

**CHARACTERIZATION OF RARE-EARTH MONOPNICTIDE
NANOPARTICLES GROWN BY INERT GAS CONDENSATION**

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Degree in Chemical and Biomolecular Engineering with Distinction

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ABSTRACT

The incorporation of rare earth monpnictide (RE-V) nanoparticles in III-V semiconductor matrices has created a new class of materials called semiconductor nanocomposites. These materials exhibit enhanced properties for thermoelectric and terahertz radiation applications compared to conventional materials. A new method by which these materials are grown has been proposed using the combined use of inert gas condensation (IGC) and liquid phase epitaxy (LPE) in which nanoparticles are produced by IGC and then grown into a semiconductor film with LPE. This new method allows for scalability, fast growth rates, flexibility, and the ability to grow and characterize the nanoparticles and films separately. However, the development of this growth method is dependent on a fundamental understanding of both IGC and LPE growth methods individually. Furthermore, the characterization of the nanoparticles grown by IGC is necessary before they are inserted into the III-V semiconductor matrix by LPE.

In this work, the investigation of various IGC growth parameters in RE-V nanoparticle growths is investigated including laser fluence, inert gas pressure, collection distance, and source composition. Furthermore, size characterization is performed to understand the average size and size distribution of nanoparticles grown by IGC. Size control of the nanoparticles is investigated. Lastly, preliminary work is performed to develop a Scherrer correlation.

It was found that ErAs nanoparticle growths are benefitted from a laser fluence higher than 0.9 J/cm^2 , He pressure higher than 30 torr, small collection distances ($\sim 1.25 \text{ cm}$), and a source pellet composition of 4:1 Er:As (at %). No significant size change occurred with varying growth parameters. The average ErAs nanoparticle size was $5 \text{ nm} \pm 2 \text{ nm}$. The shape factor (K) for the Scherrer correlation was determined to be 0.124 but more work is required to determine the validity of this value across a range of nanoparticle sizes.

Chapter 1

INTRODUCTION

The incorporation of dissimilar materials in nanostructured materials is an area that has sparked rapid growth in scientific exploration. These materials take advantage of nanoscale interactions producing new and improved properties compared to conventional materials. Specifically, a new class of materials called semiconductor nanocomposites has shown to exhibit properties unobserved in conventional materials in areas of electronics, optics, and thermoelectrics. This class of material is composed of metallic/semimetallic nanoparticles incorporated in a semiconductor matrix.

Semiconductor nanocomposites have been grown, mainly, by a method called Molecular Beam Epitaxy (MBE). While the MBE provides the control and accuracy required to fabricate these materials, it suffers from high cost, slow growth rate, and a lack of flexibility in the source materials. These drawbacks have made MBE unfit for growing nanocomposites at an industrial scale. It is therefore crucial for the future of nanocomposites (i.e. the implementation of these materials in everyday applications), that a new technique to grow these materials is developed as an alternative to MBE.

Developing a new approach to grow semiconductor nanocomposites will improve understanding of this class of material in many ways. A new method of growth will allow for the ability to make materials for practical applications in energy conversion (i.e. thermoelectrics and solar), sensing (i.e. terahertz applications), and various other electrical applications while overcoming the hurdles associated with MBE.

Dr. Joshua M. O. Zide has proposed the combined use of two well established techniques, inert gas condensation (IGC) and liquid phase epitaxy (LPE) as a new method by which semiconductor nanocomposites can be grown. The proposed technique calls for a two-step approach in which nanoparticles are grown by IGC and are then incorporated into a semiconductor matrix grown by LPE.

In order to develop the proposed growth method, a comprehensive understanding of both growth methods is required. Specifically in this work, the study of the IGC growth process will be performed in order to better understand the parameters that should be used and what the results of the growth process are.

The goals of this work are as follows:

Study the growth parameters that are used in the IGC growth process including:

- Laser Fluence
- Inert Gas Pressure
- Collection Distance
- Source Pellet Composition
- Size characterization of the particles grown by IGC
- Development of the Scherrer Correlation.

Successful completion of these goals has impacts on many different levels. The immediate impacts of this work are an understanding of the compositions and size distributions of the IGC growths and the development of a powerful tool by which the size of the nanoparticles can be easily determined. At the scale of the Zide Lab's

work, the importance of control of the IGC process and the characterization of the growths cannot be understated. Only if the properties of the particles grown in IGC are known before they are incorporated into the semiconductor matrix (by LPE) can the properties of the semiconductor nanocomposite be correlated to the properties of the nanoparticles used. At the broadest level, the characterization of RE-V nanoparticles independent of a larger host matrix has never been done before. The results in this work represent the first ever characterization of ErAs nanoparticles grown independently of any semiconductor matrix. Furthermore, this work develops insight into the IGC growth process for RE-V material systems, which have never been grown using IGC before.

Chapter 2

GENERAL BACKGROUND

2.1 RE-V Nanoparticles

Nanoparticles are clusters of atoms that have diameters ranging from about 1 to 100 nanometers. Due to their larger proportion of surface area to bulk, they exhibit distinctly different properties than their bulk counterparts. This is due to a high concentration of surface states in the material.

Rare-earth elements have interesting properties due to their unfilled f shells. These rare earth elements are combined with group V elements to make materials with interesting properties. Almost all RE-V materials have a rock salt structure. Furthermore, the lattice parameters of these RE-V materials are close to those of III-V materials used in common semiconductor technology. This agreement of lattice parameters facilitates a good epitaxial relationship between RE-V and III-V materials.

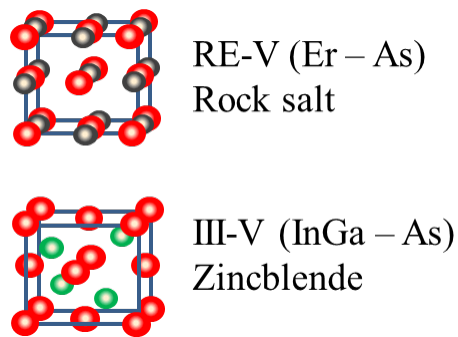


Figure 1: ErAs rock salt structure (top), InGaAs zincblende lattice (bottom). Arsenic atoms shown in red, cation atoms (Er, In, Ga) shown in green or black. [1]

Additionally, the continuation of the anion sub lattice in the structure shown in Figure 1 stabilizes an epitaxial interface as well.

RE-V nanoparticles have been incorporated in III-V semiconductors to make RE-V:III-V nanocomposites. RE-V nanoparticles such as ErAs and TbAs within III-V matrices such as GaAs and InGaAs have been shown to improve electrical, optical, and thermal properties compared to conventional materials [1]. One example of this is in thermoelectrics. These materials are able to convert a temperature gradient to a voltage difference. An important quality for an effective material is high electrical conductivity but low thermal conductivity. More specifically, the material needs effective phonon scattering while having sufficient carrier mobility. Studies of RE-V:III-V nanocomposites have shown drastic improvement in these properties compared to conventional materials. A diagram of a thermoelectric material is provided below in Figure 2.

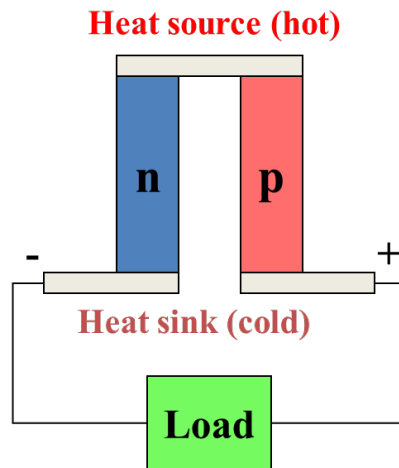


Figure 2: Diagram of a thermoelectric. N and p-type semiconductors with a temperature gradient across them are able to produce a voltage. [3]

Other applications of these classes of materials are multijunction solar cells, high-speed transistors, lasers, photomixers for terahertz sources and photoconductive switches for terahertz receivers.

2.1.1 Erbium Arsenide

Erbium arsenide nanoparticles epitaxially embedded in GaAs semiconductors has been shown to pin the Fermi level and act as a Schottky barrier [2]. This results in a material that is extremely resistive, has short carrier lifetimes, and has lots of recombination sites. Materials with these properties can be used to make materials for photometers and photoconductive switches for terahertz generation and detection and thermoelectrics.

ErAs nanoparticles embedded in $In_xGa_yAl_{1-x-y}As$ have been shown to exhibit high electrical conductivity and low thermal conductivity.

2.2 Alternative RE-V Nanoparticle Growth Methods

Nanocomposite materials have been grown in the past by simultaneously growing the host matrix and nanoparticles. The main technique used to do this has been Molecular Beam Epitaxy (MBE). A schematic showing the inner workings of an MBE growth process is shown below in Figure 3.

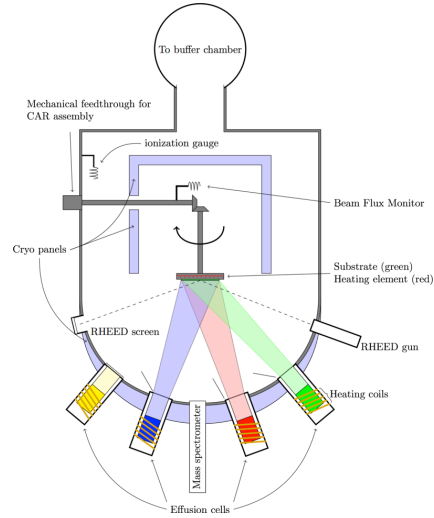


Figure 3: Diagram of a MBE system. [4]

In a growth, beams of atoms are shot at a wafer and assemble into atomic layers. This is done under ultra-high vacuum to ensure that the mean free path of the atoms in the beams is much longer than the distance between the source and the wafer. MBE has proven to be a very precise tool by which highly complex and finely tuned materials with exceptionally low defect densities can be made. In this work, RE-V nanoparticles are made using a technique called Inert Gas Condensation.

