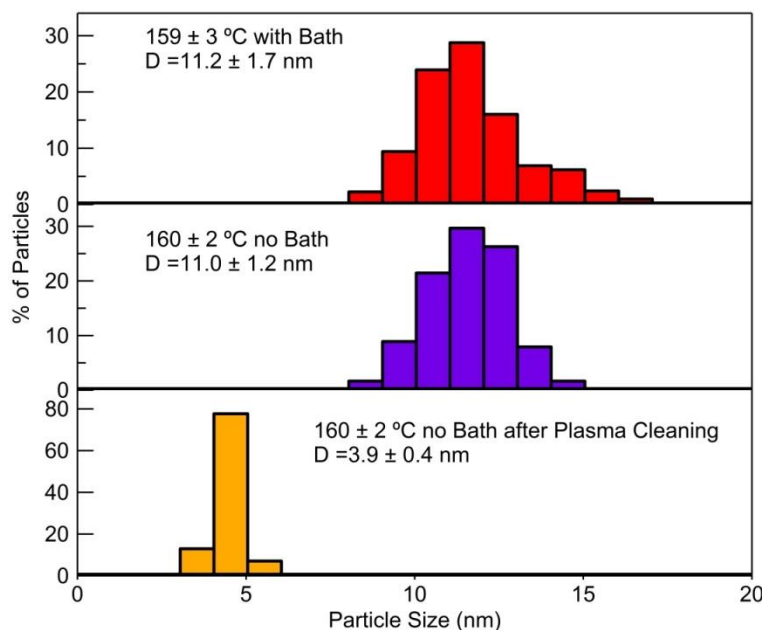


Figure 4-11 Histograms of particles produced at 159 °C with the growth zone, 160 °C without the growth zone before plasma cleaning and after plasma cleaning.

4.1.1 Batch Method

As discussed previously, several factors influence the size, shape, and size distribution of PbSe NCs. The PbSe NCs synthesized using the batch microwave reactor had a larger average particle diameter 17.4 ± 5.2 nm, and large $V_{ps} = 30$ % when compared to the $V_{ps} = 5-15$ % for most hot injection synthesis. The chemistries used were adapted from the methods used by Yu et al. for hot injection [58]. The

cubic shape of the majority of PbSe NCs shown in the TEM images may be due to the lower surface energy of the exposed (100) plane. Larger particles with the truncated octahedral shape are also observed in the TEM images. This shape is suspected to form when a large excess of ligand is available, and coordinates with the (100), (110) and (111) surfaces causing nearly equal growth. The larger size may indicate an increased growth time. Here it is expected that the large truncated octahedral shaped PbSe NCs were nucleated early on in the synthesis when a large excess of ligand is available, and the smaller cubic particles are nucleated later in the synthesis. Probably the largest factor influencing V_{ps} was the 3-4 minute ramp to 140 °C. This may have caused a drawn out nucleation event, as the rate of monomer creation slowly increased even after nucleation began caused nucleation to occur even after other particles were growing.

The most comparable result in literature was from Sliem et al., who synthesized smaller NCs using the same chemistries as in for both hot injection synthesis, and batch microwave synthesis [82]. Examination of PbSe NCs synthesized at 100 °C for 1 minute showed an average NC diameter of 5.8 nm with irregular morphologies, and a $V_{ps} = 37 \%$, while PbSe NCs synthesized at 160 °C for 1 minute and 5 minutes had a V_{ps} of 16 % and 11 %, respectively. The PbSe NC size was observed to increase with reaction time from 7.3 nm at 1 minute and 14.4 nm at 5 minutes. The smaller V_{ps} is expected to be due to a shorter nucleation event and less coarsening during the synthesis [82]. Sliem et al. used heating rates greater than

160 °C per minute, which may have led to rapid nucleation. Additionally, the rapid quench used by Sliem et al. stopped particle growth and coarsening much more quickly than the relatively slow air cooling used in the batch microwave synthesis presented here. In the batch microwave synthesis presented in this work, the growth temperature of 140 °C was reached in ~3.5 minutes giving a much slower heating rate, and the slow air cooling to 80 °C in the microwave may have allowed additional coarsening at the end of the reaction. The TEM Images in both studies showed cubic PbSe NCs indicating accelerated growth in the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions versus the $\langle 100 \rangle$ direction.

4.1.2 Microwave Assisted Segmented Flow Method

There were several differences between the microwave systems used for the microwave assisted segmented flow versus the microwave batch method. The Sariem microwave had a dummy load of water so that the microwave no longer required a minimum load to use up the microwave energy in order to protect the magnetron. This allowed use of a higher excess of microwave power without fear of damaging the magnetron, which allowed much faster heating and may have provided more even application of microwave energy. A total residence time of 25.3 seconds was determined for the 4 cm length of 1/16" inner diameter tubing (~0.079 cm) at a flow rate of 0.75 mL per minute. The temperature measured in the center of the microwave zone was 160 °C, providing a heating rate greater than 341.5 °C per minute at 250 W.

These experiments used a maximum power of 250 W, but the maximum output of the microwave system was 3 kW. It is expected that much greater heating rates could be achieved by increasing microwave power.

Control over PbSe NC size using the microwave assisted segmented flow by varying the nucleation temperature was demonstrated. It is suspected that rapid heating in the microwave zone allows creation of a burst nucleation event similar to that in the hot injection method. The rate of monomer creation in the mixed solution due to the temperature jump was similar to that present immediately after injection.

The microwave system also had water cooling directly before and after the microwave nucleation zone. As a result, the solution outside of the tubing directly below the chimney was near room temperature. This may have resulted in a sudden decrease in the rate of monomer creation. Then an oil bath was used to heat the solution to growth temperature.

Micro T-mixers were used immediately before the microwave to provide a more homogenous solution for the nucleation process, while segmented flow increased mixing during the reactor and decreased the distribution of residence times in the reactor.

The average diameter of PbSe NCs increased with decreasing nucleation temperature. This result may be explained based on equation 2-5, where the critical radius is inversely proportional to the temperature, and increased rates of monomer

creation with increasing temperature. This results in faster nucleation of a greater number of small nuclei leading to smaller NC size.

The variation in particle size was found to be 15 %, 16 %, and 15 % for PbSe NCs synthesized with particle sizes of 13.9 ± 2.1 nm, 12.5 ± 2.0 nm and 11.2 ± 1.7 nm, respectively. These are comparable to those presented by Sliem et al. of 11 % and 16 % for PbSe NCs synthesized via microwave heating at 160 °C with sizes of 7.3 nm and 14.4 nm, respectively. Currently, the smallest reported values for V_{sp} are approximately 5 % in PbSe NCs produced by hot injection process, but often are a result of size selective processes starting with a V_{sp} of 10-15 % [57, 58].

The particles collected directly after the microwave region had an average of 93 atomic percent Pb as shown by EDX analysis. This suggests that the dominate reaction in the microwave assisted segmented flow involves reduction of $Pb(OA)_2$ to Pb^0 . Additionally the lack of Se in the EDX analysis, may indicate that the TOPSe is not reduced in the reaction and the Se is in the Se^{2+} oxidation state rather than Se^0 in the microwave region. The reduction of $Pb(OA)_2$ may be due to DPP and other impurities in the TOP or directly by excess TOP.

