Synthesis and Consolidation of Metal Oxide Nanocrystals via Nonthermal Plasma

Austin Cendejas
Washington University in St. Louis

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Synthesis and Consolidation of Metal Oxide Nanocrystals via Nonthermal Plasma
by
Austin J. Cendejas

A dissertation presented to
the McKelvey School of Engineering
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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Austin J. Cendejas

Washington University in St. Louis

December 2022
Dedicated to my parents.
ABSTRACT OF THE DISSERTATION

Synthesis and Consolidation of Metal Oxide Nanocrystals via Nonthermal Plasma

by

Austin J. Cendejas

Doctor of Philosophy in Energy, Environmental & Chemical Engineering

Washington University in St. Louis, 2022

Assoc. Professor Elijah Thimsen, Chair

Nonthermal plasmas offer a unique nonequilibrium environment that has been leveraged in a wide variety of applications in the fields of material processing, lighting, and waste management to name a few. In all of these cases, the plasma serves as a source of high energy electrons, ions, reactive gas species, and radicals that interact in several ways with surfaces brought into contact with the plasma. Specifically, nonthermal plasmas have been shown to be very successful in achieving continuous, high-throughput, monodisperse nanocrystals of a wide variety of materials. The crystallinity of nanoparticles synthesized in nonthermal plasmas can be attributed to the selective heating of the particles immersed in the plasma to temperatures well in excess of 1000 K. As a result, nonthermal plasmas are a promising synthesis environment for nanocrystals of high melting point materials, such as many metal oxides. As the material library accessible via nonthermal plasma extends ever wider, understanding critical processing parameters (i.e. reactor geometry, pressure, gas composition, applied power, etc.) for designing new synthetic processes is necessary. In addition, many applications of nanocrystalline materials achievable through plasma synthesis require consolidation into dense morphologies. While a number of methods of consolidation have been attempted in the past, there is a need to develop intentional consolidation
methods with the aim of retaining nanocrystalline grain size and the monodispersity in the size distribution achieved via the nonthermal plasma.

The first aim of this dissertation is to couple external plasma synthesis parameters to desired nanoparticle properties. A nonthermal plasma synthesis process to produce Al₂O₃ nanocrystals was developed. An analytical model for particle heating during plasma synthesis was extended to incorporate only external plasma parameters as inputs. Crystallization behavior of the Al₂O₃ nanocrystals showed agreement with the predictions of particle temperature calculated by the model. In addition, the model was used to successfully predict the power required to synthesize Cr₂O₃ nanocrystals demonstrating the generalizability of the model. Ultimately, this work resulted in a predictive model that can aid in designing nonthermal plasma nanocrystal synthesis processes.

The second aim of this dissertation is to develop a method for consolidation of these nanocrystals and to explore the properties of dense, structural ceramic nanocomposites. A unique approach to consolidation was taken in which nanocrystals were first deposited by established aerosol deposition techniques followed by complete densification via atomic layer deposition (ALD) infill. The method retains the initial nanocrystal morphology from the nonthermal plasma synthesis while allowing for complete removal of porosity in the nanocomposite by ALD. Subsequent thermal post treatments were conducted in which a seeding effect on the crystallization of the ALD matrix was observed. This behavior along with the mechanical properties of the resulting nanocomposite films were investigated in detail.
Chapter 1

Introduction

1.1 Nonthermal Plasma Fundamentals

Plasma is the fourth state of matter, consisting of a partially ionized gas containing molecules, ions, radical species, and free electrons.\textsuperscript{1} The term plasma was coined by the physicist Irving Langmuir who noted the discharges he observed reminded him of the way blood plasma “carries around white and red corpuscles and germs”.\textsuperscript{2} There are several types of plasmas that exist naturally in the universe, such as stars, solar wind, and lightning (Figure 1.1 a-c).\textsuperscript{3–5} These plasmas vary greatly from the more technologically relevant artificially generated plasmas used in the laboratory and industry. Specifically, plasmas are prominently utilized for fusion research,\textsuperscript{6} material processing,\textsuperscript{7–9} spray-coating,\textsuperscript{10} and lighting devices (Figure 1.1 d-f).\textsuperscript{11}

Due to the variability in the plasmas used for various applications, it is useful to classify them based on distinct parameters. For example, the most common distinction for artificially generated plasmas is based on the relative temperatures of the plasma species. In thermal plasmas,
the ions, electrons and neutral gas atoms are all present at one temperature.¹ In other words, the plasma constituents are at thermal equilibrium and are very hot, with temperatures exceeding 10,000 K. Thermal, or high temperature plasmas have found extensive use in material synthesis and spray coating.¹²,¹³ Thermal plasmas are typically generated at atmospheric pressure in the form of an arc or torch.¹⁴ An advantage of using thermal plasmas is that they can achieve very high temperatures often needed for the synthesis of structural materials such as carbides or nitrides. One key drawback to these systems is that they behave similarly to other equilibrium aerosol methods which suffer from highly polydisperse particle size distributions and substantial agglomeration.¹⁵

![Figure 1.1. Examples of natural and artificial plasmas.](image)

The Pillars of Creation (a) are part of the Eagle Nebula, which can be observed as it emits light mostly from hydrogen.³ The northern lights (b) and lightning strikes (c) are two examples of naturally occurring plasmas we experience on earth.⁴,⁵ Artificial plasmas such as etching plasmas (d), plasma torch cutters (e) and neon lights (f) are all examples of intentionally generated discharges utilized for either material processing or lighting.⁸,⁹
Plasmas whose species are not in local equilibrium are referred to as nonthermal (or low-temperature) plasmas. The characteristic property of a nonthermal plasma (NTP) is that the ions and neutral gas species are at low-, near ambient temperatures while the free electrons are extremely hot, with temperatures typically exceeding 20,000 K. This discrepancy in temperature in the same spatial location is indicative of a highly nonequilibrium environment. The cause of the difference in these two temperatures is the disparity in the relative masses of the two species being considered, ions/neutrals and electrons. When these two species collide elastically, collisions between ions/neutrals and electrons are highly inefficient whereas collisions between ions and neutrals with other ions and neutrals have sufficient energy transfer and equilibrate. Due to the lack of collisional momentum transfer from the electrons to the heavier species, they are preferentially accelerated in the electric field and reach energies sufficient to ionize neutral species and sustain the plasma.

This nonequilibrium environment has been leveraged in several applications in laboratory generate plasmas. Specifically, NTPs have found use in several novel application areas such as water treatment, ion thrusters, and gas-phase chemical processing. In addition to these areas, the most notable example of industrial application of NTPs is in the semiconductor industry, whereby plasma-based techniques have allowed for the deposition of high-quality materials with nanometer precision at relatively low process temperatures. Such plasma processing techniques are utilized to produce a large portion of the microscopic devices that underly the integrated circuits in consumer electronics.

As early as 1989, Selwyn et al. described the presence of nanoparticles that were synthesized and levitated above the semiconductor wafer during a chlorofluorocarbon plasma etching process. These particles were deemed unwanted contaminants as they had the potential
to cause negative effects in subsequent steps of the semiconductor device fabrication process after falling down to the substrate upon extinguishing the plasma discharge. As a result, much focus on plasma generated nanoparticles in the beginning was focused primarily around mitigating the production of particles or devising ways to remove the particles from the reaction environment. It did not take long however for researchers to start to leverage the synthesis capabilities of plasmas to intentionally produce nanoparticles with Vollath and Sickafus first reporting metal oxide nanoparticle synthesis using a microwave plasma in 1992. Over the last three decades, there has been a number of groups internationally who have developed numerous types of plasma-nanoparticle reactors and chemistries in addition to exploring the underlying mechanisms responsible in order to exploit the unique capabilities of NTPs. The following section provides a brief introduction to the use of NTP as an intentional reaction media for production of nanocrystals.

1.2 Dusty Plasma Particle Synthesis

The prototypical NTP synthesis reactor operates in a flow-through configuration where the discharge is maintained in a dielectric tube. The plasma is maintained by supplying power to a ring electrode surrounding the dielectric tube, often with the addition of another grounded electrode downstream of the powered ring. In the typical configuration, shown schematically in Figure 1.2, a continuous stream of gas is fed to the reactor at a pressure between 1 Torr and atmospheric pressure. The NTP plasma is typically generated by supplying electricity to the electrodes in the radiofrequency (RF) range at a frequency of 13.56 MHz. A nice feature of this arrangement is that the electrodes are completely removed from the plasma itself, leading to very little contamination during operation of the power delivery system. This reactor geometry has
proven itself to be a useful tool in synthesizing high-quality nanocrystals in many research labs worldwide in recent years.²⁴–³⁴

Figure 1.2.1. Schematic representation of prototypical NTP reactor.

To synthesize nanocrystals in a flow-through NTP, a variety of feedstocks have been demonstrated such as metallic aerosols,³³,³⁵,³⁶ reactive gases,²³,²⁴,³⁴ and metalorganic vapors.³²,³⁷,³⁸ One of the earliest and subsequently most widely studied examples of this is the synthesis of Si nanocrystals from SiH₄. A key reason for the attention paid to NTP synthesized Si nanocrystals is the relative difficulty of producing silicon nanocrystals in the liquid phase.³⁹ Additionally, the relatively high-throughput capabilities of the continuous flow-through arrangement provide another advantage over traditional colloidal synthesis techniques for other semiconductor nanocrystals. The synthesis environment in NTPs is also relatively clean compared to the environment experienced during colloidal synthesis due to the lack of need for a solvent and capping ligands which enables nanocrystals with high purity to be achieved in NTPs.³⁹

Nonthermal plasmas also have significant advantages compared to other gas-phase synthesis methods (e.g. flames) that have also been utilized for high-throughput, continuous, ligand-free nanocrystal synthesis. One unique characteristic of a NTP containing nanocrystals (dusty plasma) is that the particles obtain a unipolar negative charge when suspended in the plasma.⁴⁰,⁴¹ This phenomena and the mechanism underlying it will be discussed in detail in Chapter 2. This result has several consequences, one of which being that particle agglomeration is
suppressed in NTP synthesis, a distinct advantage over the equilibrium environment experienced during a thermal gas phase synthesis method such as a flame. An added benefit of suppressing agglomeration is that the particles do not sinter in-flight, leading to very narrow size distributions.\textsuperscript{39}

The capability of NTPs to produce nanocrystalline materials at gas temperatures significantly lower than the crystallization temperature of the material is another distinct and unique advantage when compared to either gas-phase or solution based alternative synthesis approaches. The ability to crystallize nanoparticles stems once again from the complex interactions between the plasma media and the particle surface that will be elaborated on in Chapter 2. Briefly, nanoparticles have been shown to be selectively heated in the plasma when compared to the background gas.\textsuperscript{42} Understanding and leveraging this particle heating to produce materials such as Si, or Al\textsubscript{2}O\textsubscript{3} which crystallize well above 1000 K in a reaction media several hundred degrees cooler provides many benefits. Practically, the ability to use fluid handling components (i.e. glass tubes, o-rings, etc.) that are not rated for exceedingly high temperatures makes construction and operation of these systems more accessible. Nevertheless, the rational design of plasma synthesis processes is still lacking. The predominant method for development of a new plasma synthesis route is almost entirely empirically driven, by first picking a possible precursor and then varying one of several external parameters that have “knobs” associated with them. These parameters typically include pressure in the range 1-100 Torr, the applied RF power in the range 1-500 W, the background gas composition, and electrode geometry. With almost every reported plasma reactor having slight differences in electrode configuration and feed gas delivery, it becomes a challenge to quantitatively compare one synthesis process to another. To this end, there is a need for
predictive models which researchers can use to relate their prospective synthesis process to material properties produced.

1.3 Consolidation of Nanocrystals

Fabrication of dense, nanocrystalline materials is of interest in several research areas for a substantial number of reasons. One such reason is that materials tend to exhibit distinctly different properties at the nanoscale than their bulk counterparts. However, realizing these properties for a realistic application requires retaining the nanoscale dimensionality while scaling the material into a useable device or part at the macroscale. A field of significant research over the last several decades to this end is the consolidation of nanocrystalline metal oxide powders. Motivating these efforts are a number of material properties that are improved with decreasing grain size, such as hardness, toughness, and optical properties. The Hall-Petch relationship that dictates a material’s yield stress, $\sigma_y$, increases with decreasing grain size according to the relation:

$$\sigma_y = \sigma_0 + \frac{k_y}{d^2}$$

where $\sigma_0$ and $k_y$ are material-dependent constants and $d$ is the grain size. This relationship presents a clear benefit to reducing the grain size in structurally relevant ceramic materials. Beyond the yield stress, similar Hall-Petch type behavior has been observed for other mechanical properties such as hardness and fracture toughness.\textsuperscript{43–45} There are also a number of methods both synthetically and through size reduction processing techniques such as ball-milling to achieve free standing nanopowder of ceramics. However, the difficulty lies in the capability to press these powders and subsequently remove porosity without resorting to extreme conditions.
Historically, the extreme conditions necessary in hot-pressing and sintering ceramics have led to the inability to retain grains much smaller than a few hundred nanometers. While this is sufficient to study the existence of phenomena such as the Hall-Petch effect, the question of how small can grains get while maintaining these relationships needed further investigation. To that end, novel sintering techniques such as lower temperature pressure assisted sintering and spark-plasma-sintering (SPS) have been explored as techniques to retain nanograin size. Techniques similar to these have been leveraged in recent years to explore material properties down to the single nanometer grain size regime. Interestingly, the existence of an inverse in the Hall-Petch relationship has been observed in multiple systems including MgO and MgAl2O4 spinel whereby the hardness and fracture toughness begin to decrease with a further decrease in grain size beyond a critical threshold size. This optimal grain size for ceramics appears to exist in many ceramic materials and thus the location and presence of this parameter is crucial to understanding how to design an optimal structural ceramic for a given material.

1.4 Overview of the Dissertation

Nonthermal plasma synthesis of nanocrystals is a promising avenue to realizing nanocrystalline materials of a wide variety of classes such as semiconductors, metals/alloys, and metal oxide ceramics. However, key aspects surrounding intentional design of plasma synthetic processes require focusing on fundamental plasma-nanoparticle interactions. Furthermore, the consolidation of nanocrystals produced by nonthermal plasmas is necessary for leveraging the unique properties observed at the nanoscale in many applications. The primary challenge associated with nanoparticle consolidation is retention of the nanograin morphology amid densification. This dissertation aims to address these gaps by developing a plasma synthetic approach to production of metal-oxide nanocrystals that couples predictive models with
experimental validation. In the second part of this work, a platform for consolidation of plasma-
synthesized nanocrystals is described in which dense nanocomposites are fabricated. Finally, the
crystallization behavior and mechanical properties of these nanocomposites are investigated in
order to elucidate the potential of this platform in realizing consolidated nanocrystals. The
structure of the dissertation is as follows.

Chapter 2 describes fundamental interactions between the NTP media and the suspended
aerosol of nanocrystals. Chapter 3 follows from this description and develops an extension to the
current model of nanoparticle heating in nonthermal plasmas which allows the introduction of
external reactor parameters as opposed to the difficult to measure plasma properties. Chapter 3
also describes the experimental synthesis of Al₂O₃ nanocrystals used to validate the model
predictions.

Chapter 4 describes an approach to consolidate the nanocrystals synthesized in Chapter 3 by
first leveraging aerosol deposition techniques to deposit a highly porous nanocrystal film and
subsequently infilling the void space using atomic layer deposition (ALD). A detailed analytical
model describing the process is developed and experimentally verified.

Chapter 5 describes the crystallization behavior of the nanocomposites fabricated via the
method presented in Chapter 4. Specifically, the capability of the nanocrystals to direct the ultimate
structure of the ALD matrix and significantly reduce the energetic barrier to crystallization.