2.3 Inert Gas Condensation

2.3.1 Process Mechanics and Inputs

Inert gas condensation was developed in the 1930s [2]. This technique has been well established both in industrial and laboratory processes. The process by which particles are grown in IGC is as follows: 1) a source material is evaporated either by laser ablation or resistive heating, 2) the evaporated material is released into an inert environment usually consisting of Helium gas, 3) the evaporated atoms

condense in the inert environment forming particles which are then collected. The basic setup of the IGC chamber is illustrated in the Figure 4 below.

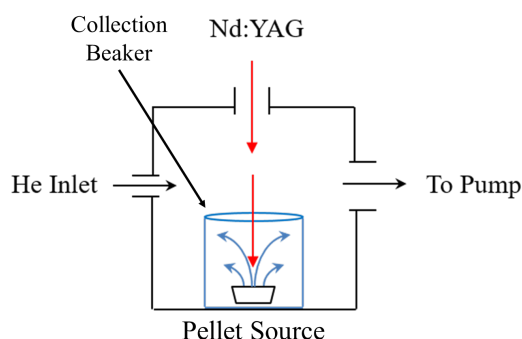


Figure 4: IGC chamber setup. Adapted from [3]

The inert gas has many important functions in the growth process. It is present to cool the evaporated material, prevents large-scale agglomeration by cooling the particles quickly and prevents any undesired reactions or oxidation from occurring.

Particle formation occurs in steps that are illustrated in Figure 5 below.

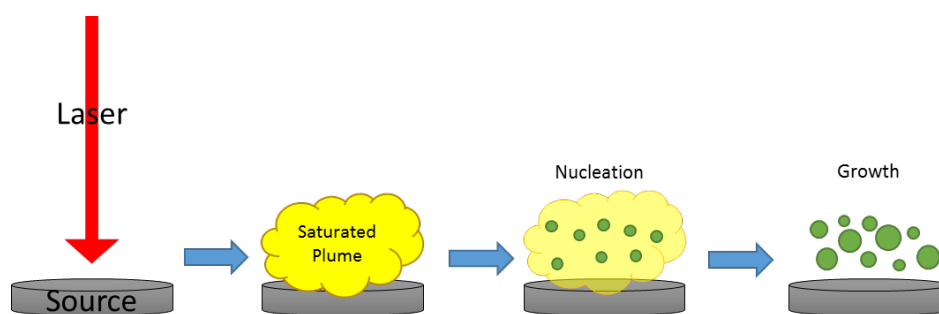


Figure 5: Diagram of the first 4 steps of nanoparticle growth: 1) laser ablation, 2) formation of saturated plume, 3) nucleation, 4) growth. Only one laser pulse is shown for clarity of other growth steps.

Shown above in Figure 5 are the major steps that occur in IGC nanoparticle growth. First, the evaporation/ablation creates loose atoms in the inert environment, forming a saturated plume. These atoms then nucleate forming the centers on which growth will occur. Following nucleation, loose atoms in the plume are consumed as they grow on nucleated particles. As opposed to what is shown in Figure 5, in actual IGC growth, source material is constantly ablated.

There are many knobs by which the quality, quantity, size, and morphology of the particle growth can be controlled.

The first of this is evaporation rate (i.e. laser fluence or resistive heating rate). By increasing the rate of heating or laser fluence, more material is released into the inert atmosphere allowing for larger particles and more of them to be grown. Additionally, some materials have a larger fluence threshold than others for ablation. These materials require more energy to be released from their sources. In order to ablate all species in a source, a laser fluence high enough to ablate the material with the highest ablation threshold is required. It has been shown in literature that an increase in evaporation correlates to an increase in particle size [2]

Collection distance is another control parameter that can be used to influence the results of the growth. A larger collection distance gives particles a longer time to interact. With longer times to interact, the particles are allowed to grow producing larger particles. However, producing larger particles must be done while balancing the agglomeration of those particles.

Inert gas type and pressure can be used to control the cooling and confinement of the vaporized gas of atoms. Inert gases with higher atomic numbers have been shown to facilitate the growth of larger particles more than smaller atomic number

inert gases due to more efficient confinement of the ablated vapor [2]. It follows that an increase in pressure also benefits the confinement of particles to the growth region also leading to larger particles. This has been correlated and studied in the literature [2].

Source composition is another crucial input to the IGC process. Source composition directly affects the composition of atoms that exist in the vapor. An optimal ratio of source material can be determined for particular cases.

2.3.2 Advantages of IGC

Inert gas condensation has many advantages over other particle production processes. First and foremost, IGC growths are relatively simple in terms of the operation, equipment used, and the general growth/collection process. Additionally, easy control over the input parameters associated with the process allows for fine-tuned control over the results of the process as well as ease of systematic studies performed in laboratory experiments. IGC can also be used to form core-shell nanoparticles.

In the scope of our overarching goals, growing RE-V nanoparticles separate from the host matrix growth cannot be done with contemporary methods. This will allow for independent control over nanoparticles and semiconductor growths. IGC is also readily scalable, allowing for mass production of particles required for an industrial scale process.

2.3.3 Disadvantages of IGC

Despite the many advantages of IGC growth, the technique also suffers from some distinct disadvantages. Compared to MBE growths, IGC is not as precise and

suffers from impurities being present in the nanoparticle growths (i.e. unreacted material and oxidized material). For materials being investigated in this paper, oxidation is a constant threat and is difficult to prevent, particularly when collecting. Finally, the growth conditions for the materials being studied are unknown and prove to be a critical area of study before progress can be made on the nanocomposite front.

2.3.4 Our System

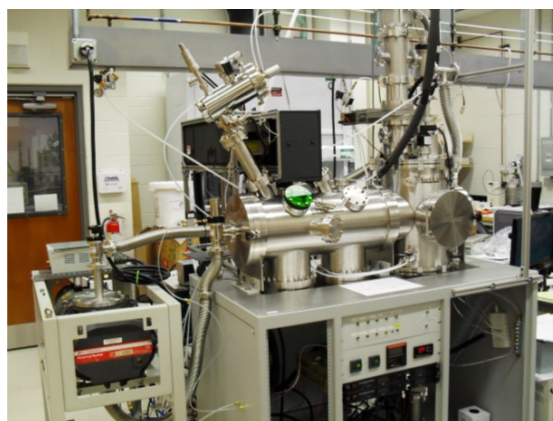


Figure 6: Picture of the IGC chamber used to produce the nanoparticles characterized in this work.

Our IGC system is fitted with a 1064 nm Nd:YAG laser used for laser ablation of the source material. It is fitted with a Helium gas inlet and Nitrogen gas inlet used for purging the system. A turbo pump is employed to enable the chamber to reach low pressures before being filled with Helium. A glove box is attached to the chamber hatch to enable minimal exposure of the particles to atmosphere when collecting. Source material is placed in a glass beaker and is then ablated. Material is collected off of the beaker wall.

The growth method used to produce nanoparticles is as follows:

1. Source material in the form of pressed pellets containing pure Er and pure As powders in a predetermined ratio are centered in the beaker.
2. The chamber is pumped down to 10^{-5} - 10^{-6} torr and then filled with He to the desired pressure.
3. Source material is ablated with the laser to begin growth.
4. After growth is completed, chamber is opened with an inert environment glove box, and sample is collected off of the walls of the beaker.

All growths for this work are performed by Doctoral Candidate Matthew Lewis.

Chapter 3

X-RAY DIFFRACTOMETRY

3.1 Background and Motivation

3.1.1 Motivation

X-Ray Diffractometry (XRD) is the most accurate and useful tool to study the effects of different growth parameters on the results of the IGC growth. XRD, in combination with Rietveld analysis, can be used to quickly, easily, and quantitatively measure the composition of the IGC growths. Specifically, XRD will be used to study the effect of laser fluence, pressure, collection distance, and pellet composition on ErAs growth. These four parameters represent the most easily tunable and controllable knobs by which the growers of ErAs nanoparticles can control the growths. Only after a comprehensive study of these parameters and their effects on the growth process is performed can consistent and well-characterized growths be performed.

3.1.2 General Overview

X-ray diffractometry is a powerful and easy to use technique by which the crystal structure of a material can be probed. In short, x-rays are produced in an x-ray source which are then directed at a sample. The interaction of the x-rays with the sample can result in a diffraction of the beam into a detector. This general process is illustrated below in Figure 7.

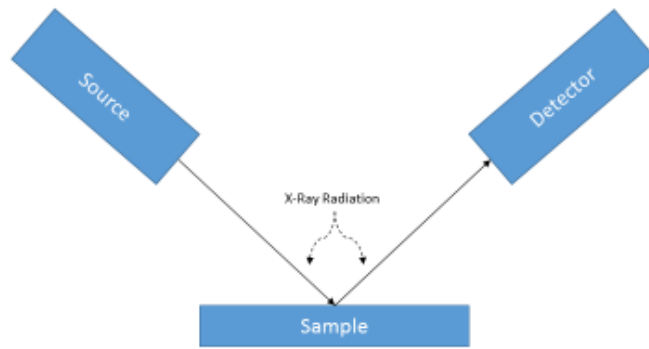


Figure 7: General Process of XRD. X-ray radiation is emitted from a source, which interacts with the sample. At certain Bragg angles, radiation will be diffracted strongly and collected by the detector

X-rays are commonly produced in the form of Copper K-alpha radiation: electrons in the K shell of copper atoms are excited and released, when a higher shell electron in the L shell moves to the K shell, it loses energy in the form of monochromatic x-ray radiation with a wavelength of 0.154056 nm. When the x-rays interact with the sample, a coherent diffraction signal will form only when a large number of atomic planes scatter the x-rays in phase. This occurs at specific crystallographic orientations where the wavelength of the x-ray matches in a favorable way with the lattice spacing of the crystal allowing for constructive interference between the rays. The set of cases for coherent diffraction is described by Bragg's law. It is this dependence on crystal spacing and orientation that allows XRD to be used to identify different crystals and their structures.