5 **PbSe Nanocrystal Synthesis: Conclusions**

In this research, a batch microwave method and a microwave assisted segmented flow method were utilized to make high quality PbSe NCs using microwave heating. The synthesized NCs were shown to have the rock salt structure for PbSe with a composition close to the ideal 1:1 ratio of Pb to Se. The PbSe NCs synthesized using the batch microwave method showed a variation in particle size of 30 %, while the PbSe NCs synthesized using the microwave assisted segmented flow method showed a variation in particle size around 15 %. While the PbSe NCs synthesized in this study showed a larger variation in particle size than the 5-10 % reported for various hot injection methods for PbSe NC synthesis, the variation in particle size was similar to the microwave based synthesis that was reported by Sliem et al. [82]. It is expected that further optimization of the microwave assisted segmented flow method and size selective precipitation can be used to obtain smaller variation in particle size.

The hot injection method reported by Yu et al. [58] was modified to synthesize PbSe NCs with small variations in particle size in the microwave assisted segmented flow reactor. The rapid heating in the microwave nucleation zone was used to create a burst nucleation event similar to the rapid injection of a precursor into hot solution. It is suspected that other hot injection chemistries could be easily adapted for the microwave segmented flow reactor. The microwave assisted segmented flow

method developed is a possible route to the scale-up in the manufacturing of a wide range of nanomaterials.

Control over the size of PbSe NCs synthesized was demonstrated by varying the microwave nucleation temperature. The NC particle size was observed to decrease from an average particle diameter of 13.9 nm to 11.2 nm with increasing nucleation temperature from 124 °C to 159 °C.

The goals of synthesizing high quality nanocrystals using microwave heating, developing a microwave assisted continuous flow technique for nanocrystal synthesis, and demonstrating control over nanocrystal size in microwave assisted continuous flow synthesis were met during this research. This work presented the first reported continuous flow synthesis of PbSe NCs, and demonstrated a novel microwave-assisted segmented flow synthesis technique for nanomaterials, which represents a possible route to scale-up for nanomaterial manufacturing.

6 ZrCuAlNi Oxidation: Introduction

The motivation of undertaking this study was to investigate thermal annealing and initial oxidation of zirconium copper aluminum nickel (ZCAN) metallic glass (MG) to facilitate the understanding interface properties and allow further the application of thin film metallic glasses for electronic devices. The goal of this study was to observe the oxide growth and compositional changes in the ZCAN MG thin film in order to obtain a better atomistic understand the initial oxidation process. This study specifically investigated the thermal oxidation of $\text{Zr}_{45}\text{Cu}_{35}\text{Al}_{10}\text{Ni}_{10}$ metallic glass thin films in ambient air. Characterization was performed using secondary ion mass spectroscopy, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy to observe oxide growth and changes in composition with nanometer scale resolution.

In contrast to crystalline metals, MG has no long range order. The lack of crystalline grains and defects allow MGs to form nearly atomically smooth surfaces. MG also offers unique properties including high yield strength, low elastic modulus, and high resistance to corrosion [102, 103, 104]. MG composition can be used to control the material properties. Vapor to solid techniques allow creation of MGs with a greater range of compositions than can be made using the traditional method of rapidly cooling the molten metal alloy [104]. This allows an increased ability to engineer MGs with ideal properties for intended applications. Sputtering deposition, a

vapor to solid technique, has been used to create high quality thin film metallic glass (TFMG) with controlled stoichiometry. Sputter deposition and nanoscale patterning [105] enables the creation of TFMGs with nanoscale features and tailored properties for thin film applications increasing the potential applications TFMGs. Understanding processing effects on TFMGs is a key step in the application of TFMG in commercial devices. Thin film processing often requires high temperatures and controlled oxidation. This research focused on the effects of thermal annealing and thermal oxidation of ZCAN TFMG.

This study of the thermal oxidation of ZCAN TFMG in this thesis is presented as follows. Chapter 7 contains a review of ZCAN literature and discussion of the possible applications of TFMGs, which will establish the technical background for discussion of the experimental results. Chapter 8 provides details of the tools and techniques used in this research, followed by the experimental methods used during this research. Chapter 9 presents the experimental data obtained and a discussing of the pertinent information. Finally, Chapter 10 will summarize the research, the conclusions drawn and propose possible directions for future investigations of metallic glass thin films.

7 **ZrCuAlNi Oxidation: Literature Review**

This chapter covers the motivation for using thin film metallic glasses (TFMGs), and the concepts required for discussion of this work are presented. This section is divided into an overview of MGs, and oxidation and diffusion in MGs.

7.1 **Overview of Metallic Glass**

Crystalline materials are known to have both long range order (LRO) and short range order (SRO). In contrast, non-crystalline or amorphous materials have no LRO. Glass is a non-crystalline material where the solid state and liquid state share the same SRO [106] and show a structural relaxation upon heating called the glass transition. Bulk glasses are often formed by rapid cooling of a melt at a critical cooling rate (R_c), which is much larger than the rate of diffusion and crystal formation. Any crystalline material could form a glass with fast enough cooling rates. For example, Ni has been shown to vitrify when the melt is cooled at a rate of 10^{10} K/s [107].

The first MG, an alloy of gold and silicon, was discovered in the 1960's using splat cooling to reach cooling rates 10^6 K/s [108]. Since the discovery of this bulk MG, there have been numerous publications on the properties, formation, and stability of bulk MGs [109]. The large critical cooling rate (R_c) required to make

many early MGs limited the maximum size of the structures that could be made to a few millimeters until the late 1980s [102].

Several modern MGs have been discovered that exhibit high glass forming ability (GFA), low $R_c < 100$ K/s, and unique properties including high specific strength, super plasticity, and wear resistance [102]. In general these high GFA alloys consisted of three or more elements, with a large difference in their atomic radii, and negative heats of mixing [110, 109]. In addition, the GFA of an alloy has been shown to increase with the reduced glass transition temperature (T_g/T_m), and temperature range of the supercooled liquid region (T_x-T_g) [111].

A MG alloy containing Zr, Cu, Al, and Ni (ZCAN), which was first studied by Inoue et al. [109] in 1990, has been found to have a large GFA with a reduced glass transition between 0.5 and 0.65, and a large supercooled region between 84 K and 127 K at various compositions [111]. This leads to high resistance to crystallization and separation in the amorphous and supercooled liquid regions of ZCAN. The ability to adjust the composition of the ZCAN MG enables tailoring the properties of the MG. Several groups have studied the glass forming ability, oxidation, and thermal stability of ZCAN with a variety of compositions [102, 112]. ZCAN MGs exhibit high mechanical strength, hardness, elastic energy and impact resistance [102, 113].

ZCAN MG's lack of grain boundaries, mechanical properties, and high stability has created interest in its application in micro and nanoscale devices. Sharma et al. first reported the sputter deposition, and nanoscale patterning of ZCAN in 2005

[105]. Near atomically smooth surfaces (maximum deviation of 1.7 nm over a $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ area) have been observed in ZCAN TFMGs [105, 114], good adhesion characteristics [115], and high corrosion resistance [103]. Sputter deposition also allows greater flexibility in the ZCAN composition [104].