Chapter 6 probes the mechanical properties of the as-prepared and crystallized
nanocomposites through nanoindentation experiments. Additionally, the platform described in
Chapter 4 is used to investigate the nanocrystal size-dependence on the hardness of the resulting
composite films.
Finally, Chapter 7 concludes the work by providing a summary of key results described in each of the chapters and provides the author’s commentary on the outlook of this line of research.
Chapter 2

Plasma-Nanoparticle Interactions

2.1 Introduction

The underlying physics of plasma interactions with matter is an entire field of study unto itself and a presentation of the entirety of this body of work is beyond the scope of this dissertation. This chapter therefore aims to act as a primer on the key fundamental interactions between laboratory nonthermal plasmas and nanoparticles immersed in the plasma media. First, a brief description of how the introduction of a surface to the otherwise homogeneous plasma affects the media will be explored. Subsequently perhaps the most important artifact of the plasma-nanoparticle interactions, the unipolar negative charging of particles, will be outlined and a quantitative description presented. Finally, the mechanism through which NTP can selectively heat nanoparticles to temperatures well in excess of the background gas temperature will be illustrated.
2.2 Plasma-Surface Interactions

Almost every plasma utilized in a laboratory setting is subject to some surface, whether it be the discharge chamber walls, a substrate upon which deposition is occurring, or a diagnostic probe, the plasma and species generated in the nonequilibrium environment interact with the surfaces in they are in contact with. Breaking down how these plasma generated species interact with the surfaces they impinge upon allows one to predict and perhaps control phenomena observed on the material surface. For example, in the field of plasma etching, the first realization that plasma contacting a material substrate could volatilize the material was made in 1974 by Hosokawa et al.\textsuperscript{48} They noted the etch rate was substantially higher in discharges containing halogen ions when compared to a pure Ar discharge, but no underlying mechanism was known. It is now widely accepted that ion bombardment increases the reaction probability of neutral and radical species at the surface being etched, and has led to an exploitation of the compounding effects of ions and radicals in the application of reactive ion etching.\textsuperscript{49,50} Another crucial surface phenomena is the buildup of charge on surfaces that come into contact with plasmas, arising from the significantly larger thermal velocity of the electrons when compared to positive ions and/or neutrals in the plasma.

If we consider a surface exposed to the plasma which is initially charge neutral, then that surface will immediately be exposed to a larger flux of electrons than ions and begin to accumulate a negative charge. As the charge builds, two distinct effects begin to emerge as the potential of the wall becomes more negative. First, the electrons are repelled by the increasingly negative potential at the surface thus reducing the electron current to the wall. Simultaneously, the positive ions in the plasma are accelerated towards the wall, increasing their respective speed above the background thermal velocity. Ultimately, the surface achieves a steady-state charge such that the
ion and electron currents are equivalent. The magnitude of the resulting potential is referred to as the floating potential of the surface and is defined as the potential required to equate the two currents. The region near the surface is distinct from the quasineutral bulk plasma, that is to say the ion density and electron density are equal in the bulk, while they are not in the so-called sheath. In dusty plasmas containing nanoparticles, each particle has a floating surface that develops a sheath around it, and thus each particle attains a negative charge that is determined by the plasma properties as detailed in the following section.

2.3 Particle Charging

As a result of nanoparticles being significantly smaller than the mean free paths of electrons and ions in the plasma, one-dimensional analysis proves insufficient to capture the true charging behavior of the particle surface. The most common treatment of small spherical particles suspended in the plasma is based on orbital motion limited (OML) theory. The theory describes the trajectory of ions and electrons in the potential near the surface as they travel on collisionless paths to the particle surface.\(^{51}\) The result is that effective collection cross-sections can be calculated and the resulting electron and ion currents to the particle surface can be expressed as:

\[
\begin{align*}
    j_e &= \frac{1}{4} n_e \left( \frac{8 k_B T_e}{\pi m_e} \right)^{\frac{1}{2}} \exp \left( \frac{e \Phi_p}{k_B T_e} \right) \\
    j_i &= \frac{1}{4} n_i \left( \frac{8 k_B T_i}{\pi m_i} \right)^{\frac{1}{2}} \left( 1 - e \frac{\Phi_p}{k_B T_i} \right)
\end{align*}
\] (2.1,2.2)

where \(k_B\) is the Boltzmann constant, \(\Phi_p\) is the particle potential, \(e\) is the elementary charge, and \(T_{i/e}, n_{i/e},\) and \(m_{i/e}\) refer to the ion and electron temperatures, densities, and masses, respectively.\(^{51,52}\) By setting Eq 2.1 and 2.2 equal, the floating potential of the particle can be calculated numerically. For typical laboratory plasmas, this floating potential is equal to several to a few tens of volts with respect to the plasma.\(^{39}\) Interestingly, the floating potential of particles in the plasma is not size-dependent as predicted by OML theory. This means that the absolute charge
particles must obtain to achieve the floating potential scales with the particle radius. The total charge on the particle, \( Z_p \), can be calculated based on the floating potential if solved numerically, but it can also be approximated to reasonable accuracy by:

\[
Z_p = 0.73 \frac{4\pi \epsilon_0 a k_B T_e}{e^2} \ln \left( \frac{n_i (m_e T_i)}{n_e (m_i T_i)} \right)^{1/2}
\]  (2.3)

where \( \epsilon_0 \) is the permittivity of free space. An immediate consequence of this expression is the dependence of the charge on the electron temperature of the plasma. To give an idea of the magnitudes of charges particles acquire in a dusty plasma, Figure 2.1 shows the absolute charge as a function of particle size for various electron temperatures in an Ar discharge.

**Figure 2.1. Particle charge in a plasma.** Particle integer charge as a function of particle diameter for three electron temperatures in an Ar discharge.
2.4 Selective Particle Heating

Particles suspended in plasmas are constantly bombarded by a number of complex species, including ions, electrons, radicals and photons generated by the plasma discharge. As a result, a number of heating (and cooling) mechanisms exist for an aerosol in the plasma that are not present in a typical aerosol which are depicted in Figure 2.2. Among the several heating processes are ion recombination on the surface, kinetic energy transfer from ions/electrons, UV light absorption, condensation surface reactions, and quenching of metastable species. The cooling processes that balance these heating mechanisms are thermal radiation, thermionic electron emission, conduction to the background gas, and for some particles evaporation. The relative contributions of these heating and cooling mechanisms depends significantly on the specific system of interest, but in general for synthesis plasmas at low pressure (1-50 Torr) the dominant mechanisms are ion-electron recombination at the particle surface and conduction to the background gas.\textsuperscript{41,42}

![Dusty Plasma Diagram](image)

**Figure 2.2. Particle Heating Mechanisms.** Select heat transfer mechanisms present for particles suspended in nonthermal plasma. Red arrows indicate a heating mechanism while blue indicate cooling.
This phenomena has been exploited over the last two decades to produce nanocrystals of many materials at temperatures well below expected crystallization temperatures.\textsuperscript{39} The following chapter provides a more detailed application of a relatively simplified heating model applied to synthesis of ~10 nm Al\textsubscript{2}O\textsubscript{3} particles, but there have been many attempts to use more complicated models in the literature. For example, Vekselman et al. recently modeled time-dependent energy fluxes and charging for particles produced in an oscillating arc discharge between graphite electrodes.\textsuperscript{53} The results suggest that the carbon particles do not remain unipolar negative in their charge during the oscillations of the plasma and that their heating and cooling have significant contributions from radiation from the arc and thermionic emission, respectively.\textsuperscript{53} This is one example of a slightly more complex plasma than the prototypical tubular flow through reactor showing dramatic differences in the necessary treatment of the underlying phenomena responsible for the heating of immersed nanoparticles. It is clear that when discussing phenomena such as particle heating, care must be placed to account for the correct heating/cooling mechanisms for a given system. Additionally, translating predictive models to new plasma systems should be done with consideration of the similarity to that used in the original validation of the model.
Chapter 3

Plasma Synthesis of $\gamma$-Al$_2$O$_3$ Nanocrystals

3.1 Introduction

Nonthermal plasma (NTP) is a well-established means of synthesizing high-purity size controlled nanocrystals.\textsuperscript{39} The unique nonequilibrium environment of NTP provides many advantages when compared to liquid-phase nanocrystal synthesis. For example, the unipolar negative charging of particles in the plasma prevents agglomeration without the need for surface ligation by long organic molecules.\textsuperscript{39,40} Over the last two decades, the material library accessible by NTP has increased significantly. There has been much work surrounding the NTP synthesis of Group IV semiconductor nanocrystals\textsuperscript{23–26,54,55} and their alloys,\textsuperscript{27,56,57} as well as transparent conductive oxides.\textsuperscript{28–30,38,58,59} More recently, NTP synthesis has been extended to include Group III-V semiconductor nanocrystals\textsuperscript{36,33,35} and ceramic nanocrystals.\textsuperscript{31,32,34,37,60} However, despite the rapidly growing material library accessible via NTP, there lacks a straightforward approach to designing synthesis processes for unexplored materials. For example, the ability to predict synthesis conditions (i.e. reactor geometry, gas composition, pressure, and power) that avoid amorphous material and instead yield crystalline nanoparticles would aid greatly in designing new
synthesis techniques; and perhaps more crucially, would drastically reduce the amount of trial and error necessary in order to realize a new material via NTP.

One significant advantage of NTP compared to other gas-phase synthesis methods (e.g. flames) is the ability to synthesize crystalline materials at gas temperatures significantly lower than the temperature required for crystallization.\textsuperscript{39,61} It is known that nanoparticles suspended in the plasma are selectively heated, often to several hundreds of Kelvin higher than the surrounding gas. Several groups have investigated the particle heating and cooling mechanisms in NTP both numerically\textsuperscript{42,62} and experimentally.\textsuperscript{63–66} The primary source of particle heating in NTP has been shown to be ion-electron recombination on the particle surface, while the primary cooling mechanism is conduction to the surrounding gas.\textsuperscript{63} Additionally, particles undergo large temperature spikes on the 100 microsecond timescale due to the stochastic nature of recombination events; however, the magnitude of these spikes decreases with increasing particle diameter.\textsuperscript{42} Despite the size-dependence of the transient fluctuations, it has been shown that particle temperature reaches an average value that is higher than the background gas and nominally independent of size.\textsuperscript{42}

Kramer et al. have demonstrated that for Si nanocrystals, when the plasma conditions are such that the average particle temperature exceeds the crystallization temperature, the entire population of particles is crystalline.\textsuperscript{64} In order to design a NTP synthesis reactor, it is therefore desirable to be able to predict the synthesis conditions under which the particle temperature will exceed this threshold and nanocrystals will be formed. Previous studies suggest that power delivered to the plasma and total pressure in the plasma are two key tuneable process parameters that significantly impact particle temperature, with increasing power and decreasing pressure leading to an increase in particle temperature.\textsuperscript{64,67,68} These trends can be understood in terms of the
heating and cooling mechanisms: an increase in plasma density with increased power causes increased particle heating through larger rates of exothermic surface reactions such as electron-ion recombination, and a decrease in conductive cooling rate with decreasing pressure. While monitoring and controlling pressure is straightforward in low pressure NTP systems, conventional means of measuring the plasma density (i.e. Langmuir probes) are nontrivial in dusty plasmas. From this perspective, the capability to predict average particle temperature using only external, tuneable process parameters would be useful for designing synthesis approaches to further extend the material library accessible via NTP.

In this work, we present a simple nanoparticle heating model that can be used to predict the threshold plasma power necessary for NTP synthesis of nanocrystals. The model requires only four inputs: the pressure, temperature, and composition of the background gas, and plasma volume to determine particle temperature as a function of applied power. Given the unique potential of NTP to yield nanocrystals of very high melting point materials at low background temperature, Al\textsubscript{2}O\textsubscript{3} was chosen as a target material. Al\textsubscript{2}O\textsubscript{3} has a reported crystallization temperature between 1100-1300 K\textsuperscript{37,70,71} The crystallinity of Al\textsubscript{2}O\textsubscript{3} nanoparticles was used as a probe for the particle temperature while suspended in the plasma. In this approach, the entire population of particles is expected to become crystalline when the average particle temperature exceeds the crystallization temperature (see Figure 3.1).
3.2 Experimental

3.2.1 Al2O3 Nanocrystal Synthesis

Al2O3 nanocrystals were synthesized in a flow-through tubular nonequilibrium plasma reactor similar to one recently described by our group. A detailed schematic of the experimental setup can be seen in Figure 3.2. In brief, the Al2O3 nanocrystals were synthesized in an Ar/O2 plasma maintained in a fused-quartz tube with inner and outer diameters of 20 and 25 mm, respectively. Trimethylaluminum (TMA, Strem, Newburyport, MA) served as the aluminium precursor and was introduced into the reactor via a gas bubbler maintained at 225 Torr and swept by 20 standard cubic centimetres per minute (SCCM) Ar (Praxair, UHP 5.0). The resulting TMA feed rate was calculated to be 1.1 SCCM. Just upstream of the plasma zone, an additional stream containing 120 SCCM Ar and 10 SCCM O2 (Praxair, UHP 5.0) was co-fed with the diluted TMA stream into the
plasma. All flow rates were regulated using mass flow controllers (Type 1159, MKS Instruments, Andover, MA). The plasma was maintained via capacitively coupled radiofrequency power (RF, 13.56 MHz) applied to two stainless-steel ring electrodes, with the upstream electrode being powered and the downstream serving as the ground. The electrodes had inner and outer diameter of 25.4 mm and 38.1 mm, respectively, with a thickness of 15.9 mm and were separated by 30 mm. The input power was maintained at the setpoint using a 13.56 MHz RF power supply (AG0613, T&C Power Conversion, Rochester, NY) and impedance matching network (AIT600, T&C Power Conversion, Rochester, NY). All values for plasma power reported are the setpoint power as indicated on the RF power supply. The pressure during synthesis was measured immediately downstream of the plasma zone by a capacitance manometer (DMA Baratron, MKS Instruments, Andover, MA). Background gas temperatures, $T_{gas}$, were estimated by thermal imaging (SEEK Thermal Compact LW-AAA, Santa Barbara, CA) of the plasma reactor during discharge (see Figure 3.3) as previously reported. The background gas temperature was taken as the value at the midpoint between the two ring electrodes.
Figure 3.2. Al2O3 nanocrystal synthesis reactor. Schematic representation of the NTP apparatus used to synthesize alumina nanoparticles.

The as-synthesized aerosol stream was diverted from the bypass line into a collection path where powder was collected on removable stainless steel 400 mesh filters or lacey carbon transmission electron microscopy (TEM) grids (part number 01824, Ted Pella, Redding CA). During powder collection on stainless steel filters, a diaphragm valve immediately before the rotary vane vacuum pump was adjusted to maintain the pressure in the plasma zone at 7.1 Torr. Stainless steel filters were weighed before and after powder collection to calculate mass production rates, which were between 125-250 mg/hr.

Post treatment annealing of alumina nanoparticles was carried out using a tube furnace (Lindberg Blue M, ThermoFisher Scientific, Waltham, MA) under 500 SCCM Ar flow. The crucible (CoorsTek, Golden CO) was 1.5 x 1.7 cm in size and comprised of grade AD-998 alumina (min. 99.8% pure). The furnace tube was evacuated after sample loading and subsequently backfilled with Ar; this process was repeated two times followed by a 15-minute period of purging with Ar before the furnace was turned on. The ramp rate during heating of the tube furnace was
approximately 2.5 K per minute. After annealing, the samples cooled down to room temperature over several hours while remaining under the inert atmosphere.

![Image](image.png)

**Figure 3.3. Digital and thermal photograph of reactor.** Digital photograph of Al2O3 synthesis plasma in operation (top) and infrared thermal image (bottom) during operation.

### 3.2.2 Electron Microscopy

All images of the particles and selected-area electron diffraction (SAED) patterns were collected using a thermal emission transmission electron microscope (TEM) equipped with a LaB6 filament (JEOL JEM-2000 FX) operated at an accelerating voltage of 200 kV. Particle size distributions were obtained using the ImageJ software package by fitting an ellipsoid around the particle and calculating the diameter of a circle with the same area. A minimum of 150 particles were counted for every size distribution and the subsequent histograms were fit with a lognormal distribution to calculate mean diameter and geometric standard deviation.