3.1.3 Bragg's Law

3.1.3.1 Derivation of Bragg's Law

Bragg's law describes the particular case in which constructive diffraction will occur in the case of incident radiation interacting with a crystal structure. Assuming each plane of atoms partially reflects the incident x-ray wave [5], a diagram can be made to mathematically describe this relationship:

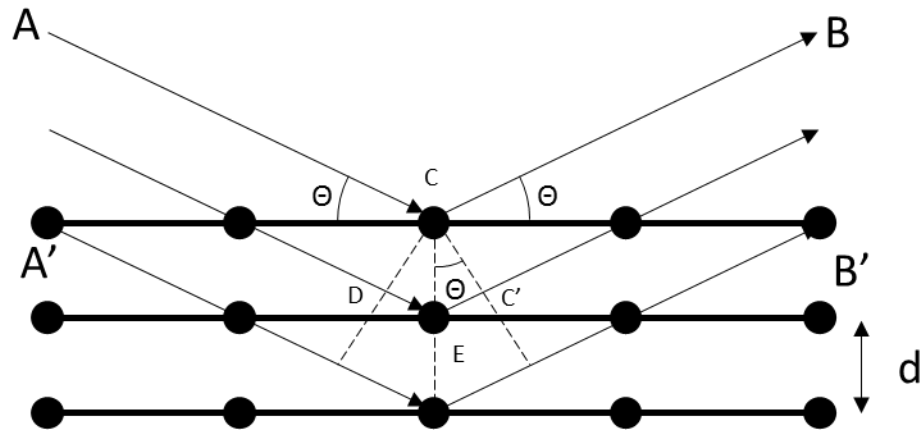


Figure 8: A diagram of X-ray radiation diffracting at the Bragg angle θ . Points D and C' denote points on the x-ray radiation path that intersect the dotted line. Adapted from [5].

It follows that the condition for existence of a coherent scattered wave occurs only when the path lengths between AB and A'B' differ by exactly an integral number n of the incident radiation wavelength [5]. Using this relationship, a mathematical requirement for diffraction can be derived [5]:

$$\delta = n\lambda$$

$$\delta = DE + EC' = 2EC'$$

$$\delta = 2CE\sin(\theta)$$

$CE = d'$, where d' is the interplanar spacing

$$\delta = 2d' \sin(\theta)$$

$$n\lambda = 2d' \sin(\theta)$$

$$\lambda = 2d\sin(\theta)$$

The equation showed above in bold is Bragg's Law.

3.1.3.2 Assumptions of Bragg's Law

Bragg's law is derived using two major assumptions [5]. The first of these conditions is the fact that the crystal quality is perfect. Second, it is assumed that the incident beam is composed of perfectly parallel and monochromatic radiation. According to Bragg's law, an ideal XRD peak would have infinitesimally small width, and only reflect at exactly at the Bragg angle. However, these conditions are never truly met in practice. As a consequence, the results of XRD experiments deviate from the predictions of Bragg's law in particular ways [5]. Signal peaks are subject to broadening due to non-idealities. The source of this broadening can be attributed to three distinct sources: 1) instrumental effects, 2) crystallite size, 3) lattice strain [5]. In addition, deviation from Bragg's law predictions are due to the fact that incident x-rays are never truly monochromatic or perfectly parallel. The analysis of peak broadening will be discussed in more detail in the Scherrer Analysis chapter of this work.

3.1.4 Single Crystal vs. Polycrystalline Samples

When scanning a sample the orientation of the crystal with respect to the incident x-rays is of critical importance. For these reasons, there are fundamental differences between the method, advantages, and disadvantages associated with single crystal diffraction and polycrystalline samples.

In single crystal diffraction, one must position the crystal in a specific orientation in order to acquire a meaningful result. This orientation can be difficult to find and requires a lot of work in order to determine. Additionally, only a small part of the diffraction pattern will be acquired with one orientation. To acquire the entire diffraction pattern, multiple orientations must be scanned and analyzed independently. However, when a pattern is acquired for a single crystal sample, no information is lost as would be in polycrystalline samples.

Polycrystalline samples analyzed with XRD, or powder diffraction has a big advantage of being quick and easy. In powder diffraction, the sample consists of randomly oriented grains. By this method, no orientation or multiple scans are required. With one scan, powder diffraction reveals the entire diffraction pattern. However, there exist limitations of powder diffraction [6]: 1) overlapping diffraction peaks occur due to symmetry, 2) overlapping of peaks caused by experimental resolution, 3) difficulty of refinement of the background of the scan, 4) possible preferred orientation existing in the sample. These limitations can lead to a loss of information in the powder diffraction scan. A method by which some of this information can be salvaged is discussed below in the section titled Rietveld Refinement.

3.1.5 Indexing a XRD Pattern

By indexing an XRD pattern, Miller indices (used to label and identify different crystallographic planes) are assigned to each peak in the diffraction pattern. By this method, the crystallographic structure of the sample can be determined which allows for identification and characterization of the sample. Correct indexing is done only when all the peaks in the diffraction pattern are accounted for and no peaks expected are missing [5]. To index a plane, an equation for the interplanar spacing and lattice parameter is used in combination with Bragg's law:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

where d is the interplanar spacing of the crystal, a is the lattice parameter, and hkl are the miller indices. The equation given above is used only for cubic crystal structures. For other crystal structures, slightly different equations are used. Using these equations, a ratio of $\sin^2 \theta$ and hkl s can be assigned to each peak. The hkl 's are determined to be the allowed diffraction conditions for a particular crystal structure (i.e. simple cubic, BCC, FCC).

3.1.6 Rietveld Refinement

Rietveld refinement is a technique by which extra information can be extracted from an XRD scan. Information is lost in polycrystalline samples as a result of random orientation and the overlap of independent diffraction peaks [7]. Rietveld refinement is a method that uses the total integrated intensities of the separate groups of overlapping peaks in the least square refinement of structures [7].

The Rietveld method is performed by modeling the crystal structures of material and then simulating the diffraction results that those materials would yield [6]. To this end, Rietveld refinement can only be performed if the crystal structure of

the components in a sample are known. In addition to the crystal structure models, one needs initial values for all variable parameters in those models, an XRD scan, 2-Theta limits, and data regarding the wavelength of the radiation used in the experiment [6].

After crystal structures are modeled, the parameters that determine the shape and scale of the integrated diffraction pattern must be refined. These parameters include lattice parameters (a, b, c, alpha, beta, gamma), atomic positions (x, y, z), atomic site occupancies, atomic thermal vibration parameters (isotropic or anisotropic), preferred orientation, background functions, 2Theta-Zero correction, overall scale factor and an overall isotropic thermal B.

3.1.6.1 Criterion for a Successful Refinement

Refinement is considered complete after a successful fit has been performed. There are many criteria and mathematical tools that can be used to determine the accuracy of the fit. One of these tools is a difference plot that takes the difference in count between the observed XRD spectrum and the calculated Rietveld spectrum. If no max deviation occurs at any part of the refinement, then one can apply a X^2 check to determine the “goodness” of the fit. X^2 is a quantified error measurement that takes the ratio between the best fit that could possibly be achieved and the actual fit [6]. These fits are quantified with R values. The equation for X^2 is denoted below.

$$X^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2$$

where R_{wp} is the weighted profile and R_{exp} is the best R_{wp} that can be achieved. It follows that a X^2 value has a perfect fit at a quantity of one. Therefore, the goal of refinement should be to bring X^2 as close to unity as possible.

It should be mentioned that these difference plots and the X^2 value, while useful tools in determining the validity of one's fit, are subject to some error themselves. One can achieve a very good fit spectrum by allowing all parameters to refine beyond logical bounds, yielding a spectrum with a shape very close to the experimental spectrum but without good quantitative validity. Therefore, one should not use the tools mentioned above as the final determining factor of the quality of a fit.

3.2 Methodology

3.2.1 Equipment Used

All XRD scans for this work were performed using a Bruker D8 XRD, shown in Figure 9 below.



Figure 9: Image of the Bruker D8 X-ray Diffractometer. This machine was used to gather all the XRD data used in this work. [8]

This XRD uses monochromatic Cu K-alpha x-rays. No sollar slit or other filters were used in order to achieve the highest count rate possible. A LYNXEYE detector was used. Scan parameters were as follows: step time — 0.2 s, 2Theta start — 20 degrees, 2Theta end — 80 degrees, step size — 0.05 degrees.

3.2.2 Sample Preparation

The sample powder is collected off the side of the beaker in a glove box. Scotch tape is used to remove the sample from the side of the beaker and is then placed onto a microscope slide. The scotch tape plays a dual role as it helps in collection and prevents oxidation. It should be mentioned that experiments were done to see if Kapton tape (a commonly used material to improve S-N ratio in diffraction experiments) would improve our signal. It was found that there was no improvement versus normal scotch tape. The samples are then placed into the XRD and scanned. It should be noted that all sample collection was performed by Doctoral Candidate Matthew Lewis.

3.2.3 XRD Pattern Matching

Scans are indexed and crystals in the sample are identified using the software provided on the XRD computer. The XRD computer database is stocked with theoretical and experimentally determined XRD peaks of many different crystals. Possible elements included in the matching process are erbium, arsenic, and oxygen. Suitable materials that fit well within the XRD pattern are then selected. After the composition of the sample is known, Rietveld refinement is performed on the pattern to achieve additional compositional data.

3.2.4 Rietveld Refinement

Full scans are imported into Profex software. Knowing the present species in the sample from the XRD matching done with the computer software, structure files for each are imported for each species. Structure files include the following information: chemical formula, space group, Hermann Mauguin Space Group lattice type, lattice parameter, values for shape texture/orientation, Lorentzian size broadening, Gaussian size broadening, microstrain, and element positions in crystal basis. After an initial refinement is run, values for B1 and k1 (Lorentzian and Gaussian size broadening, respectively) are adjusted to achieve a correct peak form and lattice parameters are adjusted to achieve the right 2Theta position of the peak for each species. Refinement is performed until X^2 is minimized and the fit is deemed acceptable. The compositional information reported by Profex is in weight percent. Weight percent is then converted into atomic fraction to allow for more meaningful analysis.