ZCAN TFMGs are a material of interest in applications including metal-insulator-metal (MIM) devices [114], nanoscale laminates [116], micro-mechanical patterning [117], micro-electro-mechanical systems (MEMS) [104] and catalysis, where metal and metal oxide catalysts are widely used.

7.2 Oxidation and Diffusion in Metallic Glass

Thermal annealing and thermal oxidation are common processes used with thin films. Thermal oxidation of TFMGs is also important for applications in catalysis, coatings and laminates [116], and electrical devices. The oxidation of ZCAN is expected to be limited by diffusion. Parabolic rates of oxidation have been observed between 300-450 °C [118]. At temperatures below the glass transition point, oxidation of ZCAN is controlled by the back diffusion of Cu and Ni into the film [119], while at temperatures above the glass transition point, the oxidation is controlled by the diffusion of oxygen to the interface [120, 121]. Dhawan et al. reported an increase in the parabolic rate constant for oxidation of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ from $8.13 \times 10^{-7}\text{ g cm}^{-2}\text{ s}^{-1/2}$ at 591 K to $8.96 \times 10^{-5}\text{ g cm}^{-2}\text{ s}^{-1/2}$ at 681 K, an increase greater than two orders of magnitude [118]. The increase in the rate of oxidation is

expected to be due to the transition between the Cu back diffusion limited process to an oxygen diffusion limited process. The mechanism of the Cu and Ni back diffusion limited oxidation of ZCAN is expected to be similar to the mechanism described for oxidation of binary alloys containing a noble metal such as GeAu [122].

Dhawan et al. reported a parabolic rate of oxidation that followed the Arrhenius law with an activation of 1.8 eV [118] for $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ in the amorphous state. Similarly, Sun et al. reported an oxidation activation energy of 1.7 eV for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ [123] in the amorphous phase. Sharma et al. reported an oxidation activation energy 1.2 eV for $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ in the supercooled liquid phase [124]. The diffusion of Ni in ZCAN has been reported to be 1.9 eV in the amorphous phase and 2.9 eV in the supercooled liquid phase [125]. The similarity in the activation energy for Ni diffusion and oxidation support the theory that the oxidation is limited by Ni and Cu back diffusion in the amorphous phase. The lower activation energy for oxidation in the supercooled liquid phase is similar to the activation energy for O_2 diffusion in ZrO_2 , which is reported to be 1.0 eV [126], suggesting that oxygen diffusion limits the rate of oxidation in the supercooled liquid phase. The activation energy for Cu diffusion was not reported but is expected to be similar to Ni based on atomic size.

The formation of oxides of Zr and Al are expected to be due their strong affinity for oxygen. The heats of formation for ZrO_2 , Al_2O_3 , NiO , CuO and Cu_2O at 300 °C were estimated using data from the NIST chemistry WebBook [127] and were

-1130.9, -1688.1, -255.1, -172.6, -212.2 kJ/mol, respectively. The large difference in the heat of formation for the oxides of Al and Zr when compared to those of Cu and Ni can be used to support the observed preferential oxidation of Al and Zr. Al has often been added to BMG to help scavenge oxygen impurities. Oxidation performed at temperatures below the glass transition temperature show no Cu or Ni in the oxide, while oxidation above the glass transition temperature show Zr, Cu, and Al in the oxide [119, 125, 128]. The absence of Ni in the surface oxide may be due to the much lower concentration of Ni in the MG.

Oxygen impurities in the film have been shown to influence the thermal stability of MGs. Oxygen may help to stabilize various crystalline phases and influence chemical segregation in MGs. Icosahedral NCs consisting of Zr_2Cu , Zr_2Al have been precipitated in various BMG systems by heating [129]. The growth of the metastable icosahedral NCs is expected to be diffusion limited [130].

Oxidation is also important in electrochemistry and corrosion resistance. Anodized ZCAN was found to form an anodic protective film with high resistance, mostly expected to be ZrO_2 with other mixed oxides. Auger electron spectroscopy depth profiles showed an increase in the atomic ratio of Cu/Zr directly after the interface of the oxide film and ZCAN [131].

8 ZrCuAlNi Oxidation: Materials and Methods

This chapter covers the methods used for preparation of the ZCAN TFMG samples, and the methods and tools used for characterization of the samples. The ZCAN TFMG samples for this research were deposited using DC magnetron sputtering. Half of the samples were annealing under high vacuum before thermal oxidation in air. The thermal oxidation was carried out in air using a tube furnace. The as deposited and oxidized ZCAN TFMGs were analyzed using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and high resolution TEM with Chem STEM. ZCAN TFMG was deposited on 3-inch Si wafers with approximately 140 nm of thermal SiO₂. Samples were cleaved into 1 cm² pieces for annealing, oxidation, and characterization.

8.1 Deposition

In sputter deposition high energy particles impinge on a target composed of the MG, and these particles deposit their kinetic energy and cause a collision cascade in the material. When the recoil from the collision cascade reaches the surface with energy greater than the binding energy of an atom or molecule, that atom or molecule is ejected from the surface. This process is called sputtering. Sputtering can be used to etch materials, analyze materials or deposit materials. In this work, sputtering is used by three different unique processes: sputter deposition, SIMS, and XPS.

All of the ZCAN TFMG samples examined in this research were deposited using DC magnetron sputter deposition. Sputter deposition is a well understood deposition technique that has been commonly used in industry for creation of both small and large area films. Since sputter deposition is a vapor to solid deposition technique it allows greater control over the composition of metallic glass thin films than traditional melt to solid techniques. Understanding the physical process of sputtering is important to this and future research on TFMGs.

A negative voltage great enough to cause electrons to be ejected from the surface of the target was applied. The ejected electrons traveled from the negatively biased target towards the grounded substrate. Electrons that collide with atoms in the carrier gas giving rise to the processes that sustain plasma between the target and substrate. Due to the mass difference between electrons and ions, electrons have a higher thermal velocity and diffuse much more quickly. This causes an excess of electrons to impact the sputter target and substrate creating a slightly positive potential in the bulk plasma compared to that of the negatively biased sputter target and grounded substrate. The difference between the slightly positive plasma potential and the negative bias on the sputter target causes positively charged ions to be accelerated towards the sputter target and electrons to be repelled from the sputter target back to the bulk plasma. Accelerated ions inelastically collide with the sputter target, causing a cascade of collisions in the material and ejecting an atom or

molecule from the surface. Ejected atoms travel until they deposit on a surface or are scattered by collisions in the gas phase.

The substrate was 4" away from a 3" ZCAN target (Kamis Incorporated) during the deposition of the ZCAN film. Deposition was carried out at a pressure of 3 mTorr, with 20 SCCM of Ar gas, and 60 W of DC power for 6 minutes to create a film thickness of approximately 50 nm (~8.33 nm per minute). In addition the composition of these films was close to $\text{Zr}_{45}\text{Cu}_{35}\text{Al}_{10}\text{Ni}_{10}$, where the subscripts are the atomic percent of each element in the alloy.

8.2 Vacuum Annealing

Vacuum annealing was performed at Pacific Northwest National Laboratory (PNNL) using an integrated XPS tool with a temperature controlled sample stage. Samples were cleaned using acetone, methanol and de-ionized water, and then dried with nitrogen (AMD process) before the vacuum annealing process. The vacuum annealing process involved loading the sample on the temperature controlled stage, and pumping the vacuum chamber down to 1.3×10^{-6} Pa. XPS analysis of the samples was performed before and after the annealing process. The samples were then heated at a rate of 20 °C per minute from room temperature up to 460 °C. The temperature was held at 460 °C for 15 minutes, and then cooled at 20 °C per minute back to room temperature.