### 3.2.3 X-Ray Diffraction

After powder collection, a sample of the powder was taken from the stainless-steel filter and characterized by x-ray diffraction (XRD) to determine the crystal structure of the
powder. Approximately 5 mg of dry powder was packed on a miscut Si wafer (MTI Corporation, Richmond, CA) with low-background signal and spectra were acquired using a d8 Advance diffractometer (Bruker, Billerica, MA) equipped with a Cu radiation source (Cu Kα, λ = 1.541 Å). All XRD patterns were collected for 2θ values in the range 20-80 degrees, with a step size of 0.02 degrees and a dwell time of 0.5 seconds per step.

3.2.4 Solid State NMR

For $^{27}$Al solid-state NMR (SSNMR) measurements, approximately 75 mg of dry powder of each sample was collected for analysis. The powder was packed into zirconia rotors (with low-aluminum background). NMR experiments were executed on a 14 Tesla instrument, $^{27}$Al Larmor frequency of 156.00 MHz, at magic-angle spinning (MAS) rotational frequencies of 35 kHz. A Bloch decay sequence with a short tip angle pulse ($\pi/18$) was used with typical pulse lengths of 0.2 $\mu$s, collecting 8k transients, and using a recycle delay of 0.1 s. Samples were referenced to $\gamma$-$\text{Al}_2\text{O}_3$ as a secondary reference. Spectra were deconvoluted using the Dmfit program, employing both the Czjzek model as well as an analysis of spinning sidebands (from quadrupolar satellites) that underlie the central transition resonances.

3.3 Results and Discussion

Nanoparticle temperature while suspended in NTP can be calculated by performing an energy balance on the particle using the heating and cooling mechanisms in the plasma. Specifically, the ion-electron recombination rate and the conduction to the background gas are the two dominant mechanisms for nanoparticles in which melting is not occurring. The particle energy balance as described by Mangolini and Kortshagen can be written as

$$\text{equation}$$
\[
\frac{4}{3} \pi r_p^3 \rho C \frac{dT_p}{dt} = G - L
\]

(3.1)

where \( \rho \) is the material density, \( C \) is the specific heat, \( r_p \) is the particle radius, and \( T_p \) is the particle temperature. The terms \( G \) and \( L \) are the heat generation and heat sink terms, respectively. The heat generation term, \( G \), is considered as the energy deposited to the particle at the surface through ion-electron recombination events. We are here neglecting additional energy release through surface chemical reactions, as these are poorly known. We can rationalize this choice by assuming that most of the chemical precursors have already been consumed by the formation of the particles. The rate of energy deposition through electron-ion recombination can be calculated as \( G = J_{ion} \Delta H_{ion} \), where \( J_{ion} \) is the ion flux to the particle surface and \( \Delta H_{ion} \) is the ionization energy of Ar, which is 15.76 eV. The ion flux is calculated by assuming the particles collect ions with the orbital motion limited (OML) current.\(^{75}\) The resulting heat generation term is thus,

\[
G = \frac{\Delta H_{ion}}{4} S_p n_i \left( \frac{8k_B^2 T_{i}}{\pi m_i} \right)^{1/2} \left( 1 - \frac{e\Phi_p}{k_B T_i} \right)
\]

(3.2)

where \( S_p \) is the particle surface area and \( n_i \), \( T_i \), and \( m_i \) are positive ion density, temperature, and mass, respectively. The particle surface potential is denoted \( \Phi_p \) and can be found by equating the positive ion and electron currents at the particle surface. The particle potential was found to be \( \Phi_p = -4.5k_B T_e/e \), which is a reasonable value for a nonequilibrium argon plasma. The ions were considered to have the same temperature as the background gas, \( T_{gas} \), and only singly charged positive ions were considered. The heat
sink term due to conduction, \( L \), can be calculated in the same way previously reported\(^{42}\) as,

\[
L = \frac{1}{4} \eta_{Kn} n_{gas} S \sqrt{\frac{8 k_B T_{gas}}{\pi m_{gas}}} \times \frac{3}{2} k_B \left( T_p - T_{gas} \right)
\]  

(3.3)

where \( n_{gas} \) is the total background gas density, \( m_{gas} \) is the atomic mass of the background gas, and \( \eta_{Kn} \) is the Knudsen accommodation coefficient which is expected to have a value between 0.1-1.\(^{76}\)

By equating the heat generation and sink terms, a steady state temperature can be calculated. This temperature can be thought of as the average temperature a particle experiences while suspended in the plasma. The fluctuations from this average particle temperature are relatively small for particles larger than 10 nm in diameter, which is the case in the present work.\(^{42,62}\) The average particle temperature can thus be calculated for an argon plasma as

\[
T_p = T_{gas} + \frac{2 T_{gas} n_i \Delta H_{rec}}{3 \eta_{Kn} P} \left( 1 - \frac{e \Phi_p}{k_B T_{gas}} \right)
\]  

(3.4)

where \( n_i \) is the ion density and \( P \) is the total pressure. We call the second term on the right-hand side, the “excess particle temperature”, defined as the difference between the particle and the background gas temperature. Thus, particle temperature in NTP depends on four key parameters: ion density, electron temperature, background gas temperature, and pressure. Both pressure and background gas temperature can be measured in straightforward ways, but the ion density and electron temperature typically require complex plasma diagnostic techniques. However, typical methods of measuring the plasma
density such as Langmuir probes and optical emission spectroscopy are often not suitable for dusty plasmas or when complex gas mixtures often used in synthesis processes are employed. To avoid the need for complex plasma diagnostics entirely, the ion density is estimated by considering the collision frequency of electrons in the discharge to determine the average power absorbed per electron. First, the electron energy distribution function (EEDF) must be obtained. A Boltzmann solver was used to determine the electric field where ionization balances electron losses by ambipolar diffusion for the background gas composition and pressure used in this work. Given the EEDF, the associated energy loss due to collisions can be calculated as the product of the collision frequency and the threshold energy of each inelastic collision. The average electron is thus found to absorb 

\[ \theta = 1.17 \times 10^8 \text{ eV/s}. \]

The electron density can then be calculated as,

\[ n_e = \frac{P_{\text{abs}}}{e\theta V} = \eta_{\text{pwr}} \frac{P_{\text{set}}}{e\theta V} \]  

where \( P_{\text{abs}} \) is the power absorbed by the discharge and \( V \) is the plasma volume. The absorbed power is defined as the product of the setpoint power and the efficiency of the power delivery, \( \eta_{\text{pwr}} \). Previous characterization of the power delivery in a similar reactor using the same power supply and matching network revealed the power delivery to be approximately 65% efficient. Using the glow visible to the naked eye during synthesis, the plasma volume was determined to be approximately 60 cm\(^3\). The result is an expression that can be used to calculate the electron density as a function of power, which is assumed equal to the positive ion density. If Eq. 5 is substituted into Eq. 4 for \( n_i \), then the excess
temperature has a factor $\eta_{\text{pur}}/\eta_{Kn}$. These efficiencies are system specific. In our system, the ratio is assumed to be unity and experimental agreement was found with particle temperatures calculated using the setpoint power (\textit{vide infra}). The assumption of positive ion density equal to electron density is justified by the feed gas being greater than 90% argon. In addition to the ion density, the EEDF can be used to determine the electron temperature, $T_e$, which is taken as $2/3$ of the mean electron energy.\textsuperscript{68} Finally, the background gas temperature was estimated by infrared imaging of the reactor walls during operation. A previous study by our group in a similar reactor compared the wall temperature measured by infrared imaging to the centreline temperature measured by a fibre optic fluorescence decay probe.\textsuperscript{68} In Figure 3.4, the wall temperature measured by infrared imaging is taken as the lower bound of $T_{\text{gas}}$, while the upper bound is calculated by adding the fractional error reported in our previous work as a function of wall temperature. The average particle temperature of 10 nm diameter Al$_2$O$_3$ nanoparticles, which is the experimentally measured size in this chapter (\textit{vide infra}), is presented as a function of absorbed power in Figure 3.4. Nanoparticle synthesis at conditions at which the calculated particle temperature is above the crystallization temperature are expected to result in the synthesis of an entirely crystalline population of Al$_2$O$_3$ nanoparticles.
In Figure 3.4, complete crystallization is expected to occur when the power supplied to the plasma exceeds approximately 325 W. To test that prediction, experiments were conducted in which the RF power supplied to the plasma was adjusted from 100 W to 400 W. At all powers, spheroidal particles between 8-10 nm were synthesized as seen in Figure 3.5. The SAED patterns of nanoparticles synthesized at low power (Figure 3.5a) revealed the particles to be amorphous while those synthesized at high power (Figure 3.5d) exhibited an SAED pattern consistent with crystalline $\gamma$-$\text{Al}_2\text{O}_3$. The particle size did not significantly increase at higher synthesis powers (Figure 3.5e). Thus, the higher particle temperature experienced during synthesis at elevated power did not lead to significant sintering, which is consistent with the expectation of suppressed aggregation in the plasma due to unipolar negative charging.\textsuperscript{39,75}

**Figure 3.4. Al$_2$O$_3$ nanoparticle temperature as a function of power.** Particle temperature for 10 nm Al$_2$O$_3$ nanoparticles as a function of applied power (red). The particle temperature is the sum of the excess particle temperature (blue) and the linear fit (black dashed line) to the background gas temperature measurements (black squares). The shaded bands for background gas temperature and particle temperature account for the error associated with the use of the wall temperature to estimate the background gas temperature. The area bounded by gray dashed lines represents the reported values for crystallization temperatures of 10 nm Al$_2$O$_3$ nanostructures.
To determine the crystallization temperature of the Al$_2$O$_3$ nanoparticles, post-synthesis annealing experiments were carried out. Samples containing amorphous alumina nanoparticles synthesized at 100 W were examined by XRD as seen in Figure 3.6. The as-

**Figure 3.5. Representative TEM of Al$_2$O$_3$ NCs at various synthesis power.** Transmission electron microscopy images and SAED patterns (a)-(d) of alumina nanoparticles synthesized at various powers. Size distributions (e) for alumina nanoparticles shown in (a)-(d), average particle diameter and geometric standard deviation of the lognormal fit is presented.

To determine the crystallization temperature of the Al$_2$O$_3$ nanoparticles, post-synthesis annealing experiments were carried out. Samples containing amorphous alumina nanoparticles synthesized at 100 W were examined by XRD as seen in Figure 3.6. The as-
deposited powder did not exhibit clear peaks in the XRD spectrum, consistent with the SAED pattern and thus confirming the powder was predominantly amorphous. As the annealing temperature was increased from 900 K to 1200 K, peaks consistent with the $\gamma$-\(\text{Al}_2\text{O}_3\) crystal structure emerged. Based on the clear presence of the $\gamma$-\(\text{Al}_2\text{O}_3\) peaks in the samples annealed above 1100 K, that temperature can be taken as the crystallization temperature of the \(\text{Al}_2\text{O}_3\) nanoparticles synthesized in this study. A crystallization temperature of 1100 K is within the range of values reported for similar nanostructured \(\text{Al}_2\text{O}_3\) in the literature.\textsuperscript{37,70,71} As a result of the particle heating in the nonthermal plasma, an increase in plasma synthesis power should eventually result in the crystallization of nanoparticles synthesized in the plasma. Alumina nanoparticles were synthesized at increasing powers between 100 W and 400 W at 50 W increments. The XRD patterns of these as-deposited powders can be seen in Figure 3.7.
For samples synthesized at 150 W or higher, peaks corresponding to γ-Al₂O₃ can be seen. Additionally, the peaks become more intense with increasing power between 150 W and 300 W, indicating that the crystalline fraction of the powder sample is increasing. At synthesis powers above 300 W, the XRD patterns remain unchanged, indicating that complete crystallization of the nanoparticles occurred at 300 W. The calculated particle temperature at 300 W is 1050 K, which is in good agreement with the crystallization temperature determined by the thermal annealing experiments in Figure 3.6. Interestingly, for the nanoparticles synthesized at powers between 150 W and 300 W, the samples clearly show the presence of diffraction peaks, indicating that a portion of the population is crystalline, which is unexpected given the calculated average particle temperatures and the results from the thermal annealing experiment. This discrepancy can be explained in one

Figure 3.6. XRD spectra of Al₂O₃ NC annealing. XRD spectra of Al₂O₃ nanoparticles synthesized at 100 W both as deposited and after annealing at the indicated temperature for 3 hours. Pattern for γ-Al₂O₃ (PDF 10-0425) shown for reference.

For samples synthesized at 150 W or higher, peaks corresponding to γ-Al₂O₃ can be seen. Additionally, the peaks become more intense with increasing power between 150 W and 300 W, indicating that the crystalline fraction of the powder sample is increasing. At synthesis powers above 300 W, the XRD patterns remain unchanged, indicating that complete crystallization of the nanoparticles occurred at 300 W. The calculated particle temperature at 300 W is 1050 K, which is in good agreement with the crystallization temperature determined by the thermal annealing experiments in Figure 3.6. Interestingly, for the nanoparticles synthesized at powers between 150 W and 300 W, the samples clearly show the presence of diffraction peaks, indicating that a portion of the population is crystalline, which is unexpected given the calculated average particle temperatures and the results from the thermal annealing experiment. This discrepancy can be explained in one
of two ways. First, the nanoparticle heating model described here is an obvious simplification of all the heating and cooling mechanisms occurring during nanoparticle synthesis in a low-temperature plasma. Specifically, it has been shown that surface reactions can have a significant impact on the heating of relatively large particles (i.e. particles greater than 5 nm in diameter) in the Si/H system. However, a recent report on Al₂O₃ atomic layer deposition on Y₂O₃-stabilized ZrO₂ nanoparticles found that temperature excursions due to the formation of Al₂O₃ on the surface are only on the order of 10s of Kelvin for nanoparticles of a similar diameter, suggesting the contribution from surface reactions may be less significant in the Al/O system. Second, the particles in this

Figure 3.7. XRD spectra of Al₂O₃ NCs at various powers. XRD spectra for alumina nanoparticles synthesized at various RF powers. The particle temperature calculated by Eq. 3.4 corresponding to each synthesis power is in parentheses.
process are growing while being heated and the growth mechanism is not completely understood. As a result, it is possible that the particles experience large excursions from the average particle temperature as they are growing and could become partially crystallized before growing to a point at which the average particle temperature is less than the crystallization temperature. Regardless, the power required to fully crystallize the population agrees well with the predicted particle temperature; and lesser applied powers appear to result in some amorphous fraction in the powder.

To characterize the amorphous fraction of the alumina nanoparticles as a function of the synthesis power, $^{27}$Al SSNMR experiments were carried out (under MAS) to determine the local coordination environment of the aluminium cations in the nanoparticles. The SSNMR spectra (showing just the central transitions) of samples prepared between 100 W and 400 W can be seen in Figure 3.8. In the case of alumina nanoparticles synthesized at 100 W, three peaks are present, appearing at approximately 2, 30, and 60 ppm corresponding to $^{[VI]}$Al, $^{[V]}$Al, and $^{[IV]}$Al species, respectively. Fitting of these peaks yielded the expected isotropic chemical shifts for the respective aluminium coordination numbers (Appendix 1). The presence of $^{[V]}$Al is an indication the sample has an amorphous structure.$^{80-82}$ At 200 W, the $^{[V]}$Al peak diminishes almost entirely consistent with crystalline phases of Al$_2$O$_3$, with a small presence of an amorphous fraction, in agreement with the XRD analysis. At powers of 300 W and 400 W, the SSNMR patterns are similar and contain only 4- and 6-coordinate aluminium cations, consistent with the crystal structure of $\gamma$-Al$_2$O$_3$.$^{82,83}$ The SSNMR peaks were fit using the Czjzek model,$^{84-86}$ in a similar method to previous studies on amorphous and $\gamma$-Al$_2$O$_3$ (Appendix 1).$^{74}$ The ratio of tetrahedral to octahedral aluminium sites is found to be similar for all samples. The disappearance of the 5-coordinate $^{[V]}$Al
resonance at 300 W and 400 W further supports the conclusion that the particles become crystallized in the \( \gamma \) phase at powers 300 W or greater. Taken together with the XRD patterns in Figure 3.8, the results indicate the absence of other crystallographic phases of alumina such as: \( \delta \)-, \( \theta \)- and \( \alpha \)-\( \text{Al}_2\text{O}_3 \) in these samples.