3.3 Results

3.3.1 Fluence Growth Series

XRD was performed on 6 samples grown with varying laser fluence ranging from 0.66 J/cm^2 to 1.33 J/cm^2 . The other parameters used in the growth process are as follows: 10 torr He, 1.25 cm collection distance, 1:1 (Er:As at %) source pellet. Composition of each sample was calculated using Rietveld refinement of the XRD spectra. All erbium containing components (i.e. elemental erbium and its oxides) are reported collectively as atomic fraction Er. All arsenic containing components (i.e. elemental arsenic and its oxides) are reported as atomic fraction As. ErAs

composition is reported as ErAs atomic fraction. The results of the laser fluence growth series is provided below in Figure 10:

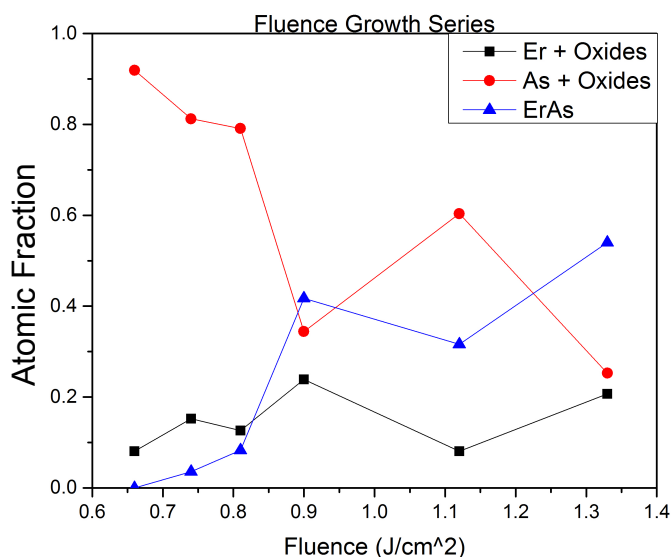


Figure 10: Results from Rietveld refinement of XRD scans taken of fluence growth series samples. All values are reported in atomic fraction. Erbium and its oxides are reported together. Arsenic and its oxides are reported together.

3.3.2 Pressure Growth Series

XRD was performed on 7 samples grown with varying He pressure ranging from 6 torr to 61 torr. The other parameters used in the growth process are as follows: 1.33 J/cm² laser fluence, 1.25 cm collection distance, 1:1 (Er:As at %) source pellet. Composition of each sample was calculated using Rietveld refinement of the XRD spectra. All erbium containing components (i.e. elemental erbium and its oxides) are reported collectively as atomic fraction Er. All arsenic containing components (i.e.

elemental arsenic and its oxides) are reported as atomic fraction As. ErAs composition is reported as ErAs atomic fraction. The results of the pressure growth series is provided below in Figure 11:

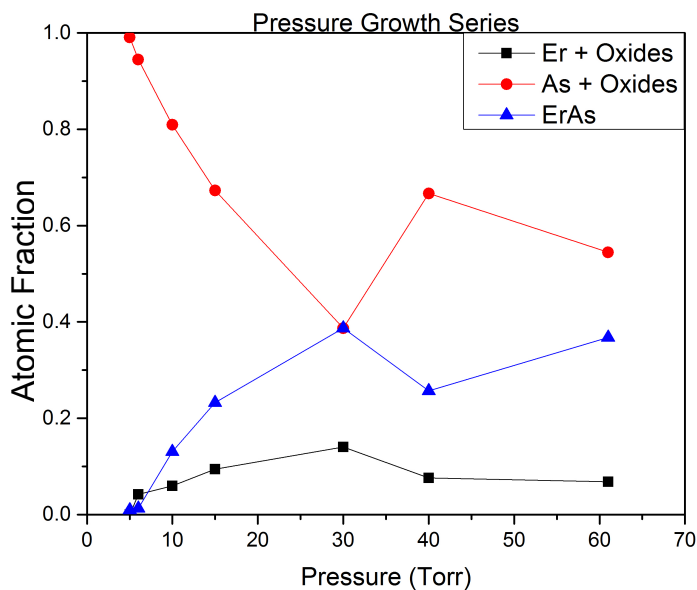


Figure 11: Results from the Rietveld refinement of XRD scans taken of the pressure growth series. All values are reported in atomic fraction. Erbium and its oxides are reported together. Arsenic and its oxides are reported together.

3.3.3 Collection Distance Growth Series

XRD was performed on 5 samples grown with varying collection distances ranging from 1.25 cm to 4 cm. The other parameters used in the growth process are as follows: 10 torr He, 1.33 J/cm² laser fluence, 1:1 (Er:As at %) source pellet. Collection distance was measured as the radius of the beakers in which source pellets were placed and ablated in. Composition of each sample was calculated using

Rietveld refinement of the XRD spectra. All erbium containing components (i.e. elemental erbium and its oxides) are reported collectively as atomic fraction Er. All arsenic containing components (i.e. elemental arsenic and its oxides) are reported as atomic fraction As. ErAs composition is reported as ErAs atomic fraction. The results of the collection distance growth series is provided below in Figure 12:

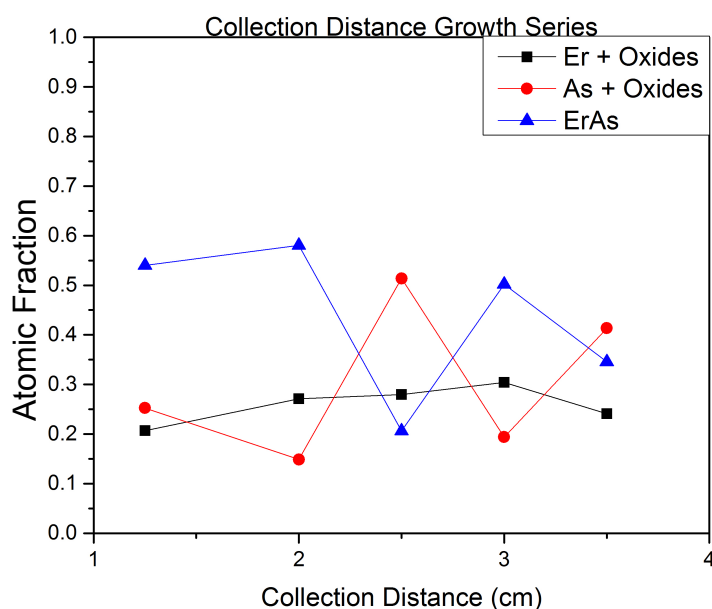


Figure 12: Results from the Rietveld refinement of XRD scans taken of the collection distance growth series. All values are reported in atomic fraction. Erbium and its oxides are reported together. Arsenic and its oxides are reported together.

3.3.4 Pellet Composition Growth Series

XRD was performed on 3 samples grown with varying source pellet compositions ranging from 1:1 (Er:As atomic %) to 4:1 (Er:As atomic %). The other

parameters used in the growth process are as follows: 10 torr He, 1.33 J/cm² laser fluence, 1.25 cm collection distance. Composition of each sample was calculated using Rietveld refinement of the XRD spectra. All erbium containing components (i.e. elemental erbium and its oxides) are reported collectively as atomic fraction Er. All arsenic containing components (i.e. elemental arsenic and its oxides) are reported as atomic fraction As. ErAs composition is reported as ErAs atomic fraction. The results of the pellet composition growth series is provided below in Figure 13:

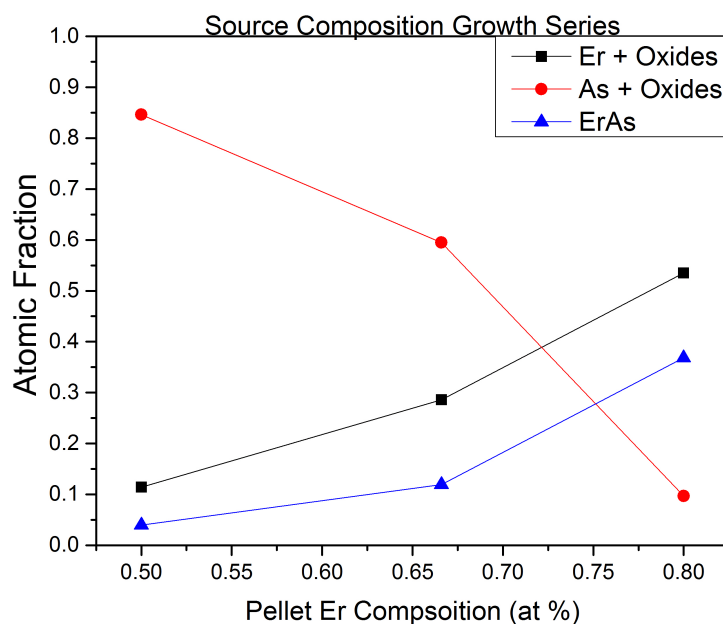


Figure 13: Results from the Rietveld refinement of XRD scans taken of the source composition growth series. All values are reported in atomic fraction. Erbium and its oxides are reported together. Arsenic and its oxides are reported together.

3.4 Discussion

3.4.1 Laser Fluence Growth Series

The trends in the results of the laser fluence growth series are expressive of theoretical expectations of the growth. As has a lower ablation threshold than Er and is therefore found in very high compositions in low fluence growths. Due to its lower ablation threshold, an arsenic overpressure is always expected in the ablated plume above the source pellet. While a small amount of erbium is expected to be ablated as well, little to none of it interacts with the ablated arsenic to form ErAs. As fluence increases, the Er composition in the growth remains fairly constant. At 0.9 J/cm^2 , a large increase in ErAs composition of the growth is observed. At this laser fluence, there is enough energy and ablated Er and As in the plume to interact and form ErAs at a significant scale. The general decrease in As as fluence increases is caused by the consumption of ablated As as more Er is ablated. The interaction of Er and As in the plume can be considered a chemical reaction in which As is in excess and Er is the limiting reactant. The formation of ErAs is dependent most strongly on the presence of Er (granted there is also enough energy) in the plume.