8.3 Thermal Oxidation

Samples were cleaned using the AMD process and dried with nitrogen. An as deposited sample and a vacuum annealed sample were placed together in a clean ceramic boat with the ZCAN surface exposed. The tube furnace was heated to the desired temperature with both ends of the tubes left open to ambient air. Once the furnace was stable at the desired oxidation temperature for 10 minutes, the ceramic boat with the sample was quickly slid into the center of the tube furnace. As soon as the sample was inserted, a stopwatch was started. The ceramic boat was quickly removed when the desired oxidation time was reached and the boat and sample were allowed to cool in room temperature air. Table 8-1 shows the temperatures and durations used for thermal oxidation of the ZCAN TFMG samples in ambient air.

Table 8-1: Annealing temperatures, and times for ZCAN samples. Odd numbered samples indicate the as deposited films while even numbered samples indicate vacuum annealed samples.

Sample Label	Anneal Temperature	Anneal Time
S1, S2	N/A	N/A
S5, S6	300 °C	5 minutes
S7, S8	300 °C	15 minutes
S9, S10	300 °C	30 minutes
S11, S12	300 °C	60 minutes
S15, S16	300 °C	120 minutes
S17, S18	400 °C	60 minutes

8.4 Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy (SIMS) used a Ga^+ ion gun to sputter atoms, molecules and ions from the sample surface. The ejected ions were measured using a mass spectrometer. Since ions were only ejected from the top few monolayers, SIMS gives very detailed information about what elements are present on the surface.

A Millbrook MiniSIMS Alpha tool was used in for this research. The main parts of this tool include a vacuum system, a gallium liquid metal ion source, and a quadrupole mass spectrometer. During analysis a liquid metal ion source of Ga is

used to bombard the surface with Ga^+ ions. A bias of 5-8 keV was applied to the ion gun during sputtering. Ga^+ ions impinging on the surface caused atoms, molecules and ions to be ejected. The ejected ions were analyzed using a quadrupole mass spectrometer.

Prior to analysis the ZCAN TFMG samples, 6mm stubs, and Al foil were cleaned using the AMD process and dried using nitrogen for mounting samples. A small strip of Al foil was placed on the 6 mm sample stub. The center of the Al foil was secured using double sided conductive Cu tape (3M), and the Al foil was folded so a small section of the Cu tape was covered. The sample was secured on the Cu tape with the Al foil providing electrical contact to the back side of the sample. The Al foil was folded again in order to contact the edge of the top side of the ZCAN TFMG sample. The sample was then placed into the stage of the MiniSIMS tool, the loading chamber was closed and the stage moved into the analysis chamber. Analysis was performed once the chamber reached a base pressure around 10^{-8} mBar. The positive surface spectra of each sample was taken over a $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ area over a mass range of 10-120 m/z with a 0.2 m/z step and the electron flood gun at 75 %.

8.5 High Resolution Transmission Electron Microscope

High resolution TEM was performed using an FEI Titan TEM to examine cross-sections of ZCAN TFMG samples. The cross sections were prepared by depositing a protective layer of amorphous carbon followed by a layer of platinum on

the surface of the sample. A focused ion beam was then used to cut out a section of the sample which was welded to a TEM grid. The sample was then thinned to a thickness of 10s of nanometers using the focused ion beam.

High resolution TEM was used to image the cross-sections of ZCAN, then a line scan across the film was done using Chem STEM to help identify the chemical compositions and interfaces in the prepared cross-section. Chem STEM uses EDX with a focused electron beam which is scanned across the sample in the TEM.

8.6 X-ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS) the samples were irradiated with by a high energy x-ray source (E_{photon}), which cause electrons to be ejected from the surface of the sample. The kinetic energy (E_k) of ejected electrons was analyzed, and used to determine the binding energy (E_{binding}) as shown (Equation 8-1).

$$\text{Equation 8-1 } E_{\text{binding}} = E_{\text{photon}} - (E_k + \Phi)$$

Where Φ is the work function of the analyzer, and is used to correct for the difference in the observed and actual kinetic energy due to the energy lost between the sample surface and the detector in the spectrometer. E_{binding} was used to determine the composition and chemical state of the surface. During this process, the emitted electrons originated from the top few nanometers of the sample, since electrons

excited deeper in the material inelastically before reaching the surface. Additionally, the sample can be sputtered with an Ar^+ ion gun during analysis in order to create a detailed depth profile of the material. XPS spectra was taken concentrating on binding energies between 271-298 eV for the C 1s, 523-543 eV for the O 1s, 173-193 eV for the Zr 3d, 925-960 eV for the Cu 2p 110-130 eV for the Al 2s, and 845-880 eV for the Ni 2p photoelectrons.

9 **ZrCuAlNi Oxidation: Results and Discussion**

Deposited films were expected to have an approximate composition of $\text{Zr}_{45}\text{Cu}_{35}\text{Al}_{10}\text{Ni}_{10}$ with a 2.5 atomic percent oxygen impurity, as previously determined [132] by electron probe micro-analysis and XPS. The surface of the deposited ZCAN was a metallic silver color with a 2-3 nm native oxide of ZrO_2 .

To further characterize the films SIMS and XPS were used to examine the ZCAN surface before and after annealing. The annealing was done in the XPS tool with integrated heated stage allowing in-situ analysis of the ZCAN while the SIMS analysis was done ex-situ. The SIMS spectra of both the as deposited (AD) and vacuum annealed (VA) samples (Figure 9-1) showed peaks around 27 m/z for Al, 63 and 65 m/z for Cu and 90, 91, 92 and 94 m/z for Zr. In addition, oxides were observed at 43 m/z for AlO, and 106, 107 and 110 m/z for ZrO. Contamination observed at 23, 39, and 40 m/z were attributed to Na, K and Ca, respectively. Peaks observed at 15, 29, 41, 69 and 70 m/z were attributed to various hydrocarbon contaminates. No peaks corresponding to Ni (58, 60 m/z) were observed at the surface in SIMS analysis.

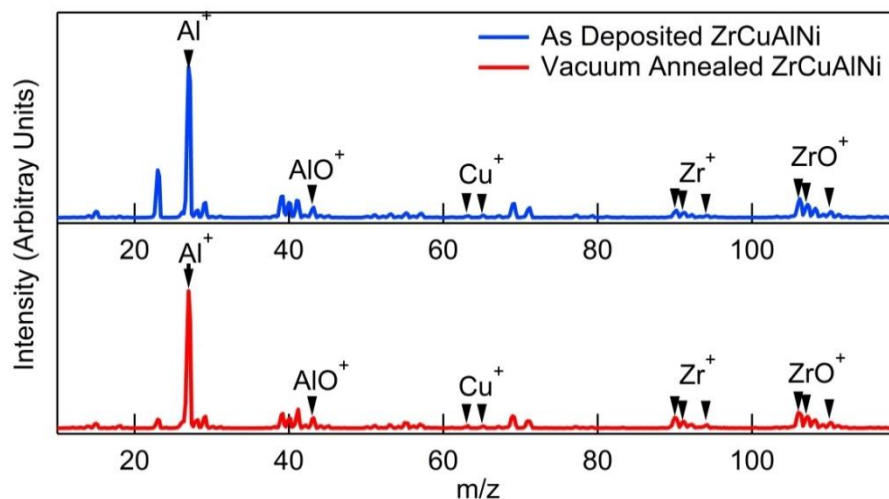


Figure 9-1 Positive SIMS Spectra of the as deposited and vacuum annealed ZCAN samples.