![Graph showing resonance at 300 W and 400 W](image)

**Figure 3.8. Solid-state \( ^{27}\text{Al} \) NMR spectra of \( \text{Al}_2\text{O}_3 \) NCs.** \( ^{27}\text{Al} \) MAS solid-state NMR spectra at 14 T of the central transitions of as-synthesized alumina nanoparticles synthesized at various applied RF power. The MAS rotational frequency (\( \nu_R \)) is 35 kHz. The data have been normalized to the highest intensity peak.

### 3.4 Conclusions

In this work, we developed an approach to predict NTP synthesis conditions that yield crystalline nanoparticles. We propose a simple particle heating model that yields an average particle temperature experienced in the NTP as a function of applied power. The model is unique in that it requires no complex plasma diagnostics for the inputs, but only depends on the reactor geometry, background gas temperature, pressure, and gas composition. The synthesis of \( \text{Al}_2\text{O}_3 \) nanoparticles was carried out to study the applicability of the model to a high crystallization temperature material. Specifically, the concept was demonstrated that there is a threshold power
at which the particle temperature is equal to the crystallization temperature, above which the entire population of particles becomes crystalline. Solid-state NMR of $^{27}$Al helped establish the aluminium cation coordination environments, in non-crystalline samples (prepared at lower RF power), when XRD was unable to lend structural insights. The Al$_2$O$_3$ nanoparticles were found to become increasingly crystalline with increases in power up to 300 W, at which point further increases in power did not have a significant effect on the crystalline fraction of the ensemble. This result is consistent with the idea of a threshold power for crystallization and was in good agreement with the predicted value of approximately 325 W from the particle heating model. This chapter provides a framework for designing NTP synthesis processes for high crystallization temperature materials by predicting conditions necessary to reach particle temperatures sufficient for nanocrystal formation.
Chapter 4

Consolidation of Nanocrystal-Based Nanocomposite Thin Films

4.1 Introduction

Thin films comprised of nanocrystals (NCs) are promising for several applications. In addition to enhanced properties at the nanoscale, high-throughput synthesis and scalable deposition techniques are also attractive features of NC-based thin films. One deposition method involves the gas-phase synthesis of NCs immediately followed by supersonic impaction onto a translating substrate, resulting in relatively dense and contamination free NC films. Several groups have built upon that foundation and utilized atomic layer deposition (ALD) to infiltrate the voids present in the NC film and form NC-based nanocomposites. Removal of the voids in the film comprised of nanocrystals has been shown to not only improve long term stability, but perhaps more interestingly, to obtain a high degree of tunability over NC film properties such as electrical conductivity, optical response, and mechanical properties. One desirable aspect of the ALD process to this end is the capability of depositing a conformal coating in high aspect ratio nanostructures, enabling a uniform modification to the
internal surface of the NC network. However, achieving the desired conformality of the ALD film on the surfaces of the nanocrystals requires judicious specification of the process parameters. Various possible process outcomes, both desirable and undesirable, are illustrated in Figure 4.1 for different combinations of ALD process parameters.

To achieve a conformal ALD coating, the precursor must be supplied in a sufficient exposure, that is pulse time multiplied by reactant partial pressure, to completely saturate the surface.\textsuperscript{96,97} One method of determining the required precursor saturation exposure is through experimental trial and error. However, optimization in this way is both time and resource expensive, especially in the context of coating high surface area nanostructures with long process times. There is a need to predict process parameters that produce a conformal coating, and significant modeling work has been done over the past two decades with that aim.\textsuperscript{97–107} Gordon \textit{et al.} introduced this concept for high aspect ratio circular vias with a kinetic model for the pulse exposure required to achieve conformal coating.\textsuperscript{98} Expanding upon this work, Yanguas-Gil and Elam derived a generalized model to calculate the pulse time required for a conformal coating of a nanostructure using only two dimensionless parameters, the precursor excess number, $\gamma$, and the Thiele modulus squared, $\alpha$.\textsuperscript{99,100}

Several numerical studies have utilized kinetic Monte Carlo simulations,\textsuperscript{101–103} which have proven successful in matching experimentally observed depth profiles. These simulations are limited in their applicability to the geometry studied (i.e. cross section and aspect ratio) and the specific ALD chemistry simulated. For these reasons, and additionally motivated by a desire to reduce computational expense, analytical approximations that allow for the prediction of ALD process parameters in high aspect ratio nanostructures are preferable.
After successful saturation of the surface during the reactant pulse step, all non-chemisorbed species, for example physisorbed reactants and reaction by-products, must be allowed to completely evacuate the nanostructure during the purging step\textsuperscript{96,97,104,105,108} Considering the feature scale diffusion-reaction model described above for the pulse step, one might think the purge step would require a similar time for molecular diffusion out of the nanostructure. However, that thought is inconsistent with experimental observations in thermal ALD processes, specifically those involving H\textsubscript{2}O\textsuperscript{96,97,109} For example, it has been demonstrated by Deshpande et al. that purge times necessary to maintain self-limiting growth during ALD of hafnium oxide onto flat Si substrates are a factor of 15 greater than reactant pulse times\textsuperscript{110}

Despite extensive work in the literature concerning reactant pulse models, significantly less effort has been put into modeling the purge step. Specifically, the purge step is commonly only modeled through macroscopic computational fluid dynamics (CFD) simulations at the reactor scale\textsuperscript{106,107} While reactor-scale models may be suitable in many instances for features such as circular vias, highly porous media with tortuous 3D networks of nanopores require substantially longer purge times to entirely evacuate the nanostructure\textsuperscript{97,104,111,112} If the purge step is too short, then it is expected that the pores in the nanocomposite will become clogged near the surface of the film (Figure 4.1e). To achieve a dense nanocomposite by ALD infilling with minimal residual porosity, the coating must remain conformal throughout the entire ALD process. The structural properties of a NC film such as the NC diameter, porosity, and film thickness all affect the requisite ALD process parameters. Required pulse and purge times increase with: increasing film thickness, decreasing NC diameter, and decreasing initial porosity. The number of cycles required for complete infill increases with increasing NC diameter and increasing porosity.
In this work, we present a simple geometric model describing a representative pore in NC films that allows for prediction of reactant pulse time, purge time, and number of cycles required to obtain a fully dense nanocomposite. This model uses three readily obtainable film parameters, which can be measured before infill, as inputs: film thickness, NC diameter, and NC volume fraction. A full set of analytical equations that allow specification of the number of ALD cycles, pulse time and purge time were obtained for fabrication of fully dense nanocomposites via ALD infill of films comprised of nanocrystals. Experiments to validate model predictions were carried out by infilling films comprised of either gallium nitride (GaN) or aluminum oxide (Al$_2$O$_3$) NCs with either zinc oxide (ZnO) or Al$_2$O$_3$, respectively.

### 4.2 Experimental

#### 4.2.1 Nanocrystal Synthesis and Film Deposition

GaN NCs were synthesized using the previously reported nonequilibrium-plasma-aerotaxy (NPA) method and apparatus. The Ga source aerosol was fed to the plasma reactor at a rate of...
1.00-1.24 mg/min, which corresponded to an evaporator temperature of approximately 1500 K. During the synthesis, total gas flow was maintained at 520 sccm with a 25:1 Ar:N₂ ratio. Pressure in the plasma region at these conditions was 4.2 torr, resulting in an estimated particle residence time in the plasma of 18 ms.

The Al₂O₃ NCs were synthesized in the reactor described in Chapter 3 and depicted in Figure 3.2. Pressure in the headspace of the bubbler was maintained at 225 torr by adjusting a needle valve immediately downstream, resulting in an estimated TMA feed rate of 1.2 sccm carried by 20 sccm Ar. Just upstream of the plasma zone, an additional stream containing 125 sccm Ar and 7 sccm O₂ was co-fed with the diluted TMA stream into the plasma. The plasma was maintained via capacitively coupled radiofrequency power at 400 W and the reactor pressure was 7.1 torr. An additional 700 sccm of Ar was introduced after the plasma along the centerline of flow to adjust the residence time in the plasma to 370 ms.

Films comprised of GaN and Al₂O₃ NCs were deposited by accelerating the aerosol streams exiting the plasma zone through a rectangular slit nozzle. The custom-made nozzle had a cross-section of 1.2 mm x 20 mm and was 10 mm in length. This geometry resulted in a pressure ratio across the nozzle of 5.28 in the case of GaN and 5.91 in the case of Al₂O₃, resulting in a particle beam with velocities on the order of hundreds of m/s. Particle beams were then impacted on 1 cm x 1 cm solvent cleaned Si substrates 5 mm downstream of the nozzle exit that were translated back and forth until the desired thickness was obtained.
4.2.2 Nanocomposite Fabrication by ALD

ALD was carried out in a home-built, tubular, hot-wall reactor described in a previous publication and depicted in Figure 4.2. Prior to carrying out a deposition, the NC films were loaded into the hot zone of the reactor and allowed to degas and reach thermal equilibrium for a minimum of 30 minutes. All depositions were carried out at 180 °C unless stated otherwise under a constant gas flow of 30 sccm Ar. Diethylzinc (DEZ, Strem, Newburyport, MA) and TMA were used as the metal-containing precursors for ZnO and Al₂O₃ depositions, respectively. In each case, a complete ALD cycle consisted of a deionized water (18.2 MΩ · cm) pulse in the range of 0.2 to 1.0 s, an Ar purge in the range of 2.0 to 150 s, a metalorganic (DEZ/TMA) pulse in the range of 0.2 to 1.0 s, and a final Ar purge in the range of 2.0 to 150 s. The growth rates for the ZnO and Al₂O₃ processes were determined by spectroscopic ellipsometry performed on films prepared using 300 cycles on polished Si to be 1.7 Å/cycle and 1.1 Å/cycle, respectively.

4.2.3 Electron Microscopy

Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were collected with a thermal emission microscope with a LaB₆ filament (JEOL JEM-2000 FX) operated at 200 kV accelerating voltage. The samples were prepared by mounting carbon-coated copper grids (part number 01824, Ted Pella, Redding CA) to the translating...
substrate holder in the impaction stage. Size distributions were obtained using ImageJ software to calculate the spherical equivalent diameter of at least 150 particles.

Both as deposited NC films and NC/ALD nanocomposites were cleaved using a diamond scribe to obtain cross-sectional scanning electron microscopy (SEM) images allowing for film thickness measurements. All SEM images were obtained edge-on using a ThermoFisher Quattro S ESEM operating at an accelerating voltage of 15 kV. Elemental mapping and line-scan profiles were also obtained in the SEM, which was equipped with an energy-dispersive X-ray spectrometer (EDXS) (Aztec Live X-Max, Oxford Instruments, High Wycombe, UK). All EDXS experiments were collected while operating the SEM at an accelerating voltage of 8 kV.

4.2.4 Spectroscopic Ellipsometry

Volume fractions of NC films and NC/ALD nanocomposites were measured using an α-SE spectroscopic ellipsometer (J.A. Woollam, Lincoln NE) with an incident angle of 70°. Ellipsometry also served as an independent measure of film thickness to cross-sectional SEM images. The ellipsometry spectra were fit with a Bruggeman effective medium approximation (EMA) in the wavelength range of 400 to 800 nm (Figure 4.3). Every sample was modeled as a Si substrate, followed by a 1.6 nm native oxide layer, and finally the EMA layer. In the case of as-deposited films and Al₂O₃ nanocomposites, the EMA layer was a two-component film consisting
of the solid material (GaN or Al₂O₃) and voids. For the GaN/ZnO nanocomposites, the EMA layer was a three-component film consisting of GaN, ZnO, and voids.

![Graph showing SE data before and after infill, dashed lines indicate EMA model fit, showing good agreement with the data.]

**Figure 4.3. Spectroscopic ellipsometry data.** SE data before and after infill, dashed lines indicate EMA model fit, showing good agreement with the data.

### 4.2.5 X-Ray Fluorescence

A Spectro Midex MID01 X-ray fluorescence (XRF) spectrometer was calibrated using thin films of GaN (450 nm, 530 nm MTI Corporation) and ZnO (prepared by ALD). All XRF spectra were collected for 120 s at an accelerating voltage of 47.8 kV and beam current of 0.5 mA. The XRF measurements provided an independent measure of GaN NC volume fraction in as-deposited NC films and the mass of Zn deposited as a function of ALD cycles. A custom MATLAB script was used to fit the emission peak areas in each XRF spectrum (Appendix 2).

### 4.3 Results and Discussion

### 4.3.1 Structural Characterization of NC Films

Process parameters required to deposit a conformal coating onto films comprised of nanocrystals by ALD depend on the geometrical properties of the film. A necessary and sufficient set of input parameters for the model described in this chapter is: 1) average NC diameter, 2) volume fraction of nanocrystals in the film before any ALD deposition, and 3) NC film thickness,
which is approximately constant during the infill process because the thickness is much larger than the nanocrystal diameter. NC size distributions were measured by analyzing TEM images. Film thickness and NC volume fraction were characterized by redundant methods to reach an accurate value. Thickness was characterized by spectroscopic ellipsometry and cross-sectional SEM imaging, while NC volume fraction was characterized by spectroscopic ellipsometry and XRF. GaN and Al₂O₃ nanocrystals were observed using TEM and SAED (Figure 4.4a).
Figure 4.4 Electron Microscopy of Nanocrystals and Films. TEM images and SAED patterns of GaN (a) and Al₂O₃ NCs. (c) Size distributions for GaN and Al₂O₃ NCs shown in (a) and (b), respectively. SEM cross-sections of films comprising GaN NCs (d) and Al₂O₃ NCs (e) deposited via inertial impaction.
In both cases, the nanocrystal size distribution was fit with a lognormal distribution (Figure 4.4b) to calculate mean particle diameter, $\langle d_p \rangle$, and geometric standard deviation, $\sigma_g$. Analysis of the SAED patterns revealed the as-synthesized NCs to be crystalline hexagonal GaN and $\gamma$-Al$_2$O$_3$. Thickness measurements of films comprised of these NCs by direct observation of cross-sections using SEM (Figure 4.4c) showed good agreement with thickness obtained from an EMA model fit of spectroscopic ellipsometry data which is consistent with a recent report demonstrating Al$_2$O$_3$ NC films of this type are well approximated by this type of EMA model. NC volume fractions obtained from EMA model were ~35% for GaN and ~30% for Al$_2$O$_3$. A complete summary of the structural parameters for the GaN and Al$_2$O$_3$ NC films is presented in Table 4.1.

Table 4.1. Structural parameters for GaN and Al$_2$O$_3$ NC films. Film thickness measured by cross-section (SEM) and spectroscopic ellipsometry (EMA) fit are presented for comparison.