3.4.2 Pressure Growth Series

The results of the pressure growth series shows great adherence to trends described by literature and theory. At low pressures, there is little confinement of the ablated vapor plume to the growth region. Additionally, the low pressure of He decreases its efficacy as a coolant of the ablated materials to help initiate nucleation. As pressure is increased, the composition of ErAs in the growth increases with diminishing returns. At about 30 torr, a tapering of the beneficial effects of increasing

He pressure is observed. A possible explanation of this result is that the rate of nucleation and agglomeration of ErAs nanoparticles compared to the rate of Er and As ablation is no longer increased as pressure increases. The effect of tapering is also observed in the results of As composition as pressure increases. At low pressures, increasing He pressure drastically increases the amount of As consumed by ablated Er. However, as pressure increases, the rate of nucleation and agglomeration roughly matches the rate of As ablation leading to an asymptotic approach of As to a value of roughly 50 at %. Similar to the results of laser fluence, Er composition in the sample is roughly constant supporting the idea that it is the limiting reagent in the ablated plume

3.4.3 Collection Distance Growth Series

The results of the collection distance growth series does not agree completely with expectations of the growth trends associated with collection distance. Collection distance was increased by ablating the source pellets in beakers of varying size ranging from 10 mL, 50 mL, 100 mL, 150 mL, and 250 mL corresponding to 1.25 cm, 2 cm, 2.5 cm, 3 cm, and 4 cm collection distances respectively. At small collection distances, tight confinement of the ablated vapor plume was expected to increase the interaction between ablated Er and As thus producing more ErAs in the growth. As collection distance increases, less interaction between the ablated species was expected due to a larger confinement volume resulting in lower ErAs compositions in the growth. As in previous results, a high ErAs concentration in the growth would be associated with a low As concentration and a low ErAs concentration would be associated with a high As concentration.

The results of this growth series follow the expected trend barring the results from the 2.5 cm collection distance growth. As collection distance increases, there is a slight decrease in ErAs concentration in the growth with a slight increase in As. However, the 2.5 cm collection distance growth shows the lowest ErAs concentration of all the growths. As of now, no explanation as to the reason for this drop in ErAs composition can be provided. Similar to other results, Er concentration in the growth remains constant throughout the entire growth series.

3.4.4 Pellet Composition

The results of the pellet composition growth series confirmed the hypothesis that increasing the Er concentration in the source pellet would benefit the result of the growth. At equivalent atomic concentrations of Er and As, the growth of ErAs is hindered by the small amount of Er present in the ablated plume compared to As. This is due to the higher ablation threshold of Erbium compared to Arsenic. It is observed that having more Er available mitigates the effect of erbium being harder to ablate. At the ratio of 4:1 (Er:As), there is a large increase of ErAs and Er in the growth while the As composition is very low. While the lower As concentration is, in part, an effect of having less As available to ablate in the material, at the 4:1 ratio a shift occurs from Er being the limiting reactant in the plume to As, shown by the smaller concentration of As in the growth than Er. While no experiments were done to test larger Er concentrations in the pellet, it can be expected that the beneficial effect of having more Er in the source pellet will taper off and eventually hurt the growth of ErAs.

3.5 Conclusion

The results of the growth series for laser fluence, He pressure, collection distance, and pellet composition reveal which growth parameters are beneficial for ErAs growths in IGC. A laser fluence of at least 0.9 J/cm^2 should be used in order to ensure Er ablation with enough energy to form ErAs. A He pressure of at least 30 torr should be used to ensure confinement of the vapor plume and enhanced interactions between ablated species. While no clear trend with collection distance was observed, a small collection distance of 1.25 cm has been used consistently in IGC growths for our system with success and should therefore be used for future ErAs growths until a clearer trend is observed. Finally, a pellet composition with higher Er compositions benefits the formation of ErAs. However, without further testing, a pellet source of compositions higher than 4:1 (Er:As) should not be used.

Chapter 4

ELECTRON MICROSCOPY

4.1 Background and Motivation

4.1.1 Motivation

Transmission electron microscopy (TEM) is the most effective method by which images of the particles grown by IGC could be obtained and analyzed. In order to accurately measure the sizes of the nanoparticles, it was crucial to be able to clearly see the grain boundaries to distinguish between agglomerated particles. Selected area electron diffraction (SAED) was used in conjunction to confirm that only ErAs nanoparticles would be counted in the size distributions. Scanning electron microscopy (SEM) was needed in order to confirm the absence of larger particles on the scale of 100 nm – 1 micrometer. The existence of particles of this size would render the distributions presented in this work invalid as well as make the use of the Scherrer correlation impossible. The Scherrer correlation will be discussed more in-depth later in this work.

4.1.2 Transmission Electron Microscopy

4.1.2.1 Components of TEM

Transmission electron microscopes have many components that are fundamental to the machine's operation. These components are labeled in Figure 14 below.

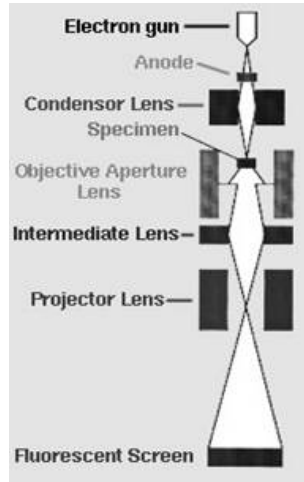


Figure 14: General schematic of a TEM. [9]

The electron gun provided a partially collimated stream of electrons. The electrons that are ejected from this source are then focused by a series of condenser lenses to produce the desired illumination. It is important to maintain a high vacuum in the TEM to minimize electron interaction with any material in the column as well as prevent any interaction of the sample with gas that could be present. The stage that the sample is attached to allows for sample movement and tilting, especially important for diffraction studies and single crystal studies in the TEM [10].

There are three sets of apparatus in the TEM that are important to imaging. The first is the condensers that are used to collimate and modify the intensity of the electron beam. Next is the objective back focal plane which is used to manipulate the magnification for bright/dark field or lattice imaging. The third set of apparatus is the objective image plane which allows the user to select the electrons from a particular area for imaging [10]. Different electrons can be used to produce images of different

types. Found in Figure 15 below, the different electron emissions that result from an electron beam interacting with a sample are illustrated.

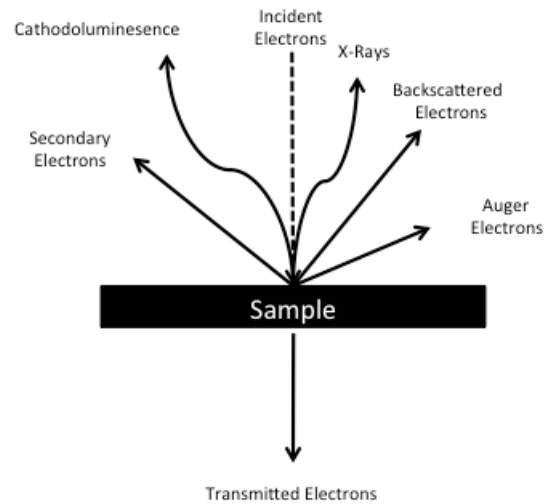


Figure 15: Diagram of different electron emissions resulting from an incident electron beam. Adapted from [11]

The experimental parameters that are adjusted in TEM to obtain a clear image are: specimen thickness, specimen orientation, accelerating voltage, objective apparatus size, objective sense aberration coefficients, and focusing conditions [10].

4.1.2.2 Imaging in TEM

There are three main functions of TEM relevant this work: 1) Bright/dark field (BF/DF) imaging, 2) High-resolution TEM (HRTEM), 3) selected area electron diffraction.

In bright field imaging, the image obtained is formed with a bright background. The contrast in the image comes from electron interaction with the

sample, leading to dark areas in the image that reveal the sample. Conversely, dark field image is formed through diffraction of the electron beam by the sample. The diffracted electrons are collected and are able to form a coherent image. Dark field imaging is particularly useful in the characterization of complex microstates such as twins and grain boundaries, but requires a significant amount of the electron beam to be diffracted. For this reason, it can provide large contrast between defects in the structure of a sample and the rest of the sample, but is not as sensitive as bright field in the imaging of a sample all together.

Sources of error and poor image quality for both dark field and bright field imaging include spherical aberration, chromatic aberration, astigmatism, improper specimen thickness and orientation, and improper focusing.

High resolution TEM is a type of imaging in TEM that allows the user to study materials at the atomic level. Compared to BF/DF imaging, HRTEM yields images with higher resolution but a smaller field of view.

SAED is a technique by which the diffraction pattern of a sample is observed. In this technique, a collimated beam of electrons passes through the crystalline specimen and is scattered according to Bragg's law [10]. This technique is very useful in determining the composition of what is being imaged in bright field or dark field images. For single crystal samples, the diffraction pattern will appear as dots corresponding to specific orientations at which diffraction can occur. In polycrystalline samples, these diffraction dots are oriented randomly and in large numbers forming rings. Examples of these ring patterns can be found in the results section of this report that detail the TEM studies performed for this work. The breadth

and spottiness of the ring pattern depends on the size and number of crystals contributing to the diffraction pattern.

Sources of error in SAED come from spherical aberration and incorrect focusing of the objective sense [10].

4.1.3 Scanning Electron Microscopy

SEM is another electron microscopy technique that is used to obtain topological information of a sample. Similar to the TEM, the SEM probes the sample with a collimated beam of electrons (produced by an electron gun) which is then collected by a detector to form an image. A general diagram of a SEM setup is shown below in Figure 16.