The surface was also examined using XPS, and the Zr 3d, Al 2s, Cu 2p, Ni 2p, O 1s, and C 1s spectra were obtained (Figure 9-2). The C 1s peak observed around 286.3-286.1 eV was expected to be from aliphatic hydrocarbon contamination at the surface [133]. The intensity of this peak was decreased during the annealing pretreatment indicating removal of contamination from the surface. The reduction of in the hydroxyl groups at the surface was further supported by the reduction in the peak around 533.6-533.4 eV in O 1s spectra, which is consistent for hydroxyl groups [133, 134]. This is shifted from the expected binding energies for adsorbed H₂O on Al₂O₃ and ZrO₂ which have been reported at 533.4 eV and 532.7 eV, respectively [135]. A second O1s peak was located between 531.2-531.4 eV, which is due to the metal oxides. A peak at 531.4 eV was observed by Sharma et al. in ZrTiCuNiBe MG

[136], while the O 1s peak for pure ZrO_2 has been reported at 530.4 eV [135] and for pure Al_2O_3 was reported at 532.0 eV [135]. It is suspected that the peak at 531.2-531.3 eV in the O 1s spectra was from a mixed metal oxide containing Zr and Al.

The Zr 3d spectra showed peaks two sets of peaks, were the separation of peaks in each set matched the 2.4 eV expected for the Zr 3d splitting [137]. The more intense set of peaks were located at 183.4 and 185.8 eV and are expected to be the $3d_{5/2}$ and $3d_{3/2}$ peaks, respectively. This is shifted above the 182.5 and 184.9 eV expected for pure ZrO_2 [135], but in good agreement with the 183.4 eV reported for Zr $3d_{5/2}$ peak by Sharma et al. [136]. There is an increase in intensity of these peaks from the AD sample to the VA sample suggesting an increase of Zr in the surface oxide. The second set of Zr 3d peaks were located at 179.1 and 181.5 eV, and were suspected to be the $3d_{5/2}$ and $3d_{3/2}$ peaks for metallic Zr [127, 136]. The shift in the binding energy in both sets of peaks from what was expected of pure ZrO_2 and Zr was likely due to binding effects of the ZCAN/oxide [119].

In the Al 2s spectrum, a peak was observed at 119.8-120.0 eV, which is in good agreement with the 120 eV expected for Al_2O_3 [133, 135]. A second peak around 117 eV may have been obscured, so the presence of metallic Al could not have been ruled out. Additionally, a peak at 122.7 eV was seen for the Cu 3s, which was suspected to be Cu^0 or Cu^{1+} [133] shifted due to the binding effects of the ZCAN/oxide.

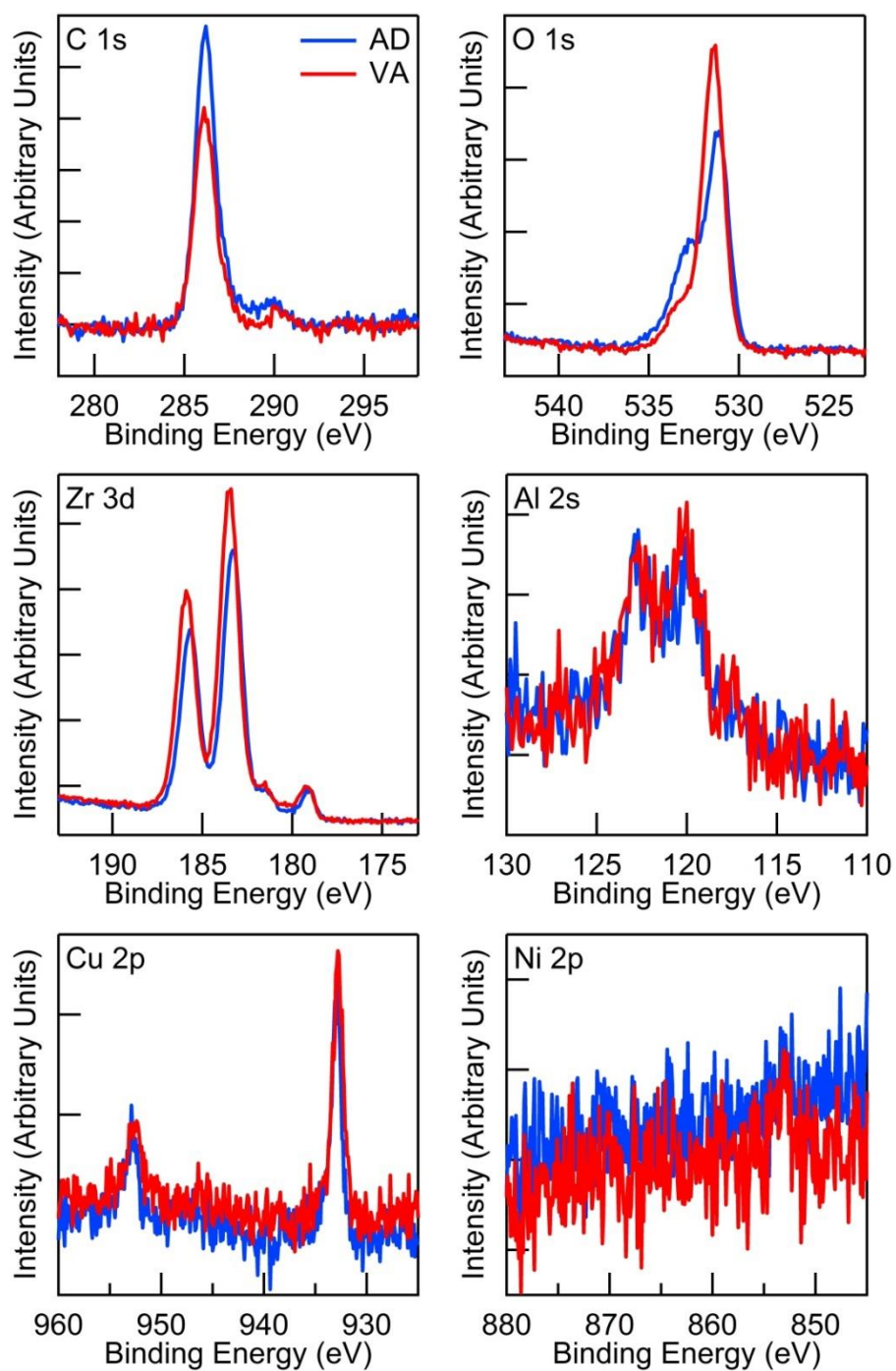


Figure 9-2 XPS spectra of a ZCAN sample taken in-situ before and after vacuum annealing.