<table>
<thead>
<tr>
<th>Property</th>
<th>GaN</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Diameter</td>
<td>15.5 nm</td>
<td>10.5 nm</td>
</tr>
<tr>
<td>SEM Thickness</td>
<td>1.05 μm</td>
<td>1.65 μm</td>
</tr>
<tr>
<td>EMA Thickness</td>
<td>1.02 ± 0.02 μm</td>
<td>1.66 ± 0.03 μm</td>
</tr>
<tr>
<td>Initial Porosity</td>
<td>64.5 ± 2.1 %</td>
<td>70.1 ± 1.9 %</td>
</tr>
</tbody>
</table>
4.3.2 Cycle Number for Complete ALD Infill

To achieve a conformal ALD coating, the precursor molecules must be allowed sufficient time to enter at the mouth of the high aspect ratio feature and then diffuse the entire length to the base. In the case of a NC film, the definition of a singular “feature” is nontrivial since there exists a complex 3D network of pores to be coated (Figure 4.1a). To resolve the situation, we consider the rate-limiting feature to be an uninterrupted path of void space from the surface of the NC film to the substrate (Figure 4.5a). It is immediately apparent that the path of molecular transport is longer than film thickness because the feature is tortuous. Percolation theory is a suitable method to quantify the tortuosity, as it describes spatial dimensions for systems consisting of large numbers of randomly connected objects.\textsuperscript{113} Furthermore, it has been shown previously that the electrical conductivity of inertially-impacted NC films can be predicted by applying a links-nodes model derived from percolation theory, and so there is confidence in the theory yielding physically meaningful results.\textsuperscript{91}

The links-nodes model can be used to determine the ratio of actual path length between two sites along a connected cluster to the straight-line path length. This ratio describes the tortuosity, \( \tau \), of the connected sites and is given by,

\[
\tau = (\phi - \phi_c)^{-\xi}
\]  

(4.1)

where \( \phi \) is volume fraction of conducting phase (i.e. porosity), \( \phi_c \) is the percolation threshold, and \( \xi \) is the critical exponent.\textsuperscript{114} The percolation threshold defines the minimum porosity at which an infinite cluster of voids (i.e. uninterrupted path of voids) exists between the surface of the NC film and the substrate. The randomly packed film can be approximated as a face-centered cubic lattice of sites, which are occupied or unoccupied with a probability that is the volume fraction of NCs
or porosity respectively. The percolation threshold and critical exponent for a face-centered cubic lattice have theoretically predicted values of 0.15 and 0.99, respectively.\textsuperscript{113,114} Thus, the path length through a representative pore in a NC film can be calculated by,

\[
L_{\text{pore}} = L_{\text{film}} (\phi_{\text{void}} - 0.15)^{-0.99}
\]  \hspace{1cm} (4.2)

where \( L_{\text{film}} \) and \( \phi_{\text{void}} \) are the thickness and porosity of the NC film, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{Schematic of Representative Pore Model. Schematic of nanostructure geometry with representative pore outlined in red (a) and depiction of stretching tortuous pore into a cylinder of diameter \( d_{\text{pore,0}} \) along the centerline (b). The height of the tortuous pore is equal to the thickness of the NC film, \( L_{\text{film}} \), and is scaled by the tortuosity factor, \( \tau \), to give the cylindrical equivalent pore height, \( L_{\text{pore}} \). The ALD coating on the pore, depicted in red, has thickness \( d_{\text{ALD}} \).}
\end{figure}

Considering the application of a percolation theory model, one might initially assume the diameter of this representative pore to be on the order of the lattice constant (i.e. NC diameter); however, simply equating the two seems implausible as the effective pore diameter should increase with an increase in porosity. To account for this, the pore diameter, \( d_{\text{pore}} \), is calculated by
\[ d_{\text{pore}} = d_{\text{NC}} \left( \frac{\phi_{\text{void}}}{\phi_{\text{NC}}} \right)^{1/3} \]  

where \( d_{\text{NC}} \) and \( \phi_{\text{NC}} \) are the NC diameter and volume fraction, respectively. Thus, the pore can be represented by a cylinder of diameter described by Eq. 4.3 and length equivalent to the distance along the centerline of the tortuous path (Figure 4.5b) described by Eq. 4.2.

To ascertain the suitability of this geometric description, XRF was used to monitor the intensity of the Zn Kα peak during the infill of a GaN NC film with ALD ZnO, and the result was compared to the expectation of the geometrical model. If the growth is conformal, then the expectation is that after a minimum number of cycles, the pores will completely fill in. The model can be used to formulate expected values for that minimum number of cycles. As the film fills in, different slopes should be observed in a plot of ALD material added as a function of the number of cycles. Experimentally, three distinct slopes were observed when the measured Zn XRF intensity was plotted as a function of ALD cycle number for pulse and purge times that resulted in conformal growth (Figure 4.6). The lower slope in the first several cycles can be described by a nucleation delay in the growth of ALD ZnO.\(^{112}\) For intermediate cycle numbers, the slope is much higher as a result of the significant surface area enhancement when coating the internal nanostructure of the film comprised of nanocrystals. Finally, the slope becomes shallower after the pores are filled and the ALD ZnO was deposited on the topmost surface of the dense GaN/ZnO nanocomposite.
The expected amount of conformal ALD coating added to the network can be modeled as a function of the initial geometrical parameters of the film comprised of nanocrystals and the number of cycles. Assuming the length of the pore is much larger than the pore diameter, the volume of the pore after a given thickness of ALD coating is deposited can be calculated by

\[
V_{pore,f} = \frac{\pi L_{pore}}{4} (d_{pore,0} - 2d_{ALD})^2
\]  

(4.4)

where \(d_{pore,0}\) is the initial pore diameter calculated by Eq. 4.3. The ALD coating thickness, \(d_{ALD}\), is the product of number of ALD cycles (\(n_{cycles}\)) and growth per cycle (\(GPC\)). Combining Eqs. 4.2-4.4, the pore volume after a given number of ALD cycles is

\[
V_{pore,f} = \frac{\pi L_f}{4} (\phi_{void,0} - 0.15)^{-0.99} \left[ d_{NC} \left( \frac{\phi_{void,0}}{\phi_{NC,0}} \right)^{1/3} - 2n_{cycles} GPC \right]^2
\]  

(4.5)

where the subscript 0 denotes the value of the parameter before ALD coating, and \(d_{NC}\) is the initial NC diameter. Given that the change in pore volume is equivalent to the negative of the volume of

---

**Figure 4.6 Integrated Zn XRF peak area as a function of ALD cycle number.** Zn XRF peak area as a function of ALD cycle number (black circles). Predicted change in mass of zinc from cylindrical pore infill model (orange band).
ALD material deposited, Eq. 4.5 can be combined with a scaling factor, $k_{\text{eff}}$, obtained from XRF calibration (Appendix 2) for ALD ZnO to predict the evolution of the Zn XRF signal as a function of ALD cycles: $I_{\text{XRF}} = k_{\text{eff}} \phi_{\text{void,0}} [1 - (d_{\text{pore,0}} - 2n \cdot \text{GPC})^2 / d_{\text{pore,0}}^2]$. The initial pore diameter was calculated by Eq. 4.3 using the void volume fraction measured by spectroscopic ellipsometry. The upper and lower bounds of the confidence interval for $\phi_{\text{void}}$ resulted in initial pore diameters of 19.7 nm and 18.2 nm, respectively, which in turn determined the band in Figure 4.6.

Agreement was obtained between Eq. 4.5 and the experimental data after a small horizontal offset was included to account for the nucleation delay (Figure 4.6). Hence, this geometric description appears to model the pores in the film comprised of nanocrystals with reasonable accuracy, and it is therefore accepted. Having accepted the geometrical description, Eq. 4.5 can be used to predict the number of ALD cycles required to achieve a desired final porosity when the growth is conformal. For example, solving Eq. 4.5 for the number of cycles resulting in $V_{\text{pore, f}} = 0$ gives the cycle number required to completely infill a NC film.

### 4.3.3 Pulse Time to Saturate Surface

The pore geometry defined in the preceding section can be used to predict the pulse time required to conformally coat films comprised of nanocrystals. GaN NCs coated with ZnO were used as a model experimental system due to their excellent complementary x-ray fluorescence spectra. The work of Yanguas-Gil and Elam\textsuperscript{99,100} demonstrates the saturation pulse time in a nanostructured substrate can be calculated as,

$$t_c = \frac{L^2}{D_T} \left(1 - \frac{\log(1-c)}{\alpha}\right) \quad (4.6)$$
where $L$ is the length of the nanostructure, $c$ is the desired fractional coverage at the base of the feature, and $D$ is the diffusion coefficient. The dimensionless parameters $\alpha$ and $\gamma$ are the Thiele modulus squared and precursor excess number, respectively. The first step in applying Eq. 4.6 to the infilling of NC films is selecting the appropriate diffusion coefficient. Given the low pressure of the ALD process, and the small pore diameter, transport takes place in the free molecular regime. Molecular transport in this regime is dominated by Knudsen diffusion and the diffusion coefficient is given by

$$D_{Kn} = \frac{D_{pore}}{3} \left( \frac{8k_B T}{\pi m_p} \right)^{1/2}$$

(4.7)

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature of the ALD process, and $m_p$ is the mass of a single precursor molecule. The pore diameter, $d_{pore}$, is taken as the pore diameter during the last ALD cycle and can be calculated by $d_{pore,0} = 2n \cdot GPC$ where $d_{pore,0}$ is calculated by Eq. 4.3. In the case of a complete infill, the pore diameter can be taken to be a molecular diameter of the precursor being considered as this can be considered the smallest possible pore diameter where transport can still occur.

In Eq. 4.6, the precursor excess number, $\gamma$, describes the ratio of precursor molecules in the nanostructure to the total number of surface reaction sites. This number is representative of the entire nanostructure surface to be coated and thus the entire film comprised of NCs must be considered. The number of precursor molecules in the nanostructure was calculated as the product of total volume of voids in the NC film and concentration of precursor at the pore mouth:

$$V_{vold} C_0 = \frac{L_{film} A_{f} \phi_{vold} P_p}{RT}$$

(4.8)
The NC film thickness and projected area on the substrate are given by $L_{film}$ and $A_f$, respectively, and $P_p$ is the precursor partial pressure measured during the pulse. The number of precursor sites was calculated by dividing the total nanostructure surface area by the average adsorption surface site area. Total surface area of the nanostructure was calculated by treating particles as spherical and estimating the total number of particles from the volume fraction of NCs in the film. The average surface site area, $s_0$, can be calculated from the measured saturation growth per cycle on a flat surface.$^{100,117}$ The Thiele modulus squared, $\alpha$, is the ratio of characteristic diffusion time to characteristic reaction time. This was calculated by assuming a constant reaction probability, $\beta_0$, due to constant temperature during the reaction as,$^{104,118}$

$$\alpha = \frac{L_{pore}^2}{D_{Kn}} \frac{v_{th} s}{4 \beta_0}$$  \hspace{1cm} (4.9)

where $v_{th}$ is the mean thermal velocity of the precursor molecule and $s$ is the surface area per unit volume in the NC film. Due to the relative size of the reactant species, the DEZ pulse can be considered the limiting half reaction as the diffusion coefficient of $H_2O$ is nearly a factor of 2 larger. The values used for calculations of saturation pulse time in the as-deposited GaN NC films are summarized in Table 4.2.
Table 4.2. Parameters used in calculation of saturation pulse time using Eq. 4.6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{DEZ} )</td>
<td>40.1 Pa</td>
</tr>
<tr>
<td>( L_{pore} )</td>
<td>2.128 μm</td>
</tr>
<tr>
<td>( d_{pore} )</td>
<td>7.15 nm</td>
</tr>
<tr>
<td>( D_{Kn} )</td>
<td>( 5.619 \times 10^{-7} \text{ m}^2/\text{sec} )</td>
</tr>
<tr>
<td>( \beta_0 )</td>
<td>( 7 \times 10^{-3} ) (ref. 41)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( 1.6917 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>855.34</td>
</tr>
</tbody>
</table>

To experimentally determine saturation pulse time, the amount of ZnO deposited on six nominally identical GaN NC films was measured after 35 ALD cycles carried out with different pulse times. Given the self-limiting nature of the ALD process, the expectation is that for pulse times greater than the saturation pulse time, there should be no dependence of the amount of material deposited on the pulse time. Below the time required for saturation of the surfaces of the nanocrystals with precursor molecules, the amount of ZnO deposited is expected to increase with pulse time. The amount of material deposited by ALD, as characterized by the measured volume fraction of ZnO by spectroscopic ellipsometry, increased with increasing pulse time until 0.5 s, above which \( \phi_{ZnO} \) remained constant with further increases in precursor pulse time (Figure 4.7).
This result suggests that a pulse time of 0.5 s is sufficient to completely saturate the surface for all of the 35 cycles, consistent with the predicted saturation pulse time of 0.48 s by Eq. 4.6. It should be noted that the prediction from Eq. 4.6 is subject to the uncertainty in the measured values of $L_{film}$ and $\phi_{void}$ as well as the estimated value of $\bar{s}$. Given the uncertainties in Table I and an assumed 10% uncertainty in $\bar{s}$, the resulting uncertainty in $t_c$ is approximately 100 ms. Additionally, the measured volume fraction of ZnO after 35 cycles is in good agreement with the prediction based on the proposed cylindrical pore geometry and Eq. 4.6. The conclusion is further supported by XRF measurements acquired from the samples, where the same trend was seen in the Zn Kα peak intensity as a function of pulse time. The extent to which the ZnO coating penetrated into the GaN NC films was characterized by SEM and EDXS (Figure 4.8). SEM-EDXS mapping of the cross section (Figure 4.8c) shows Zn penetrates the entirety of the GaN NC film.
A line scan of the same cross section (Figure 4.8d) revealed that the Ga and Zn profiles trace one another over the entire thickness of the film, consistent with a conformal coating.

Figure 4.8 Cross-sectional SEM of GaN/ZnO composites with elemental mapping. SEM cross-section of GaN NC film before (a) and after (b) infill with 35 cycles of ALD ZnO. EDXS elemental map (c) and line scan elemental profiles (d) of the composite shown in (b).

4.3.4 Required Purge Time for Evacuation

To achieve a conformal coating, the purge step must be sufficiently long that excess precursor is evacuated from the tortuous film, and pore clogging is prevented (Figure 4.1). Evacuation of the pores was modeled by considering diffusion in the gas phase and on the surface, and most importantly, desorption kinetics of excess physisorbed precursor. Films comprised of Al₂O₃ NCs infilled with Al₂O₃ was chosen as an experimental system for two primary reasons.
First, H\textsubscript{2}O mass transport in porous Al\textsubscript{2}O\textsubscript{3} is well documented in the literature\textsuperscript{119–122}. Second, the system simplifies the analysis of desorption kinetics and surface diffusion by only considering a single solid phase material. A schematic representation of the model used for the precursor transport during the purge step is depicted in Figure 4.9. The pore is considered a cylinder with length \( L\text{pore} \) and radius \( R\text{pore} \). The pore is divided into \( n \) finite slices of height \( \Delta z \), where the \( i^{th} \) slice contains the pore walls, surface phase molecules, and gas phase molecules between the heights \( z \) and \( z + \Delta z \). Molecules of water present in the pore are considered as belonging to one of two phases: gas phase molecules that undergo Knudsen diffusion, or surface phase (physisorbed) molecules that undergo surface diffusion. Partitioning between these two phases occurs via adsorption and desorption.

The diffusional molar fluxes (mol/m\textsuperscript{2} s) were calculated by Fick’s first law as \( J = -DdC/dz \), where \( D \) is the appropriate diffusion coefficient. In this case, the flux of gas phase molecules in and out of every slice can be calculated in a straightforward manner by using the Knudsen diffusion coefficient as calculated by Eq. 4.7 and using concentrations calculated by the ideal gas law \( C = P/RT \). The surface diffusion coefficient, \( D_s \), is typically represented with an Arrhenius-type dependence on temperature as:\textsuperscript{123–126}

\[
D_s = D_{s0} e^{-E_s/RT}
\] (4.10)
where $D_{S,0}$ is the surface diffusivity pre-exponential factor and $E_s$ is the activation energy for surface diffusion. The activation energy can be calculated from the adsorption energy by, $E_s = aE_{ads}$, where $0.3 < a \leq 1$ for physisorbed gas molecules.\textsuperscript{124,126} Tamon \textit{et al.} demonstrated for multiple adsorbate/adsorbent systems including H$_2$O/Al$_2$O$_3$ that the surface diffusivity pre-exponential factor can be empirically approximated as $D_{S,0} = 3.65 \times 10^{-6} S_T^{0.65}$ and $a = 0.49$, where $S_T$ is the specific surface area (m$^2$/kg) of the porous media.\textsuperscript{119} Use of those empirical relationships results in a surface diffusion coefficient of $D_s = 4 \times 10^{-5}$ m$^2$/s in the Al$_2$O$_3$ NC films infilled in this work.