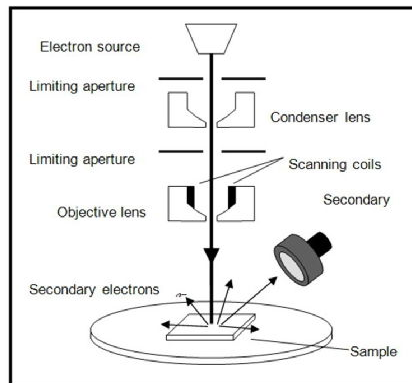


Figure 16: General Schematic of a SEM. [12]

SEM is able to form two types of images using two different detectors. The lower secondary electrons image (LEI) detector captures secondary electrons while the secondary electrons image (SEI) detector collects backscattered electrons. The LEI is generally more sensitive to the topology of the sample while the SEI can be

used to obtain higher magnification. However, the maximum magnification obtained using SEM is not comparable to the magnification obtained in TEM. For this reason, SEM can be used as a tool to view samples which have structures in the 100 nm to 1 micrometer range.

4.1.4 Log Normal Distribution

Log normal distributions will be used to describe size distributions obtained with TEM experiments in this section. For this reason, log normal distributions are described here.

A log normal distribution is a continuous probability distribution where the logarithm of a random variable is normally distributed [13]. The equation for a log normal distribution is given below:

$$\ln(y) = \left(\frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln x - \mu)^2}{2\sigma^2}\right) \right), x > 0$$

where y is the probability, x is the quantity whose probability of occurrence is being calculated, σ is the standard deviation of x , and μ is the average of all x . This type of distribution is often used to describe particle size distributions of particles in fields such as colloidal and polymer chemistry [13]. It is specifically applicable to the IGC growth process because a fundamental tenet of log normal distributions in terms of size is that relative growth rate of particles is independent of the particle size. In general terms, a log-normal process is one that contains many independent random positive variables that produce a result. In Granqvist and Buhrman, a log normal distribution was used to describe the size distributions of nanoparticles produced by IGC [2]. Additionally, they determined that the logarithm of nanoparticle sizes has a Gaussian distribution at small sizes, but deviation from this behavior occurs at larger

sizes [2]. Characteristic features of a log normal distribution are an asymmetric bell shape and a tail towards larger sizes.

4.2 Methodology

4.2.1 TEM

4.2.1.1 Equipment Used

The microscope used for TEM experiments is a JEM 3010 transmission electron microscope. This machine has capabilities of BF, DF, SAED, and energy-dispersive electron spectroscopy (EDX).

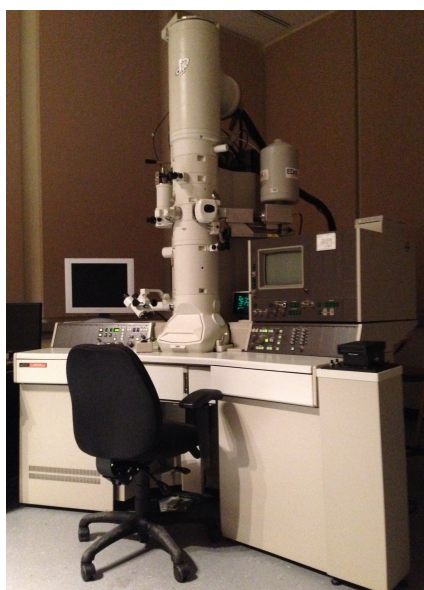


Figure 17: Image of the JEM 3010 TEM used for particle imaging. [14]

It has a 300 kV accelerating voltage and a LaB6 electron source. All TEM images were taken by Doctoral Candidate Matthew Lewis.

4.2.1.2 Sample Preparation

The sample is collected off the side of the beaker and placed in a vial with ethanol to prevent oxidation. Sample collection is performed in a glove box attached to the IGC chamber to reduce oxidation during collection. The vial of ethanol and particles are sonicated prior to TEM sample preparation to break up agglomeration of particles and to suspend the particles homogeneously in the ethanol solvent. A dropper is used to drop cast particles on the TEM sample grid. After letting the grid dry, it is placed on a TEM sample holder and then inserted into the TEM for imaging. Sample collection and preparation was performed by Doctoral Candidate Matthew Lewis.

4.2.1.3 Imaging

Prior to imaging, areas are first scanned using SAED to ensure that all crystalline material in the field of view is ErAs. High resolution TEM imaging is then performed to get images of the particles. This is done to acquire a large number of images to ensure that size distributions are statistically accurate.

4.2.2 SEM

4.2.2.1 Equipment Used

The microscope used for SEM experiments in this work is a JSM-7400F scanning electron microscope. It has SEI and LEI detectors and is also able to perform XEDS.

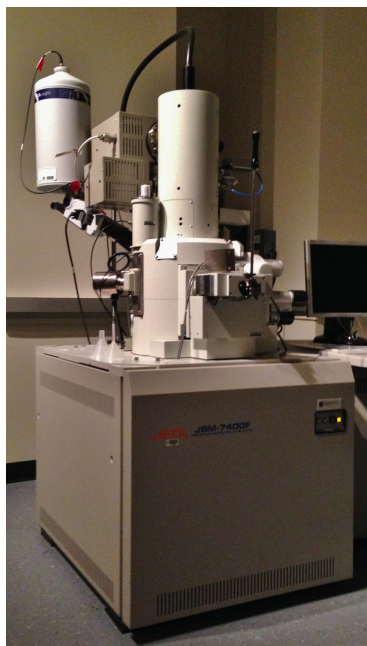


Figure 18: Image of the JSM 7400F used for the SEM experiments of this work.
[15]

An accelerating voltage of 3 kV is used for imaging.

4.2.2.2 Sample Preparation

Particles scraped off of the beaker walls and are placed on carbon tape attached to an SEM sample holder in a glove box attached to the IGC chamber to reduce oxidation. The SEM sample holder is then attached to the larger sample holder which is then placed into the SEM for imaging.

4.2.3 Selected Area Electron Diffraction

Before imaging particles in the TEM, the SAED mode is turned on and used to image electron diffraction (ED) patterns of the material in the field of view. The ED pattern is then indexed to acquire lattice spacing using the TEM computer software.

Only after a diffraction pattern corresponding to ErAs and only ErAs was found were TEM images taken. All SAED images were taken by Doctoral Candidate Matthew Lewis.

4.2.4 Size Distributions

Size distributions are obtained through analysis of multiple TEM images of particles. ImageJ software is used to do this analysis. Each particle is circled and the area of the particle is obtained. It is assumed that each particle is roughly spherical, allowing the diameter of the particle to be obtained. The mean particle size is calculated along with standard deviations and the distribution is calculated using a log-normal distribution function.

4.3 Results

4.3.1 TEM

Images of hundreds of nanoparticles were taken for each IGC growth using TEM. An example image of nanoparticles is provided below in Figure 19.

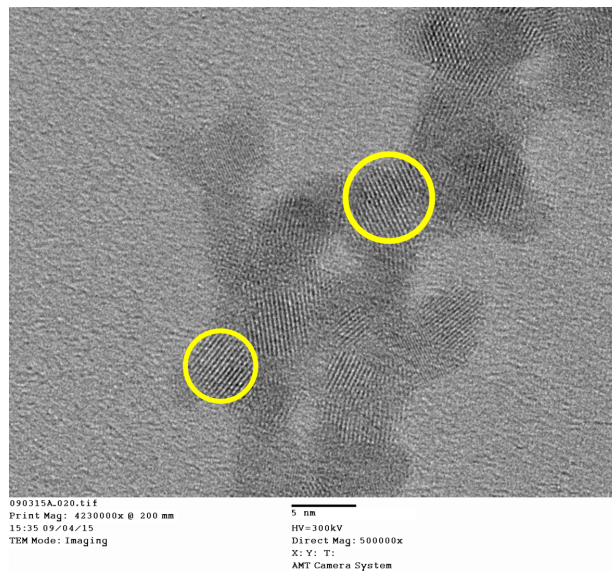


Figure 19: TEM image of ErAs nanoparticles. Nanoparticles can be found by their lattice fringes. Two nanoparticles are circled for clarity.

Each image was analyzed using ImageJ software to obtain particle diameters for the nanoparticles. The sizes of the nanoparticles were sorted into size ranges to form size-distributions and then fit with a log-normal size distribution. An example size distribution and its log-normal fit is provided below in Figure 20.

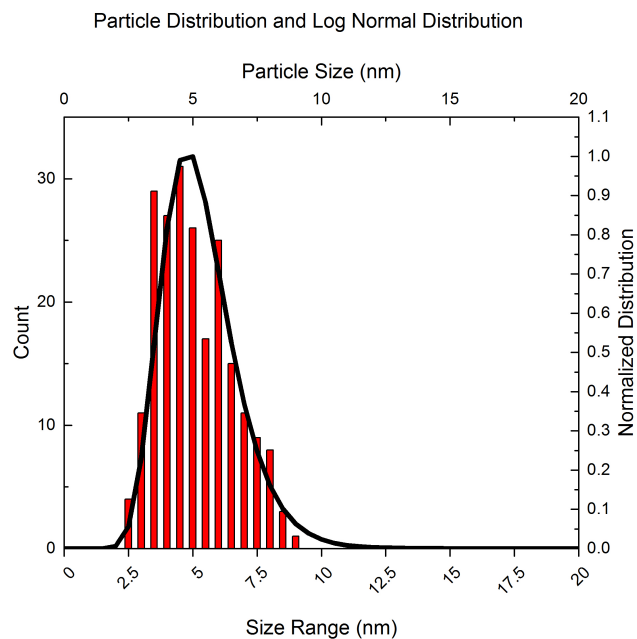


Figure 20: Size distribution bar graph overlaid with a log-normal distribution, showing good agreement between actual and modeled distribution.