Cu 2p spectra was found to the most intense peak around 932.8 eV and a less intense peak around 952.8 eV, which are due to be the $2p_{3/2}$ and $2p_{1/2}$ peaks for metallic Cu. Cu^0 and Cu^+ have been observed to have a $2p_{3/2}$ peak around 932.0-933.1 eV [133]. Sharma et al. [136] reported the $\text{Cu}2p_{3/2}$ peak at 933.2 eV as metallic Cu, Kim et al. [120] reported a peak at 933.4 eV as CuO and Dhawan et al. [119] reported a peaks at 933.6 and 932.5 eV as CuO and Cu^0/Cu^+ , respectively. A minor set of peaks were observed around 934.2 and 955.1 eV, and were suspected to be the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peak for CuO. The CuO peaks are expected to be found around 933.7 and 953.7 eV [133].

The signal for Ni was extremely low and noisy, so no well-defined peaks were observed. This was expected to be due to the lack of Ni at the surface, which was observed in the SIMS analysis of the surface. This is also consistent with results in the literature [119, 120].

XPS depth profiles performed on the AD and VA samples show depletion of oxygen in the ZCAN layer from around 10 atomic percent to 2-3 atomic percent (Figure 9-3). As this occurred, the growth in the surface oxide thickness increased from 1.7 nm to 2.8 nm. This reduction in the oxygen impurity was also observed after five minutes of thermal oxidation in air at 300 °C. Additionally, a change in the interface between the oxide layer and ZCAN layer was observed in high resolution TEM examination of the cross sections of as AD and VA samples after thermal

oxidation at 300 °C for 60 minutes. The VA sample showed a much clearer interface between the oxide and ZCAN films (Figure 9-4).

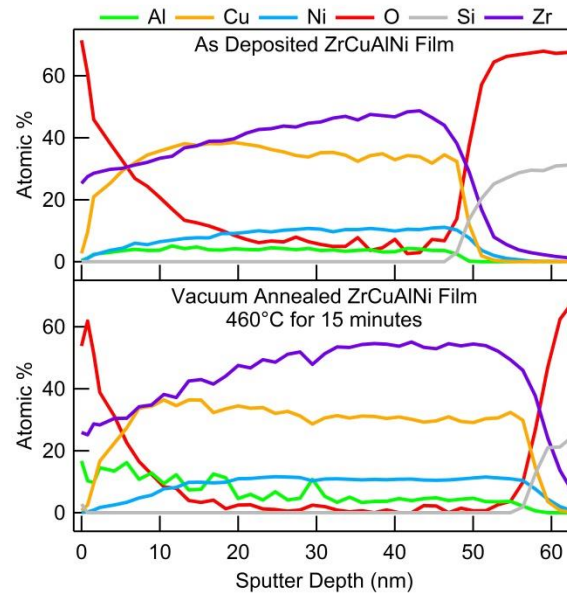


Figure 9-3 XPS depth profiles of the as deposited and vacuum annealed ZCAN samples before thermal oxidation.

High resolution TEM examination of ZCAN cross-sections was performed on AD and VA samples which were thermally oxidized at 300 °C for 60 minutes. The integrated Chem STEM analysis was used to perform a line scan across the film. Comparison of the line scan data with XPS depth profile data was used to calculate the sputter rate of the oxide and ZCAN films during XPS depth profiling. This was done by finding the interface between the oxide and ZCAN, and the interface between the ZCAN and SiO₂. The interface between the oxide and ZCAN was determined by

averaging the depth of the midpoint of the decreasing O and increase Cu relative concentrations, while the interface between the ZCAN and SiO₂ was determined using the midpoint in the increasing Si relative concentration. The HRTEM image, Chem STEM line scan and XPS depth profile are shown (Figure 9-4).

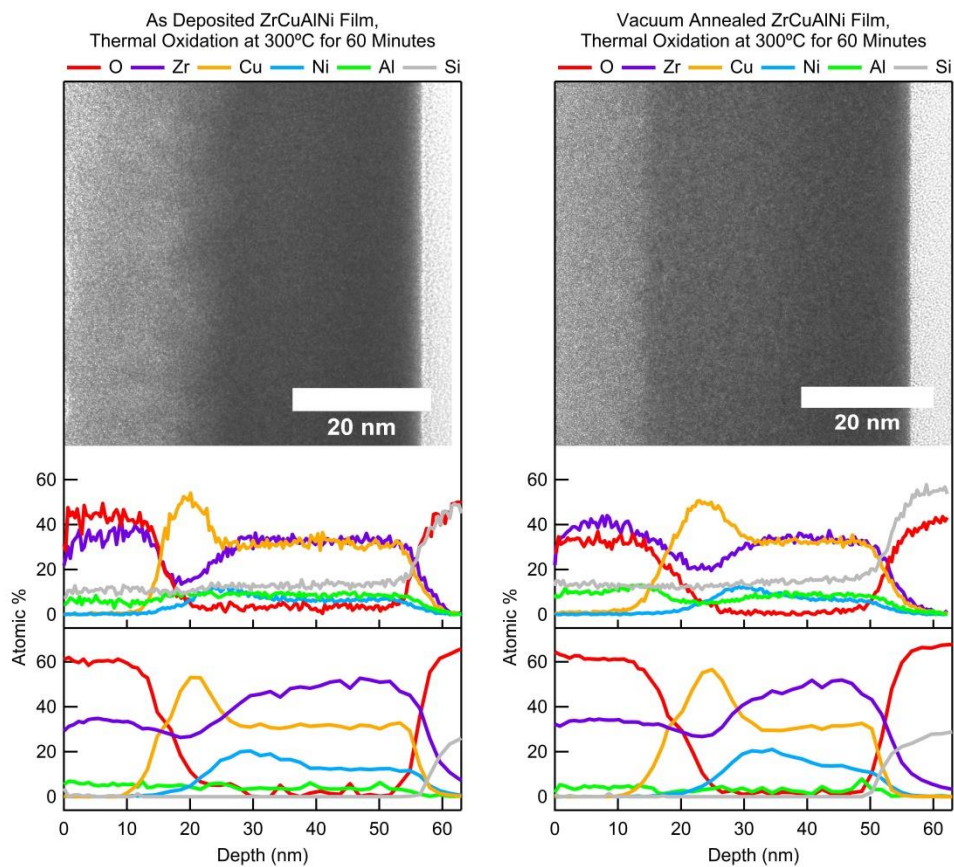


Figure 9-4 High resolution TEM image, Chem STEM line scan and XPS depth profile of the AD and VA ZCAN samples thermally oxidized at 300°C for 60 minutes.

The sputter rate was found to be 0.78 nm per minute for the oxide and 1.58 nm per minute for the ZCAN. The standard deviation in the sputter rate between the two samples were found to be 0.01 nm per minute and 0.03 nm per minute for the ZCAN film which is less than the distance between data points in the Chem STEM, 0.357 nm per data point.

XPS depth profiling was performed ex-situ on the AD and VA samples before thermal oxidation, and after 5, 15, 30, 60 and 120 minutes of thermally oxidized in air at 300 °C (Figure 4.2.E). The oxide was observed to contain Zr and Al, but was free of Cu or Ni. As the oxide grew, a Cu rich, Zr poor region was formed at the interface between the oxide and the ZCAN. Additionally, a Ni rich region was observed between the Cu rich, Zr poor region and the bulk ZCAN film. The Cu rich, Zr poor region reached a plateau at a Cu concentration around 55 atomic percent between 15-30 minutes of thermal oxidation at 300 °C. The Zr concentration in this region was reduced from ~39 to ~27 atomic percent in the first 30 minutes and ~27 to ~22 atomic percent between 30-60 minutes of thermal oxidation at 300 °C.