\textbf{Figure 4.9 Transport mechanisms in pore during purge step.} Schematic of cylindrical pore with length, $L_{pore}$, and radius, $R_{pore}$, along with transport mechanisms for water vapor considered in finite difference model of purge step. The flux due to Knudsen diffusion and surface diffusion in and out of each pore slice are given by $J_g$ and $J_s$, respectively. Partitioning between the gas and surface phases occurs due to the flux of gas phase molecules that adsorb onto the surface, $J_{ads}$, and the desorption flux of surface phase molecules, $J_{des}$.

The surface concentration of adsorbed water molecules during the purge step requires a description of the adsorption/desorption kinetics. The rate of change of surface coverage of physisorbed species, $\theta$, can be represented by a first-order Langmuir kinetic expression as,\textsuperscript{127}
\[
\frac{d\theta}{dt} = k_{ads} C_g (1 - \theta) - k_{des} \theta
\]  
(4.11)

where \( k_{ads} \) and \( k_{des} \) are temperature dependent adsorption and desorption constants, respectively, and \( C_g \) is the adsorbent concentration in the gas-phase. The adsorption and desorption constants have an Arrhenius-type temperature dependence and can be calculated as,

\[
k_{ads/des} = v e^{-\frac{E_{ads/des}}{RT}}
\]  
(4.12)

where the pre-exponential factor \( v \) is related to bond vibration frequency and can be typically assigned a value of \( v = 1 \times 10^{-13} \text{ s}^{-1} \).\text{120} Given sufficient adsorption and desorption data, this allows for a coupling of the surface diffusion fluxes and adsorption and desorption in each slice to monitor the change in surface coverage of a site during the purge step. The adsorption and desorption of \( \text{H}_2\text{O} \) on \( \text{Al}_2\text{O}_3 \) is well studied and thus the activation energies for these processes are known: \( E_{ads} = 143 \text{ kJ/mol} \) and \( E_{des} = 125 \text{ kJ/mol} \).\text{120–122} The fluxes in and out of the \( i^{th} \) slice of the pore can then be combined with partitioning between the gas and surface phase in each slice to yield the final finite difference equations for each phase,

\[
C_{i,j+1} = C_{i,j} + \Delta t D_{K_n} \left( \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta z^2} \right) - \Delta t \left( k_{ads} C_{i,j} RT (1 - \theta_{i,j}) + k_{des} \theta_{i,j} \right)
\]  
(4.13)

\[
\theta_{i,j+1} = \theta_{i,j} + \frac{\Delta t D_{S_n}}{2} \left( \frac{\theta_{i,j+1} - 2\theta_{i,j} + \theta_{i,j-1}}{\Delta z^2} \right) - \Delta t \left( k_{ads} C_{i,j} RT (1 - \theta_{i,j}) + k_{des} \theta_{i,j} \right)
\]  
(4.14)

where \( C_{i,j} \) and \( \theta_{i,j} \) are the gas phase concentration and surface phase fractional coverage, respectively, in the \( i^{th} \) slice of the pore during the \( j^{th} \) time step. The time step, \( \Delta t \), was set to 0.5 ms for all simulations while the width of each slice, \( \Delta z \), was set to 75 nm. The initial condition for the gas phase is taken to be the partial pressure of water during the pulse.
Very quickly after the purge begins, the partial pressure of water vapor diminishes. That vapor is constantly swept by an inert gas at the pore mouth and thus transport is unidirectional out of the pore during purging. The initial and boundary conditions for the gas phase can be summarized as,

\[ P(t = 0, z) = P_{p,0}, \forall z \]  
\[ P(t, z = L_{pore}) = 0, \forall t \geq 0 \]  
\[ \frac{dP}{dz} \bigg|_{z=0} = 0, \forall t > 0 \]  

The initial fractional surface coverage is taken to be that predicted by Langmuir theory for equilibrium of the surface with the initial precursor partial pressure \( P_{p,0} \). The initial and boundary conditions for the surface phase can be summarized as,

\[ \theta(t = 0, z) = \frac{\left(k_{ads}/k_{des}\right)P_{p,0}}{1 + \left(k_{ads}/k_{des}\right)P_{p,0}}, \forall z \]  
\[ \frac{d\theta}{dz} \bigg|_{z=t_{pore}} = -k_{des}\theta, \forall t > 0 \]  
\[ \frac{d\theta}{dz} \bigg|_{z=0} = 0, \forall t > 0 \]  

Temperature is a significant parameter in the kinetics of all three transport processes considered. The rates of surface diffusion and desorption increase exponentially with increasing temperature. Thus, the time required to reach a given surface coverage at the base of the pore decreases exponentially with increasing temperature. The predicted surface coverage as a function of purge time at the base of the pore is presented in Figure 4.10a for water desorbing from Al₂O₃, which limits the rate of our ALD process of interest. Temperature was found to have a significant
effect on the rate of H\textsubscript{2}O surface coverage, with a temperature increase of 40 °C resulting in an order of magnitude decrease in required purge time to reach the same fractional coverage. Considering the trend seen in temperature and the uniform predicted surface coverage across the pore, the main conclusion drawn from this finite difference modeling is that the purge time is dominated by the time required for water to desorb from the surface of the tortuous nanoporous sample. In other words, for geometrical values like the ones explored here, to achieve a conformal coating, the purge step, and indeed the entire ALD cycle, is limited by the rate at which water desorbs from the surface.

Since the purge step is limited by the rate of desorption, the required purge time to achieve a conformal film can be approximated as the time required to achieve a certain fractional coverage that is sufficiently low, which we have empirically found to be $\theta_f = 5 \times 10^{-3}$. Assuming the evacuation rate is limited by desorption, the purge time required to reach a given fractional coverage is:

$$t_{\text{purge}} = \frac{\ln \left( \frac{\theta_0}{\theta_f} \right)}{1 \times 10^{-13} e^{-\frac{E_{\text{des}}}{RT}}}$$

(4.21)

where $\theta_f$ is the final fractional of physisorbed molecules after the purge step. It is apparent that modeling desorption in this way will not predict a fractional coverage of zero in finite time, but it is a priori not clear what the desired fractional coverage should be after purging. To this end, experiments were carried out to measure residual porosity in Al\textsubscript{2}O\textsubscript{3} nanocomposites as a function of purge time at three temperatures. All ALD infills were carried out such that the total number of cycles ($n_{\text{cycles}} = 200$) and pulse times ($t_{\text{pulse}} = 1$ second) were sufficient to conformally coat the
nanostructure and completely infill the NC film with purge times for each temperature indicated in Table 4.3.

**Table 4.3.** Summary of ALD process parameters used in Al₂O₃/Al₂O₃ composite fabrication.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Predicted θ_f</th>
<th>Purge Time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.2650</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>0.1150</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>0.0425</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>0.0085</td>
<td>150</td>
</tr>
<tr>
<td>200</td>
<td>0.2650</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.1150</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.0425</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.0085</td>
<td>30</td>
</tr>
<tr>
<td>220</td>
<td>0.2650</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.1150</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.0425</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>0.0085</td>
<td>10</td>
</tr>
</tbody>
</table>

The measured residual porosity of the nanocomposite after 200 cycles of ALD infill is plotted in Figure 4.10b as a function of the expected surface coverage of water at the end of evacuation calculated using the experimental purge times. It was found that for predicted surface coverages of 0.0085 there was zero measured residual porosity. However, a decrease in purge time (i.e. increase in predicted surface coverage after purge step) resulted in an increase in residual porosity (Figure 4.10b). Another interesting result was that residual porosity followed the same trend with increased predicted fractional coverage at all three temperatures, consistent with the desorption limiting behavior predicted by the finite difference model. Thus, one can predict the purge time necessary for complete infill of a NC film with a conformal ALD coating analytically by Eq. 4.21.
after selecting a suitably low (i.e. $\theta_J = 5 \times 10^{-3}$) fractional coverage for the desired ALD process temperature (Figure 4.10c). There is a clear benefit to operating the ALD infill process at higher temperatures, since the rate of desorption, which limits the overall deposition rate, increases exponentially (Figure 4.10c) and therefore the time required to completely infill the network decreases exponentially (Eq. 21).
Figure 4.10 Purge time required to completely desorb H$_2$O. Fractional coverage (a) of H$_2$O at the base of the pore predicted in the finite difference model as a function of purge time. Hollow symbols in (a) represent purge times selected for experiments. (b) Residual porosity measured by ellipsometry after 200 cycles of ALD Al$_2$O$_3$ as a function of the predicted fractional coverage. (c) Comparison between finite difference model and Eq. (4.21) for a final surface coverage of 0.005 along with purge times required experimentally to observe dense nanocomposites with no residual porosity.
4.4 Conclusions

In this chapter, the ALD infill process of NC films was modeled to predict process parameters necessary for fabrication of dense NC-based nanocomposite films. Experiments were carried out with two nanocrystal systems: GaN NCs infilled with ALD ZnO and Al₂O₃ NCs infilled with ALD Al₂O₃. It was found that using readily obtainable NC film parameters as inputs, three criteria could be analytically approximated in order to fabricate dense nanocomposites. First, the number of ALD cycles must be greater than the number predicted using Eq. (5). Second, we demonstrated the minimum pulse time for complete saturation of the NC surface is accurately predicted using the representative pore geometry in Eqs. (2)-(4) coupled with Eq. (6). Third, a finite difference approach was demonstrated which accounts for surface diffusion, adsorption, and desorption in addition to gas-phase diffusion during purging. Interestingly, it was found in NC films of approximately 1 μm thickness, the purge step was limited by the desorption kinetics within the porous network. As a result, the purge time must exceed the value predicted by Eq. (21) to entirely evacuate the nanostructure and maintain self-limiting growth throughout the entire ALD process. In general, it was found that required pulse and purge times decrease with increasing NC diameter, increasing porosity of the NC film, decreasing film thickness, and increasing temperature; whereas, the total number of cycles increases with increasing initial NC film porosity and increasing NC diameter. These three criteria provide a basis for predicting thermal ALD process parameters necessary to fabricate dense NC-based nanocomposites.
Chapter 5

Nanocrystals as Seeds for Nanocomposite Crystallization

5.1 Introduction

Crystallization of amorphous materials is a common approach to production of polycrystalline materials of a desired composition. Understanding the behavior of this crystallization is especially important in ceramic materials, where materials are typically multicomponent and thus compositional changes may arise due to the crystallization process.\textsuperscript{129,130} In addition, reducing the energetic requirement to produce dense crystalline materials is another challenge in ceramics as the materials of most interest often have exceedingly high crystallization temperatures. One successful approach to lowering this energetic barrier is through seeding the crystallization process by introducing nanocrystals embedded in the amorphous material that act as nucleation sites for the crystallization process to propagate from.\textsuperscript{131} In the Si system for example, it has been demonstrated that nanocrystals synthesized in the vapor phase and co-deposited with amorphous CVD Si reduce the energy barrier for crystallization and increase the crystallization kinetics at the same temperature when compared to unseeded CVD films.\textsuperscript{132–134}
In the Al₂O₃ system, there has been a significant amount of effort put into lowering the barrier to producing polycrystalline α-Al₂O₃. This work primarily has focused on mixing powder of nano- or microcrystalline α-Al₂O₃ with some amorphous alumina synthesized by the sol-gel method or aluminum hydroxide precursor like boehmite and sintering. More recently, work has been done to understand the effect of a single seed on the crystallization of amorphous Al₂O₃ by drop-casting seed nanocrystals on the surface of the ALD layer. The resulting crystallization occurred as ellipses propagating outward from the seed nanocrystal and at much lower temperatures than typically required for amorphous to alpha transition in the alumina system. It is also worth noting that the typical progression of crystal structure in the Al₂O₃ system for vapor-phase amorphous films is amorphous, followed by γ, and then finally α.

One outstanding challenge facing production of nanocrystalline α-Al₂O₃ is achieving grain sizes less than 100 nm. One successful method that can produce ultrafine α-Al₂O₃ nanocrystals is through ball-milling. A major drawback to this technique however is that consolidation of the milled material results in rapid grain growth, leading to final grain sizes much larger than the starting powder. As a result, there have not been reported attempts of seeding Al₂O₃ crystallization with α-Al₂O₃ nanocrystals smaller than 50-100 nm. As an alternative approach, seed nanocrystals of grain size less than 20 nm of a suitable isomorphic material could be used.

In this chapter, the seeded crystallization of ALD Al₂O₃ grown on a network of nanocrystals is investigated. The effect of seed crystals is determined by comparing the x-ray diffraction of the same mass of ALD material grown in a planar configuration on Si to that grown supported on a network of nanocrystals. Crystallization of the ALD material was observed at temperatures where the matrix showed no signs of crystallization in the absence of nanocrystals. Furthermore, the crystal phase of the embedded nanocrystals determines the structure of the
resulting crystallized matrix. It was seen that in the presence of $\alpha$-Cr$_2$O$_3$ nanocrystals, the ALD matrix crystallized in the $\alpha$-phase and there was no crystallization in the $\gamma$-phase.

5.2 Experimental

5.2.1 Cr$_2$O$_3$ Nanocrystal Synthesis and Film Deposition

Chromium oxide nanocrystals were synthesized in a modified version of the tubular flow through plasma reactor described in Chapter 3. A representative schematic of the reactor is shown in Figure 5.1. The key modification was made in the metal-containing precursor delivery portion of the reactor, where the TMA bubbler was replaced by a sublimator containing chromium hexacarbonyl (CrCO$_6$, MilliporeSigma). The sublimator consisted of a 0.5 in. outer diameter stainless steel tube that was 2.5 in. long which contained the CrCO$_6$ powder. At either end of the 0.5 in. tube length, the sublimator was reduced to 0.25 in. outer diameter stainless steel tubing and 400 mesh stainless steel was placed in the reducers to confine the precursor powder. A sweeping flow of 100 sccm Ar was blown through the powder bed to sweep the sublimed vapor into the reaction zone of the plasma reactor. Electrical heating tape was used to heat the sublimator and gas line downstream of the sublimator until the glass discharge tube. The heated portion of the reactor was maintained at 50 °C during synthesis as measured by a thermocouple placed on the outside of the stainless steel tube housing the precursor powder. Applied radiofrequency power to the plasma was set at 175 W, and the reactor was maintained at a pressure of 7.5 Torr. The same impaction nozzle used for deposition of Al$_2$O$_3$ nanocrystal films in Chapter three was used to
accelerate the as-synthesized \( \text{Cr}_2\text{O}_3 \) aerosol onto translating Si wafer substrates with a deposition rate of \( \sim 300 \text{ nm/min} \) until a total thickness of 1.5 \( \mu \text{m} \) was achieved after 5 minutes of deposition.

**Figure 5.1. Schematic of \( \text{Cr}_2\text{O}_3 \) nanocrystal synthesis reactor.**

### 5.2.2 Atomic Layer Deposition

ALD was carried out in the previously described home-built reactor in Chapter 3. Prior to carrying out a deposition, the NC films were loaded into the hot zone of the reactor and allowed to degas and reach thermal equilibrium for a minimum of 30 minutes. All depositions were carried out at 180 °C under a constant gas flow of 30 sccm Ar. Trimethylaluminum (TMA) was used as the metal-containing precursor and \( \text{H}_2\text{O} \) provided the oxygen. In depositions where \( \text{Cr}_2\text{O}_3 \) nanocrystal networks were infilled, a complete ALD cycle consisted of a deionized water (18.2 MΩ · cm) pulse of 1.0 s, an Ar purge in of 150 s, a TMA pulse of 1.0 s, and a final Ar purge of 150 s. For depositions of \( \sim 650 \text{ nm thin films of Al}_2\text{O}_3 \) on Si, 6000 cycles of 0.2 s pulse followed by 15 s Ar purge for both \( \text{H}_2\text{O} \) and TMA half-reactions were carried out.
5.2.3 Thermal Annealing

Annealing of films were carried out in a closed-atmosphere tube furnace (Lindberg Blue M, ThermoFisher Scientific) continuously purged with 500 sccm of Ar flow. A mineral oil bubbler was positioned at the exit of the tube furnace to ensure no back-diffusion from the ambient. Films were placed in an alumina boat and loaded into the 50 mm diameter fused quartz tube which was evacuated and subsequently backfilled with Ar. After 30 minutes of Ar purging, the furnace was ramped to the setpoint temperature at a rate of 2.5 °C per minute. Samples were then annealed at the setpoint temperature for 2 hours, followed by a cooldown to room temperature over several hours while Ar remained flowing.