The distributions for multiple different IGC growths were obtained using different growth parameters to study the effect of those parameters on particle size. These distributions are stacked on the same chart for comparison. The average particle sizes for the growths are represented by the thick vertical lines. The average particle sizes +/- a standard deviation for the growths are represented by the thin vertical lines.

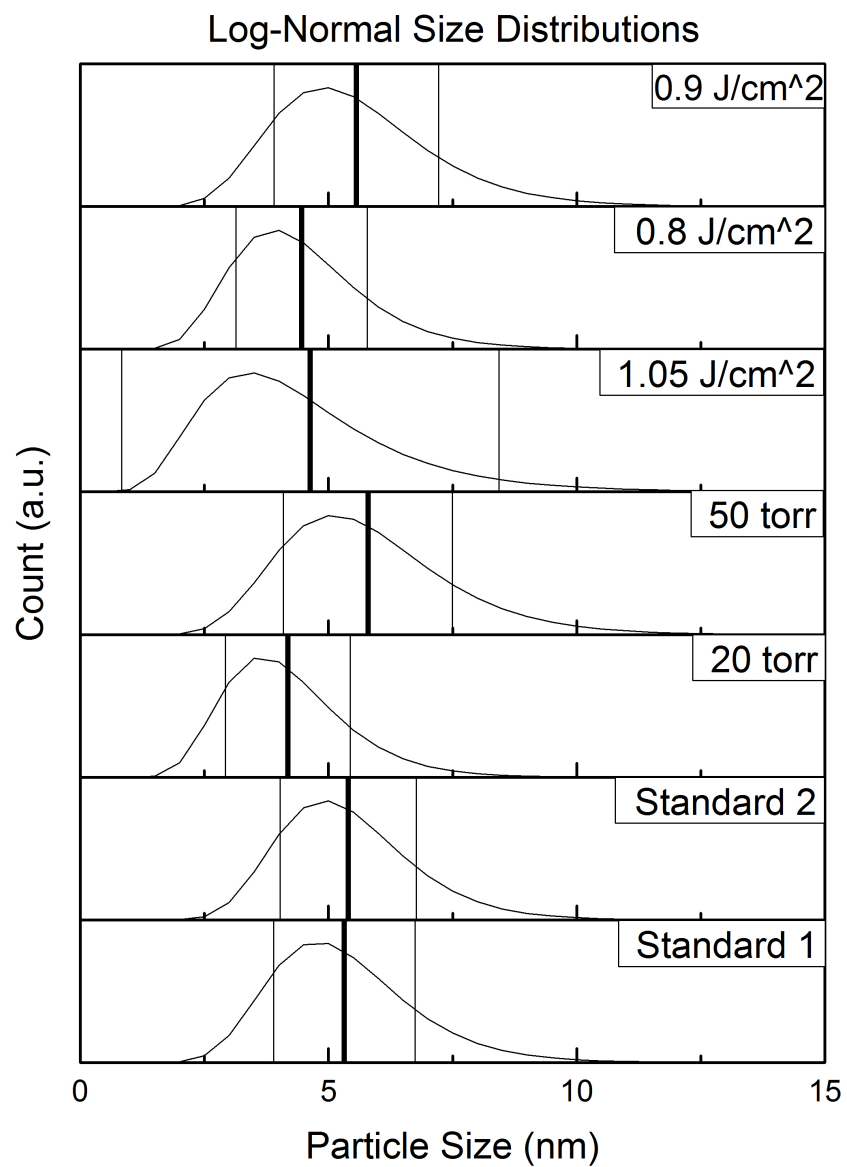


Figure 21: Stacked log-normal size distributions for a series of growths with varying growth parameters. Mean particle size is represented by the thick lines. One standard deviation away from the mean is represented by the thin vertical lines.

The values for the mean particle size and standard deviation used above in Figure 21 are provided below in Table 1.

Table 1: Particle size statistics of the size distributions shown in Figure 21.

Sample	Mean (nm)	StDev (nm)
Standard 1	5.3	1.4
Standard 2	5.4	1.4
20 torr	4.2	1.3
50 torr	5.8	1.7
1.05 J/cm ²	4.6	3.8
0.8 J/cm ²	4.5	1.3
0.9 J/cm ²	5.6	1.7

4.3.2 SEM

SEM was used to confirm the non-existence of larger particles on the scale of 100 nm - 1 micrometer. It was confirmed that no sizable amount of particles of this size range existed in the growths.

4.3.3 SAED

SAED was used to confirm that the nanoparticles imaged in TEM were all ErAs with no other major components. An unindexed SAED pattern is provided below in Figure 22.

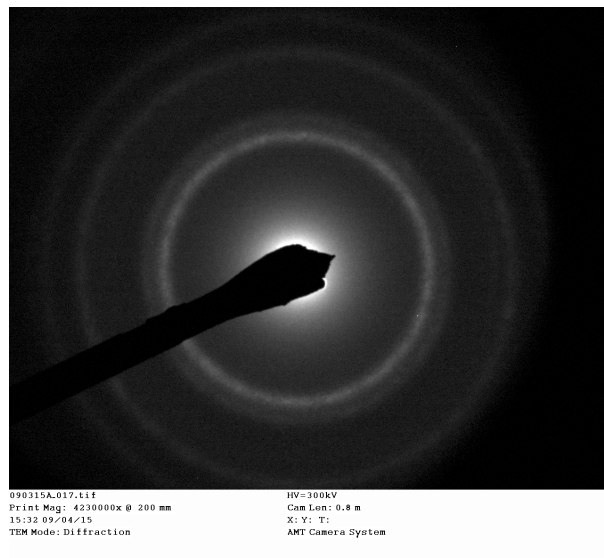


Figure 22: Unindexed SAED pattern of ErAs particles.

Computer software was used in order to quantify the ED pattern to acquire lattice spacing. The indexed ED pattern provided above in Figure 23 is shown below in Figure 23.

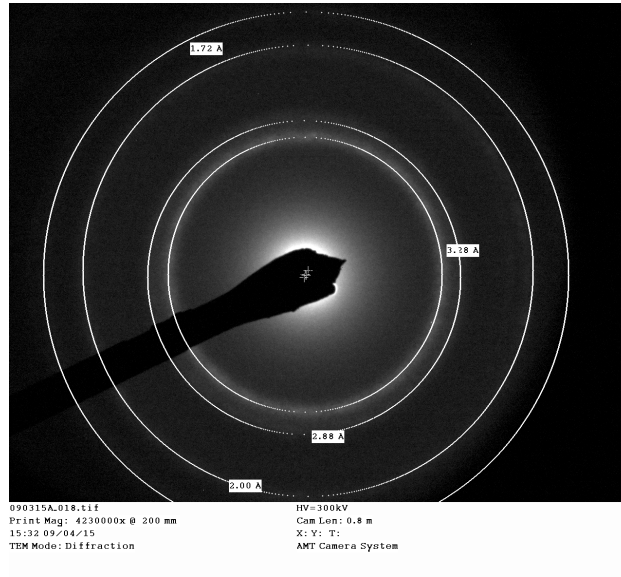


Figure 23: Indexed SAED pattern shown in Figure 23.

4.4 Discussion

4.4.1 TEM

As seen in Figure20, the fit of the log-normal distribution on the particle distribution is very accurate as it captures the shape of the actual distribution well. The log-normal distribution clearly describes the sharp increase in count towards smaller particle sizes and the longer tail towards larger sizes.

Comparing the size distributions of different growths, no clear size change is observed. While some variation in the mean particle size occurs, all growths are subject to a large standard deviation of about 30% the average particle size. One exception to this is the size distribution from the IGC growth made with a laser fluence of 1.05 J/cm^2 . At this time, no explanation as to why the standard deviation for this growth is significantly larger than other growths can be provided. In brief,

laser fluence and He pressure has no clear effect on the size of nanoparticles grown in IGC.

4.4.2 SEM

The confirmation of the absence of larger particles was crucial to the validity of the size characterizations performed in this work. The existence of larger particles would result in a bimodal size distribution making the log-normal distribution and Scherrer correlation invalid.

4.4.3 SAED

The ED pattern of the nanoparticles imaged in TEM reveals crucial information regarding the composition and nature of the growth. The circular diffraction pattern with no observable spots pattern that the sample in fact has a large number of particles and that no large-scale agglomeration or degradation of the crystals occurred during sample prep. After indexing the pattern using the computer software, it is clear that the imaged nanoparticles are ErAs with lattice spacing of 3.28 Å, 2.88 Å, 2.00 Å, and 1.72 Å. These lattice spacing correspond to the first four diffraction peaks of ErAs at lattice spacing of 3.334 Å, 2.887 Å, 2.042 Å, 1.741 Å [16]. Additionally, the diffraction pattern has no other visible rings or spots meaning that there are no crystalline materials in the field of view in the TEM other than ErAs. Therefore, all crystalline particles counted towards the size distributions are confirmed to be ErAs.

4.4.4 Conclusions

The results of the TEM image analysis reveal that particles with a size of ~5 nm are consistently made in our growths. No experiments have been made to

determine the effect of pellet composition or collection distance on particle size. It can be concluded that He pressure and laser fluence have no effect on particle size. Furthermore, SEM microscopy confirmed the absence of larger particles validating our results and allowing for the application of the Scherrer correlation.

Chapter 5

SCHERRER ANALYSIS

5.1 Background and Motivation

5.1.1 Motivation

The method by which size distributions are obtained for each IGC growth is a process that is very tedious, inefficient, and unnecessary. The Scherrer correlation is a tool that can be used to extract the average size of particles in a sample from the XRD pattern. While the Scherrer correlation is commonly used in literature, the accuracy of the results of the calculation are rarely, if at all, confirmed. In order to use the Scherrer correlation in our work, an accurate shape factor must be calculated for our growths. After this value is determined, using the Scherrer correlation to measure the size of the nanoparticles grown by IGC will be a statistically accurate and easy alternative to TEM image analysis.