Several factors are expected to determine the rate of oxidation include of the ZCAN film including: the initial oxygen impurity in the film, the native oxide thickness, the reaction rate at the oxide/ZCAN interface, the solubility and diffusion of oxygen in the oxide, Cu and Ni back diffusion in the ZCAN film, and the diffusion of Zr from the ZCAN to the oxide/ZCAN interface.

It is expected that the initial oxidation is limited by the reaction rate until the O and Zr concentrations are reduced. This results in the creation of a Cu and Ni rich region as the Zr is consumed near the oxide/ZCAN interface. The back diffusion of Cu and Ni becomes rate limiting as the Cu rich, Zr poor and Ni rich regions are formed. This is supported by observed trends in the XPS depth profiles (Figure 9-6). Rapid growth of the oxide layer was observed for 5 minutes of thermal oxidation at 300 °C, corresponding to the reduction of oxygen in the ZCAN film. Additionally, a maximum concentration of Cu was seen near the oxide/ZCAN interface. The Cu concentration increases and the Zr concentration decrease near the oxide/ZCAN interface as the thermal oxidation time is increased until reaching a plateau in the Cu concentration after 15-30 minutes. The Ni concentration directly behind Cu rich, Zr poor region also increased until reaching a plateau in the Ni concentration after 30-60 minutes. Meanwhile, the rate of oxide growth was observed to decrease.

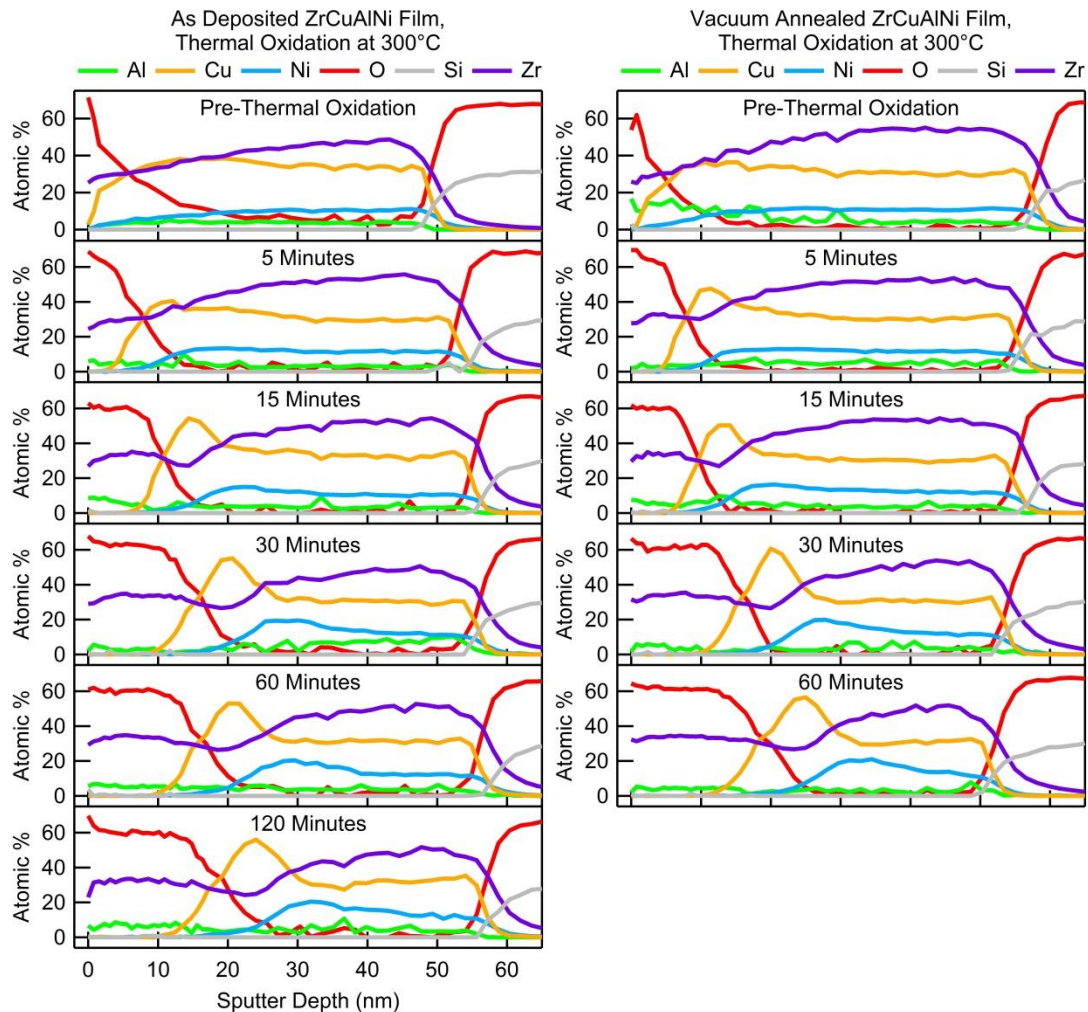


Figure 9-5 XPS depth profiles of the AD and VA samples which were thermally oxidized at 300 °C.

The rate of oxidation is expected to be linear in the initial reaction limited region, then parabolic when diffusion limited. Previous studies have reported one-stage parabolic rates [118] and two-stage rates [121] for oxidization of ZCAN alloys

over several hours. A single-stage parabolic and linear/single-stage parabolic fits were attempted in this study, but showed a large amount of error. Therefore, it is expected that a multiple parabolic rates due to the back diffusion of Cu and Ni, and possibly diffusion of Zr to the oxide/ZCAN interface are required to form an accurate model.