5.2.4 Electron Microscopy

TEM and scanning TEM (STEM) measurements were carried out on a JEOL JEM-2100F field emission transmission electron microscope. Samples were prepared by placing a TEM grid (01824, Ted Pella) on the impaction stage and quickly translating the stage once back and forth across the particle beam generated by the impaction nozzle. For both TEM and STEM measurements, the microscope was operated at an accelerating voltage of 200 kV. Bright field images were acquired in TEM mode that were used to count particles for a particle size distribution where the ImageJ software was used to fit an ellipse around particles and calculate the spherical equivalent particle diameter. Selected-area electron diffraction (SAED) patterns were also collected in TEM mode to determine crystallinity of the Cr$_2$O$_3$ nanocrystals. High-resolution images were acquired in STEM mode operating with a spot size of 1.0 nm.

5.2.5 X-Ray Diffractometry

X-ray diffraction (XRD) experiments were carried out to determine the crystallinity of as-synthesized Cr$_2$O$_3$ powder, nanocomposite films, and films comprised of entirely ALD Al$_2$O$_3$. All
XRD spectra were obtained using a Bruker D8 Advanced Diffractometer equipped with a Cu radiation source (Cu Kα λ = 1.541 Å). The spectra were collected over a range of 2θ from 33-55° with a step size of 0.02° and a dwell time of 0.75 s per step. During data collection, the sample stage was rotated at a speed of 15 revolutions per minute.

5.3 Results and Discussion

5.3.1 α-Cr₂O₃ Nanocrystal Synthesis and Film Deposition

Investigating the effect of crystal phase of the embedded nanocrystals on the seeding of crystallization in the matrix material necessitates samples with initial nanocrystal phases that align with stable crystal phases of the matrix material. To produce nanocrystals of diameter less than 15 nm that match the corundum structure of α-Al₂O₃, Cr₂O₃ was selected owing to its much lower crystallization temperature and <5% lattice mismatch as seen in Table 5.1. As-synthesized Cr₂O₃ nanocrystals were observed by TEM and SAED as seen in Figure 5.2. A size distribution of the particles was fit with a lognormal distribution of mean particle size, \( d_{p,g} \), of 13.06 nm and geometric standard deviation, \( \sigma_g \), of 1.28. STEM imaging revealed that lattice fringes extended to the edges of the particles, indicating individual particles were single crystals. Radial integration of SAED measurements indicated the nanocrystals were α-Cr₂O₃ and showed good agreement with the XRD patterns obtained from powder measurements of the nanocrystals.

Table 5.1. Crystal structure parameters and properties for α-Al₂O₃ and α-Cr₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>ρ (g/cm³)</th>
<th>T_{cryst} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃</td>
<td>4.81</td>
<td>4.81</td>
<td>13.12</td>
<td>3.87</td>
<td>~1100</td>
</tr>
<tr>
<td>α-Cr₂O₃</td>
<td>5.07</td>
<td>5.07</td>
<td>13.87</td>
<td>4.90</td>
<td>~650</td>
</tr>
</tbody>
</table>
Films comprised of nanocrystals produced by plasma-synthesis and supersonic impact deposition were from 1.5 microns in thickness and had an alumina volume fraction of 25%, as determined by spectroscopic ellipsometry using a Bruggeman effective medium approximation. Cross-sectional SEM imaging was used as a redundant means of confirming film thickness as seen in Figure 5.3. Nanocrystal networks were subsequently infilled via the ALD method detailed in Chapter 4, such that the measured residual porosity was 0%. STEM-EDX maps seen in Figure 5.3 revealed that the Al₂O₃ conformally coated the Cr₂O₃ nanocrystals as evident by the separation of the elements in addition to the stark Z-contrast in the bright field. Both SAED and HRTEM imaging indicated no signs of crystalline Al₂O₃ as-deposited, meaning crystalline α-Al₂O₃ was not grown epitaxially under these conditions. This is not surprising given previous reports of epitaxial growth on α-Cr₂O₃ requiring growth temperatures in excess of 450 °C.¹⁴³
Prior to understanding a seeding effect of the nanocrystals on the amorphous matrix material, one must first determine the crystallization behavior in the absence of the embedded nanocrystals. Thin films that were 650 nm thick of ALD Al₂O₃ were thus deposited on bare Si wafer substrates as measured by ellipsometry and SEM cross-section. Films of the unseeded amorphous ALD Al₂O₃ were then annealed at 400 °C and 700 °C for 2 hours in an Ar atmosphere. The ALD films were examined by ALD both as deposited and after thermal annealing as seen in Figure 5.4. No signs of crystallization was observed in any of the samples, indicating annealing at 700 °C is not sufficient to induce crystallization. This is consistent with previous reports of the crystallization of ALD Al₂O₃ which observed crystallization into the γ-phase at temperatures starting at 800 °C for thin films on Si.¹⁴¹

To probe the seeding effect of nanocrystals on the ALD matrix, nanocomposites comprised of 25% by volume γ-Al₂O₃ nanocrystals of 1.5 microns thick were fabricated. This thickness was selected because it results in approximately the same amount of ALD material as was deposited in the planar ALD films. This similarity in the masses of ALD material in the two morphologies

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**Figure 5.3.** SEM and EDX of Cr₂O₃/Al₂O₃ composite. SEM cross-section of Cr₂O₃ nanocrystal film. STEM image (b) and STEM-EDX map (c) of Cr₂O₃ nanocrystals coated with ALD Al₂O₃ illustrating the core-shell morphology of the coating.

### 5.3.2 Seeded Crystallization of Amorphous ALD Matrix

Prior to understanding a seeding effect of the nanocrystals on the amorphous matrix...
allows for easier comparison between XRD patterns as the diffraction intensity is proportional to the mass of the sample. Interestingly, for nanocomposites comprised of 10 nm $\gamma$-$\text{Al}_2\text{O}_3$ nanocrystals annealed at the same conditions as the planar ALD films crystallization was observed at temperatures as low as 400 °C after 2 hours. XRD patterns for the $\gamma$-$\text{Al}_2\text{O}_3$ containing nanocomposites are presented in Figure 5.5. Upon annealing at 700 °C, the peak corresponding to $\gamma$-$\text{Al}_2\text{O}_3$ at a 2θ value of 46 degrees becomes more intense, clearly indicating the crystallization of the amorphous ALD $\text{Al}_2\text{O}_3$ matrix into the $\gamma$-phase. The observation of distinct crystallization occurring under the same conditions that yielded no crystallization in the planar ALD material indicates that the nanocrystals embedded in the matrix act as seeds that lower the energy barrier required for the process. Previous efforts to seed the crystallization of amorphous sol-gel $\text{Al}_2\text{O}_3$ have focused on the production of $\alpha$-$\text{Al}_2\text{O}_3$ and have seen similar reduction in the transformation temperature in the presence of nanocrystal seeds. A more recent work by Maret et al. focused on seeding crystallization of ALD alumina grown on drop-casted $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystals and showed
successful crystallization of the α-phase, bypassing the transition γ-phase at temperatures as low as 900 °C.\textsuperscript{139}

![Figure 5.5. XRD of γ-Al₂O₃ seeded nanocomposites. XRD patterns for γ-Al₂O₃ seeded nanocomposites as-deposited after ALD infill and after thermal annealing at indicated temperature for 2 hours.](image)

Preparing nanocomposites consisting of ~10 nm α-Al₂O₃ nanocrystals as seeds is exceedingly challenging owing to the difficulty of preparing small α-Al₂O₃. Nanocomposites comprised of Cr₂O₃ nanocrystals, which are isomorphic with α-Al₂O₃, were thus prepared as a means of probing the capability of these seeding nanocrystals to direct the final structure of the ALD matrix. As in the case of γ-Al₂O₃ nanocrystal-based composites, the total nanocomposite film thickness was approximately 1.5 μm with a volume fraction of 25% α-Cr₂O₃ nanocrystals as-deposited. As seen in the XRD patterns of the α-Cr₂O₃-containing nanocomposites presented in Figure 5.6, peaks corresponding to α-Al₂O₃ at 43.4 and 35.1 degrees 2θ start to appear at annealing temperatures as low as 600 °C. The peaks increase in intensity with increasing annealing temperature up to 800 °C. Delamination of the composite films resulted for annealing temperatures
higher than 800 °C, preventing the acquisition of XRD patterns for any annealing processes at higher temperatures for the Cr₂O₃ nanocrystal-based composites. Despite such low annealing temperatures, the presence of α-Al₂O₃ peaks in addition to the distinct lack of γ-Al₂O₃ peaks after annealing at the same conditions demonstrates the importance of the crystal structure of the embedded nanocrystals. Specifically, the nanocrystals have a structure-directing effect, whereby the resulting phase of the crystallized ALD matrix is dictated by the original phase of the nanocrystals in the composite.

Figure 5.7. XRD of α-Cr₂O₃ seeded nanocomposites. XRD patterns for α-Cr₂O₃ seeded nanocomposites as deposited after infill and after thermal annealing at indicated temperature for 2 hours.

5.4 Conclusions

In conclusion, nanocrystals embedded in a matrix of amorphous ALD Al₂O₃ not only act to lower the barrier associated with crystallization of the matrix but also have the capability to direct the resulting crystal structure. By depositing size-controlled nanocrystals via inertial impaction
and subsequently infilling the pores of the network via ALD, nanocomposites of a consistent morphology with only the material and phase of the nanocrystals was varied. Upon annealing of these nanocomposites under the same conditions, it was found that the crystallization of the ALD Al₂O₃ proceeded towards the preferred transition γ-Al₂O₃ phase at a lower temperature in the presence of γ-Al₂O₃ nanocrystals while it bypassed the transition phase altogether and crystallized as α-Al₂O₃ in the presence of α-Cr₂O₃. Furthermore, in the absence of seeding nanocrystals, a dense ALD thin film did not crystallize at all when subjected to the same thermal treatment. Experimental limitations prevented the exploration of harsher annealing treatments to the α-Al₂O₃ containing nanocomposites which may result in a more complete crystallization of the matrix and warrants further exploration. This framework provides a route of directing the crystal structure of an ALD material (which are usually grown amorphous) deposited on a scaffolding of nanocrystals by selecting the appropriate nanocrystal material and phase.
Chapter 6

Mechanical Properties of Nanocrystal-Based Nanocomposite Thin Films

6.1 Introduction

Nanocrystalline ceramic materials have been widely studied for the past several decades owing to the promise of realizing superior mechanical properties that emerge at the nanoscale.\textsuperscript{145–148,44} More specifically, structural ceramic materials realize increases in hardness and fracture toughness with decreasing grain size, commonly referred to as the Hall-Petch effect.\textsuperscript{149–151} In addition, traditionally brittle ceramic materials have been shown to exhibit plasticity atypical of the bulk material when grain size is reduced to the nanoscale owing to an increase in grain boundary sliding.\textsuperscript{152–155} More recently, Ryou et al. have demonstrated that this enhancement in the mechanical properties of nanocrystalline ceramics with decreasing grain size is not indefinite.\textsuperscript{45} Rather, it has been shown that there exists an optimum in the hardness of MgAl\textsubscript{2}O\textsubscript{4} at a grain size of approximately 18 nm. In a similar vein, molecular dynamics has also recently been employed to study this behavior in nanocrystalline SiC and B\textsubscript{4}C, revealing critical grain sizes <15 nm due to
a region of deformation dominated by grain boundary sliding that is enhanced at the nanoscale.\textsuperscript{14,15} However, not all ceramic systems exhibit this inverse Hall-Petch behavior, in nanocrystalline cubic BN \textit{ab-initio} calculations revealed a nanotwin enabled strengthening in the classic inverse Hall-Petch size regime.\textsuperscript{158} Thus the existence of this critical grain size, and perhaps more importantly its value, are of crucial importance in the pursuit of designing nanocrystalline structural ceramic materials with optimal mechanical properties.

Despite being one of the most widely studied structural ceramic materials, the grain size dependence of mechanical properties of alumina are relatively unexplored in the literature at grain sizes less than 150 nm.\textsuperscript{44} This is primarily a result of the difficulty in producing dense ceramic samples suitable for mechanical testing while simultaneously avoiding rapid grain growth. Conventional consolidation methods are the step typically responsible for deleterious grain growth, necessitating new approaches to the consolidation of nanocrystalline ceramic materials.\textsuperscript{159} Several works have been carried out in an effort to examine size-dependent mechanical properties at grain sizes larger than 150 nm in Al$_2$O$_3$, which typically employ a sintering technique at temperatures in excess of 1300 K.\textsuperscript{160–163} Since these experimental techniques have difficulty in realizing small grain size in consolidated ceramics, there is a gap in knowledge of inverse Hall-Petch behavior in Al$_2$O$_3$.

In this work, we address that gap in knowledge by using a novel material synthesis method whereby a porous film comprised of size-controlled nanocrystals is consolidated via atomic layer deposition. The resulting nanocomposites can further be processed via low-temperature thermal annealing to crystallize the amorphous matrix and produce dense polycrystalline alumina ceramics with small grains suitable for nanomechanical studies. Complete crystallization of the amorphous matrix material was achievable at temperatures as low as 700 °C. Finally, nanoindentation is
employed to characterize the size-dependent hardness in nanocrystalline Al₂O₃ films with systematically controlled grain size. An optimum in the hardness of the γ-Al₂O₃ nanocomposites was observed at a nanocrystal diameter of approximately 10 nm both before and after annealing.

6.2 Experimental

6.2.1 Al₂O₃ Nanocrystal Synthesis

Nanocrystals were synthesized in the reactor described in Chapter 3 and depicted in Figure 3.2. An RF plasma was sustained in the tubular reactor using a 13.56 MHz power supply and matching network (T&C Power Supply) at a set point of 400 W. Nanocrystal size was controlled by adjusting the flow velocity through the plasma (Figure 6.2), which has been shown to be a key parameter in determining particle size produced by these plasma synthesis reactors. Control over flow velocity was achieved by introducing a diluting Ar stream immediately downstream of the plasma, allowing for the total flow through the impaction nozzle to be held constant while controlling the flow through the plasma region. Detailed flow conditions for different size nanocrystals can be found in Table 6.1.

Table 6.1. Summary of nanocrystal synthesis conditions.

<table>
<thead>
<tr>
<th>dₚ,av / nm (TEM)</th>
<th>Ar_car / sccm</th>
<th>Ar_dil / sccm</th>
<th>Ar_add / sccm</th>
<th>O₂ / sccm</th>
<th>P₂ / Torr</th>
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<td>125</td>
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<tr>
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<td>30</td>
<td>800</td>
<td>11</td>
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<td>0</td>
<td>830</td>
<td>10</td>
<td>1.45</td>
</tr>
</tbody>
</table>
6.2.2 Nanocrystal Film Deposition

The resulting nanocrystal aerosol leaving the plasma region of the reactor was subsequently accelerated across a rectangular slit nozzle (1.2 mm x 20 mm x 10 mm long in the direction of flow) and impacted onto Si wafer substrates. The substrates were fixed to a mechanical push rod that was translated in a back-and-forth motion such that a uniform film of nanocrystals was deposited on the Si wafer. Deposition in this manner was carried out for the duration that resulted in a film of the desired thickness. The relative density of films comprised of nanocrystals has been shown to depend on nanocrystal size when deposited via inertial impaction. Film density was thus controlled by adjusting the pressure ratio across the impaction nozzle, thereby controlling the velocity of nanocrystals when they struck the deposition surface, to achieve a constant volume fraction of 23% at each size (Figure 6.2). This was accomplished by adjusting a diaphragm valve just upstream of the pump. Due to the flow being choked across the nozzle, the upstream pressure ($P_1$) in the plasma region was unaffected by minor changes in downstream pressure.