5.1.2 General Background

The Scherrer correlation was developed in 1981 by Paul Scherrer [17]. As mentioned before in the XRD section of this work, non-idealities in diffraction that lead to peak broadening are instrumental effects, crystallite size, and lattice strain [5]. The mathematical correlation developed by Scherrer described the relationship between XRD peak broadening and grain particle size. This broadening occurs because as the number of lattice planes decreases, the sharpness of the diffraction

condition goes down [5]. That is, angles that usually do not diffract strongly (because of destructive interference with diffracted beams from other planes) are able to diffract enough to give a noticeable signal in the XRD spectrum.

The anatomy of an XRD peak is shown below in Figure 24.

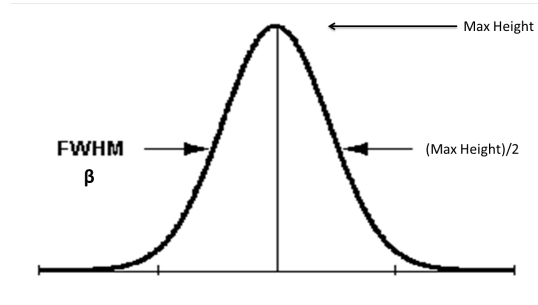


Figure 24: Diagram showing location of full-width at half max (FWHM) with respect to the max height of the XRD peak.

The Scherrer equation quantitatively relates the FWHM of the XRD peak to the crystallite size:

$$L = \frac{K\lambda}{\beta \cos \theta}$$

Where L is crystallite size, K is the shape factor, λ is the wavelength of radiation used for diffraction, β is the FWHM of the XRD peak, and θ is the Bragg angle of the diffraction peak. The definition of peak width commonly used in practice is the FWHM which is the width of the diffraction peak measured at halfway between the peak maximum and background, as shown above in Figure 24. The Scherrer equation was derived based on 2 main assumptions: 1) Gaussian line profiles, 2) small cubic crystals of uniform size (for which the shape factor, K, was determined to be 0.94).

However, the Scherrer equation has been used as a common tool to estimate the size of both cubic and non-cubic materials from their XRD spectra. The difference in crystal type was accounted for by varying the value of the shape factor. As a result, the values for this constant range drastically in literature [5]. The value calculated using Scherrer equation is very rough and should be assumed to have an error of about +/- 10 % [5].

5.1.3 K Value

It is important to understand the base assumptions of the shape factor in order to understand the accuracy of the Scherrer correlation with respect to a specific case. The K value depends on 3 main factors: 1) definition of peak width, 2) crystallite shape, 3) crystal size distribution. The crystallite shape of the sample can be assumed to have a regular shape (i.e. cube, sphere, etc) even though true uniformity is practically improbable. Finally, all growth processes produce particles with a distribution of sizes, yet the Scherrer correlation calculates a singular value for crystallite size. It is therefore up to the investigator to determine how the results of the Scherrer correlation relate to the size distribution of the particles under examination

5.2 Methodology

Using the XRD computer software, accurate calculation of the FWHM and 2Theta of the main peak at about 31.1 degrees 2Theta for ErAs is calculated. The peak at 31.1 degrees 2Theta is used for ErAs because it is the peak that has the strongest diffraction. For consistency, the 31.1degree peak is the most viable choice for analysis for the Scherrer correlation. Using the Scherrer equation and the known

mean particle size for that particular growth obtained from TEM image analysis, a value of K is calculated.

5.3 Results

The average sizes of the IGC growths were used to calculate a K value for a series of growths. Reported below in Table 2 are the growth conditions, average sizes, and calculated K value for each growth. An average K value and standard deviation K were calculated. Standard growths denote growths which used the following growth conditions: 1:1 (Er:As) source pellet, 1.25 cm collection distance, 10 torr He pressure, 1.33 J/cm² laser fluence.

Table 2: Average sizes and calculated K value for IGC nanoparticle growths with varying growth conditions. Standard growth conditions are as follows: 1.33 J/cm² fluence, 10 torr He pressure, 1.25 cm collection distance, 1:1 Er:As source pellet.

Growth Condition	Avg Size Full (nm)	K
Standard	5.3	0.125
Standard	5.4	0.145
20 torr	4.2	0.115
50 torr	5.8	0.16
1.05 J/cm ²	4.6	0.075
0.81 J/cm ²	4.5	0.1075
0.9 J/cm ²	5.6	0.14
Average	-	0.124
Stdev	-	0.0281

The growths were plotted on a graph of Particle Size vs. FWHM. The average K value, average K value + standard deviation, and average K value – standard deviation were used to graph the predicted particle size (according to the Scherrer correlation) at a series of different FWHM. The graph is provided below in Figure 25:

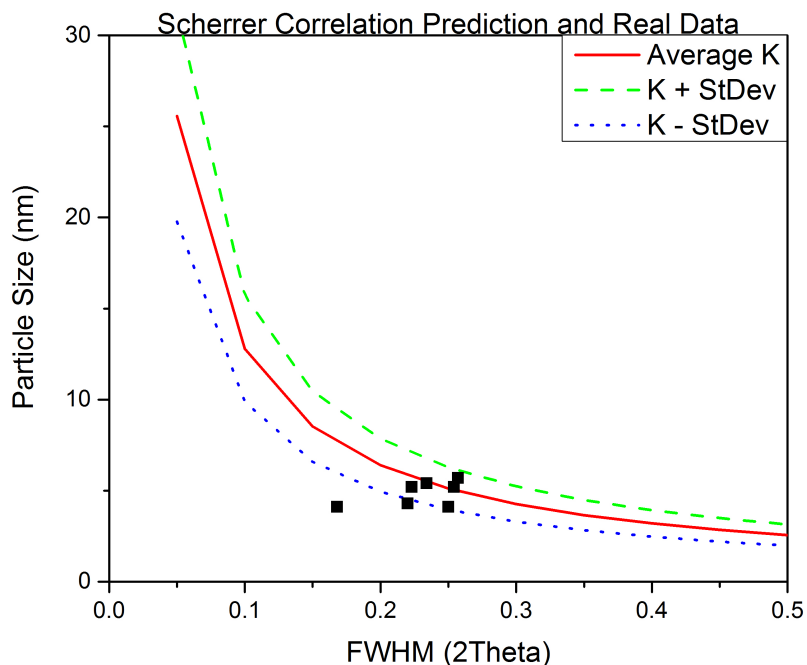


Figure 25: Scherrer correlation prediction and real data. Real data using the average sizes and FWHM for the growths denoted in Table 2 are shown as black dots.

5.4 Discussion

The calculated K values for the growths provided in Table 2 do not agree with values often reported and used in literature. As mentioned before, a K value of approximately 0.9 is used as a standard. However, the largest K value calculated in this work is 0.16 and the lowest being 0.075. It is clear that a disconnect exists between the commonly used K value and that which pertains to our growths and system. The standard deviation for the K value is about 23 % of the average K value, showing significant variation in the shape factor from case to case.

Applying the average K factor to calculate predicted particle sizes at a range of FWHM, the efficacy of the K factor in the Scherrer correlation is observed. For particle sizes of ~5nm, a K value of 0.124 will give a good estimate of the particle size. However, this K factor has not been tested at varying particle sizes. At this point, achieving statistically significant size change has been unsuccessful. As a result, no significant change in the FWHM of the ErAs diffraction peak has been observed as well. Only after significant size change has been accomplished can the validity of the shape factor be tested.

5.5 Conclusion

The shape factor calculated for particles grown in our IGC chamber is in disagreement with the commonly used value of ~0.9. Our particles satisfy the Scherrer correlation with a K value of ~0.124. However, before this value can be used universally, it must be tested and confirmed to work in predicting the size of particles that have statistically different sizes.

Chapter 6

FUTURE WORK

6.1 IGC Growths

In the Zide lab, future work for the growth of RE-V nanoparticles by IGC is directed at a few distinct goals. Most immediately, the goal of obtaining controllable and significant size change of the particles is being addressed. This includes doing further studies on various growth parameters and their effect on particle size. Of the growth parameters to be studied, inert gas pressure is the most promising. This is due to the vast amount of support from literature and the data obtained with the inert gas pressure studies performed in this work. Pressures much higher than the ones used in the growth series for this work are of particular interest. After significant size control is achieved, more work with the Scherrer Correlation can be completed. Another goal of the Zide lab is to perform growths using different material systems. The next nanoparticles to be grown are Terbium Arsenide nanoparticles. While the effects of growth parameters on nanoparticle growths has been studied in this work for ErAs, it is necessary to confirm the validity of those results with respect to new material systems. Therefore, the use of XRD and electron microscopy in future work of the Zide lab is important in understanding and characterizing growths of new material systems.

6.2 XRD

In future work, XRD will be used continually to check the results of growths, both in terms of composition and crystal structure. It remains the easiest and most powerful tool at our disposal for quickly checking the results of our growths. XRD and Rietveld analysis will be also be used to determine the effects of different growth parameters not investigated in this work as well as the effects of the growth parameters already investigated for new material systems. In brief, XRD will continue to be the first line of characterization for our work.

6.3 Electron Microscopy

Electron microscopy, specifically TEM will be used to do further size analysis. Images will be used to obtain similar size distributions and growth size statistics to determine whether statistically significant size change can be achieved. Systematic studies relating growth parameter inputs to particle sizes will be carried out. Mentioned before, growth series with inert gas pressures higher than what was studied in this work is of distinct interest. SAED will be used as it has been used in this work to identify the particles imaged with TEM.

6.4 Scherrer Correlation

A complete Scherrer correlation can only be performed after statistically significant and controllable size control can be accomplished. By correlating the particle sizes across a range of FWHMs, a K value that accurately predicts particle size can be calculated. This K value will pose to be more meaningful as it will describe the relationship of peak width to particle sizes across a large range of particle sizes. Doing this will show that the Scherrer correlation can be used as an accurate tool to determine the size of particles.

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