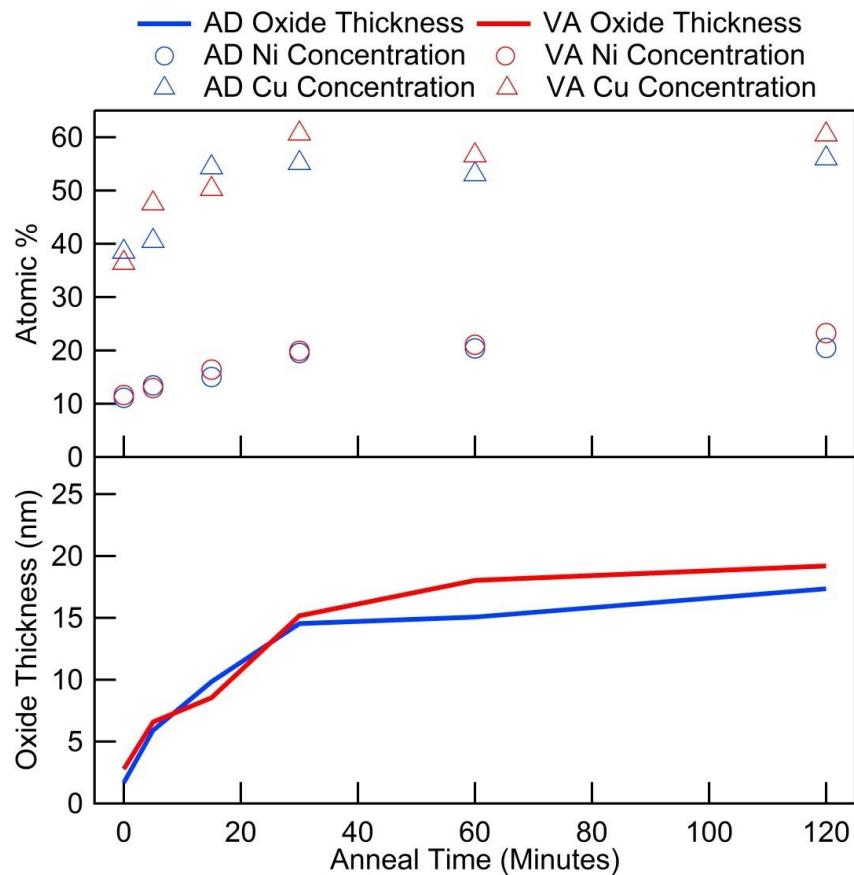


Figure 9-6 Relative concentrations of Cu in the Cu rich, Zr poor region and Ni in the Ni rich region shown above the observed oxide thickness.

XPS profiles were also performed on samples annealed at 400 °C for 60 minutes. The film was shown to be completely oxidized, indicating that the rate of oxidation was greatly increased from 300 °C to 400 °C (Figure 9-7). The increased oxidation rate is expected to occur due to the transition between the amorphous and supercooled liquid phase which has been reported for similar ZCAN materials at around 345-350 °C [121, 138], and this transition causes a large increase in the oxidation rate [118, 138]. One possible explanation for this change in oxidation rate is a switch between Cu and Ni back diffusion limited oxidation to one limited by the diffusion of O to the oxide/ZCAN interface, which Sun et al [123] supported with the by comparing the Arrhenius activation energies observed for the oxidation to that of Ni diffusion in ZCAN and O diffusion in ZrO_2 . The ratio of Zr to Al was also observed to change in the surface oxide, with the sample oxidized at 400 °C showing an increase in the Zr to Al ratio near the surface. Additionally, it was visually observed that samples oxidized above 400 °C change from a silver color before oxidation to a gold color after oxidation.

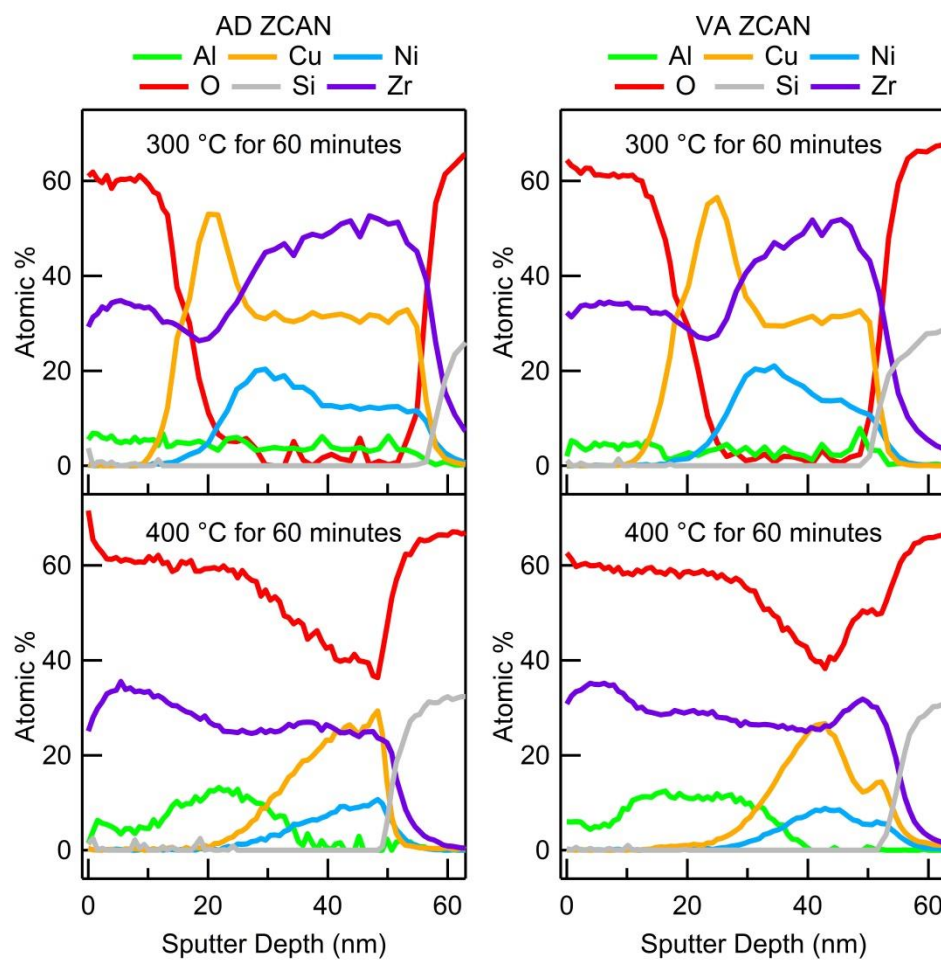


Figure 9-7 XPS depth profiles of ZCAN films oxidized at 300 °C and 400 °C for 1 hour.

10 ZrCuAlNi Oxidation Conclusion

XPS depth profiling was used to observe oxide growth in sputter deposited thin films of $\text{Zr}_{45}\text{Cu}_{35}\text{Al}_{10}\text{Ni}_{10}$. The pre-oxidized samples and samples oxidized for 5, 15, 30, 60 and 120 minutes at 300 °C showed a decrease rate of oxide growth with the creation of Cu rich, Zr poor, and Ni rich regions. The rate of oxidation is expected to be initially rate limited and then diffusion limited. Observation of Cu rich/Zr poor and nickel rich regions support the theory that Cu and Ni back diffusion is rate limiting, which was previously suggested for the oxidation of ZCAN alloys in the amorphous phase.

XPS depth profiles of ZCAN thermally oxidized at 400 °C for 1 hour showed that the ZCAN film was completely oxidized. This indicates a large increase in the rate of oxidation between 300 °C and 400 °C, which may be caused by the transition from amorphous to supercooled liquid. Additionally it was observed that Zr was preferentially oxidized over Al at the surface in the 400 °C.

The oxygen in the as deposited ZCAN films was reduced during vacuum annealing and initial thermal oxidation. High resolution TEM examination of ZCAN cross-sections showed a better defined interface between the oxide and ZCAN. Chem STEM line scans performed on the ZCAN cross-sections were used to calibrate the etch rate during XPS depth profiling to 0.78 nm per minute for the oxide and 1.58 nm per minute for the ZCAN.

Oxide growth and compositional changes in ZCAN TFMG were examined using XPS depth profiling and high resolution TEM examination of cross-sections. Results showed a rapid initial oxidation which decreased as the oxide is formed. It is expected that oxidation is initially limited by the reaction at the oxide/ZCAN surface and then by competing diffusion processes. The trend in oxidation rate appears to follow that of the back diffusion of Cu and Ni supporting Cu and Ni back diffusion as the rate limiting process.

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