![Figure 6.1. Nanocrystal volume fraction control. Volume fraction of nanocrystals contained in an inertially impacted Al2O3 NC film before ALD infill as a function of nanocrystal diameter for 4 different pressure ratios across the impaction nozzle. The higher the pressure ratio, the larger the volume](image-url)

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6.2.3 Atomic Layer Deposition

A home-built, hot-wall, tubular reactor that has been previously described was used for ALD (see Figure 4.2). Nanocrystal films were loaded into the hot zone of the reactor and allowed to equilibrate and degas for at least 30 minutes. All depositions were carried out at 180 °C under 30 sccm of Ar. Each ALD cycle consisted of an H\(_2\)O pulse of 1.5 s, an Ar purge of 150 s, a TMA pulse of 1.5 s, and finally an Ar purge of 150 s. Films were measured to have a residual porosity of < 1% by spectroscopic ellipsometry after 200 cycles of ALD infill.

6.2.4 Composite Annealing

Annealing of films were carried out in a tube furnace (Lindberg Blue M, ThermoFisher Scientific) under 500 sccm of Ar flow. Films were placed in an alumina boat and loaded into the 50 mm diameter fused quartz tube which was evacuated and subsequently backfilled with Ar. After 30 minutes of Ar purging, the furnace was ramped to the setpoint temperature at a rate of 2.5 °C per minute. Samples were then annealed at the setpoint temperature for the time indicated, followed by a cooldown to room temperature of several hours while remaining under the inert atmosphere.

6.2.5 Structural Characterization

Nanocrystal TEM images were obtained using a JEOL JEM-2000 FX thermal emission microscope equipped with a LaB\(_6\) filament operated at an accelerating voltage of 200 kV. High resolution TEM images were obtained using a JEOL JEM-2100 F field-emission microscope operating at an accelerating voltage of 200 kV. Cross-sectional SEM imaging was conducted on cleaved films using a ThermoFisher Quattro S ESEM operating at an accelerating voltage of 10
kV. X-ray Diffraction patterns were acquired using on a Bruker D8 Advance diffractometer using a Cu radiation source (Cu Kα, λ = 1.541 Å). XRD patterns were acquired for values of 2θ in the range 20-80°, with a step size of 0.02° and a fixed integration time of 0.5 s per step.

6.2.6 Nanoindentation

Nanoindentation was carried out using a Berkovich tip diamond indenter on the Hysitron TI 950 Triboindenter. For each sample, a series of 25 indents were carried out in a 5x5 array with 4 μm spacing in both directions between the indents. For each sample, the indentation load was determined such that the maximum depth of the indent was less than 10% the total thickness of the film to prevent substrate effects, resulting in peak loads between 700 and 1500 μN. Each indent consists of three segments, a 5 s load at constant rate to the peak load, a hold at peak load for 2 s, and an unload at constant rate for 5 s. The tip contact area was calibrated using a fused silica standard provided by Bruker in the load range of 100-10,000 μN before each day of indentation experiments to ensure no tip irregularities formed over the course of the work. Error bars in the reported hardness values were taken as ± 1 standard deviation of the 25-indent array for each sample.

6.3 Results and Discussion

6.3.1 Fabrication of Nanocomposite Films

Nanocomposites comprised of well-defined nanocrystal size were fabricated by deposition of a highly porous nanocrystal film via inertial impaction followed by infilling the pores by atomic layer deposition. Precise control over nanocrystal size in the porous film can be achieved by tuning the plasma synthesis parameters. It was found that increasing the flow velocity in the plasma while all other synthesis conditions were held constant resulted in a decrease of particle size, as has been
reported in other plasma synthesis systems.\textsuperscript{164,23,26,33} Nanocrystal diameter was found to increase from 6 nm to 23 nm with a decrease in flow velocity from 1.25 m/s to 0.18 m/s (Figure 6.2). High-resolution TEM imaging of the as-synthesized nanocrystals revealed showed clear lattice fringes indicative of single crystals of $\gamma$-Al$_2$O$_3$.

![Figure 6.2. TEM of size controlled Al$_2$O$_3$ nanocrystals.](image)

The as-deposited films comprised of nanocrystals produced by plasma-synthesis and supersonic impact deposition step were from 1.75 to 2.50 microns in thickness and had an alumina volume fraction of 23\%, as determined by spectroscopic ellipsometry using a Bruggeman effective medium approximation. An example of one such film before infill is presented in Figure 6.3a. The nanocrystal films were subsequently infilled completely via a method previously described.\textsuperscript{58,72} In that method, atomic layer deposition (ALD) was used to infill with alumina the interstitial voids between the nanocrystals in the as-deposited film comprised of nanocrystals. An example of a film after infill is presented in Figure 6.3b. Complete infill of the film comprised of nanocrystals to a porosity less than 1\% was confirmed by spectroscopic ellipsometry prior to nanoindentation. As
deposited, the ALD alumina infill was amorphous, and annealing in an Ar atmosphere was used for crystallization.

![Cross-sectional SEM of Al₂O₃ nanocomposites](image1.png)

**Figure 6.3. Cross-sectional SEM of Al₂O₃ nanocomposites.** Cross-sectional scanning electron microscopy images of a) as-deposited film comprised of 10 nm NCs at a volume fraction of 23% and b) Nanocomposite film comprised of the same nanocrystals as (a) after infill with ALD alumina.

### 6.3.2 Annealing of Nanocomposite Films

Crystallization of the ALD matrix was performed by thermal annealing of the composites over the temperature range from 400 °C to 1000 °C. X-ray diffraction (XRD) was performed to characterize the crystal structure as shown in Figure 6.5. The (200) peak of γ-Al₂O₃ increased in sharpness with increasing annealing temperature until 700 °C, at which point the pattern remained consistent with further temperature increases. Beyond 800 °C, severe cracking and delamination occurred, rendering subsequent nanoindentation experiments unreliable. Annealing experiments were conducted as a function of time at 700 °C to determine the fraction of the ALD matrix that
was crystallized after 1 hour at 700 °C. It was found that the ALD alumina matrix was approximately 90% crystallized after 1 hour of annealing at 700 °C and that treatment was used in subsequent experiments to prepare samples for mechanical characterization. Determination of the fraction of ALD alumina matrix crystalized after 1 hour at 700 °C involved annealing samples for different times, up to 16 hours, at 700 °C; and then identifying the time after which the mass-normalized peak area stopped changing. Mass normalization was done by integrating the peak and subsequently dividing by the product of film thickness and volume fraction of ALD material. The fraction of crystalized matrix can then be estimated as the ratio of the normalized peak area at 1 hour to the normalized peak area at long annealing times. It should be noted that this method requires an assumption that the crystallite size is constant as annealing proceeds, which was found to be the case in our experiments based upon a peak width analysis as seen on the right axis of Figure 6.4, which is inversely proportional to the grain size via the Scherrer equation.

**Figure 6.4.** Extent of crystallization of ALD matrix. XRD patterns a) acquired after annealing at indicated time at 700 °C, normalized integral area b) under the peak at 46 degrees 2θ as a function of annealing time illustrating relatively little change in the total fraction of crystalline material with increased duration of annealing. The right axis shows the FWHM of the integrated peak, indicating no significant change in the crystallite size of the ALD matrix material after annealing at 700 °C in this time range.
Achieving dense nanocomposites with ambient pressure, low-temperature annealing results in the ability to decouple the sintering conditions from the grain size. This is a critical benefit of this consolidation method, owing to the ability to select size from the nanocrystal synthesis method and retain that size post-consolidation without requiring excessive temperatures often necessary for densification. Additionally, this method provides the capability of producing dense multicomponent composites given a suitable nanocrystal synthesis approach and ALD chemistry.

6.3.3 Nanoindentation of Nanocomposite Films

Annealing the composites after ALD infill increased the hardness of the material. Nanoindentation experiments were carried out such that the maximum penetration depth was \( \leq 10\% \) of the film thickness in order to avoid substrate effects.\textsuperscript{165} Indentation was then carried out and the hardness determined using the Oliver-Pharr method\textsuperscript{166} for composites annealed for 1 hr in Ar atmosphere in the temperature range of 400 – 700 °C as shown in Figure 6.6. Unsurprisingly, the hardness of the composite increased with increasing annealing temperature similar to previous results studying the hardness of annealed and sintered \( \gamma \)-\( \text{Al}_2\text{O}_3 \).\textsuperscript{161} The increase in hardness can be explained by the crystallization of the amorphous ALD matrix into the crystalline \( \gamma \) phase, which was observed in the XRD patterns shown in Figure 6.5.

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Interestingly, the hardness of composites after annealing at temperatures below 600 °C was lower than the hardness of a pure ALD film grown in the same reactor used for infilling the composites. Given the expectation that the ALD material should be softer than γ-Al₂O₃, a volume averaging approach to describe composite hardness such as Hill’s approximation would predict a value somewhere between the pure phases. Our result is an indication that the nanostructure of the film plays a significant role in determining the ultimate hardness of the film measured by nanoindentation. This indication is consistent with previous reports on nanoindentation of nanoparticle-based films that revealed annealing, even in the absence of a matrix material.
surrounding the particles, can lead to a significant increase in the hardness of the film.\textsuperscript{168} The effect is presumably a result of stronger interparticle contacts produced by annealing.

![Graph showing hardness as a function of annealing temperature](image)

**Figure 6.6. Annealed nanocomposite hardness.** Hardness of nanocomposites after ALD infill, prepared from films initially comprised of 10 nm NCs with 23\% volume fraction, as a function of annealing temperature. The blue-to-red band represents the hardness of pure ALD matrix material as a function of temperature from as-deposited to 700 °C.

When compared to the composite samples, annealing pure ALD alumina without nanocrystal inclusions had a relatively minor effect on the hardness of the material. Annealing and nanoindentation were performed on 650 nm thick films of pure ALD Al\(_2\)O\(_3\). As discussed in the previous chapter, no crystallization was observed in the XRD patterns obtained after annealing at 700 °C (Figure 5.4). Nanoindentation of the annealed ALD films revealed a very minor increase in the hardness of the ALD material with increasing annealing temperature from 10.3 ± 0.53 GPa as deposited to 11.5 ± 0.42 GPa after annealing at 700 °C. The relatively minor increase in hardness of pure ALD material with increasing annealing temperature indicates that the increased nanocomposite hardness with annealing observed in Figure 6.6 was caused by changes in the harder crystalline phase, including strengthened interparticle contacts and increased crystalline phase volume fraction caused by crystallization of the amorphous matrix.
6.3.4 Nanocrystal Size-Dependence of Nanocomposite Hardness

To evaluate the effect of nanocrystal size on nanocomposite hardness, a series of nanoindentation experiments were carried out on composites fabricated from films comprised of nanocrystals with diameters in the range 6 to 22 nm. After infill, nanoindentation was performed on samples that were: unannealed, annealed for 1 hr at 400 °C, and annealed for 1 hr at 700 °C. As seen in Figure 6.7, all three cases exhibit a sharp increase in hardness with an increase in nanocrystal diameter from 6 to 10 nm and then a subsequent decrease in hardness with a further increase in initial nanocrystal diameter. Nanocrystal diameter of 10 nm produced the highest nanocomposite hardness. The emergence of an optimum grain size for the hardness has, to the best of our knowledge, not been previously reported in alumina; although our measured value of approximately 10 nm diameter is consistent with behavior seen in other nanocrystalline ceramics such as MgAl₂O₄. The presence of this optimum grain size has been referred to as the inverse Hall-Petch effect at very low grain sizes, however the underlying cause of this behavior is still a topic of debate. Regardless, the optimum grain size observed in this case of 10 nm is in the size range of similar ceramics where such an optimum has been reported. Given there is an optimum in the hardness of γ-Al₂O₃ with grain size, it is reasonable to expect a similar behavior in ultrafine grained α-Al₂O₃ materials as well. As a result, it is certainly of interest to pursue nanomechanical studies of fine grained α-Al₂O₃ to identify the location of the optimum grain size to achieve superior mechanical properties compared to bulk morphologies of the ceramic material.
6.4 Effect of Matrix Crystal Phase

Given the capability of seeding crystals to influence the ultimate crystal structure of the final composite, a comparison between the transition $\gamma$-Al$_2$O$_3$ and the harder $\alpha$-Al$_2$O$_3$ matrix is of interest. In order to compare the two composite morphologies, Figure 6.8 shows the hardness of composites comprised of 13 nm Cr$_2$O$_3$ nanocrystals compared to 10 and 15 nm Al$_2$O$_3$ nanocrystal-containing composites after being subjected to the same annealing conditions. Interestingly, the as-deposited composites are all of a similar hardness, despite the $\alpha$-Cr$_2$O$_3$ nanocrystals having an expected hardness of $\sim$18 GPa, which is much higher than that of the $\gamma$-Al$_2$O$_3$ of $\sim$13 GPa. However, after annealing the composites that showed the formation of $\alpha$-Al$_2$O$_3$ exhibited a roughly 50% increase in hardness compared to those containing $\gamma$-Al$_2$O$_3$. This dramatic increase in hardness coupled with the fact that the as-deposited nanocomposites had the same hardness, is a further indication that the matrix is crystallizing in the harder phase.
Conclusions

In conclusion, by preparing nanocrystalline films comprised of $\gamma$-Al$_2$O$_3$ nanocrystals in a matrix of both amorphous and crystallized ALD Al$_2$O$_3$, the grain size-dependent mechanical properties of $\gamma$-Al$_2$O$_3$ were studied. In this consolidation technique, the grain size is selected solely by the nanocrystal synthesis process while the subsequent densification is carried out at low temperature allowing for retention of this grain size. Furthermore, the volume fraction of the initial nanocrystalline phase is tunable and thus this method could be employed in the future to investigate the effect of loading fraction on mechanical properties. By decoupling the consolidation process from the grain size being studied, the prevailing issue hindering the study of Al$_2$O$_3$ at grain sizes less than 150 nm, which is rapid grain growth during consolidation, was avoided entirely.

The hardness in this $\gamma$-Al$_2$O$_3$ system was found to exhibit size-dependent behavior similar to other nanocrystalline ceramic materials in which an inverse Hall-Patch relationship has been
observed at very small grain sizes. As a result, an optimal grain size of approximately 10 nm was
identified, which is reasonable given results for similar structural ceramic materials. Additionally,
post-fabrication annealing was able to increase the composite hardness while retaining the size-
dependence. Ultimately a hardness of $13.5 \pm 0.67$ GPa was achieved, a value equivalent to high-
pressure sintering$^{161}$ of $\gamma$-Al$_2$O$_3$. The high hardness values for $\gamma$-Al$_2$O$_3$ obtained by our synthesis
method demonstrates the suitability of this approach for fabricating consolidated fine-grained
alumina at relatively low temperatures. Furthermore, by substituting the $\gamma$-Al$_2$O$_3$ nanocrystals with
$\alpha$-Cr$_2$O$_3$ nanocrystals, the composites showed a significant increase in hardness, achieving a
hardness of $17.1 \pm 0.21$ GPa. This increase in hardness is likely due to the observed crystallization
of the matrix partially into the $\alpha$-phase detailed in chapter 5.
Chapter 7

Concluding Remarks

Nonthermal plasmas provide a uniquely nonequilibrium environment that has been leveraged to enable incredible technological advancements. The fact that in spite of the complexity of the plasma environment that it has been utilized as a controlled media to perform precise material processing speaks volumes to the potential scientists and engineers recognize. Throughout this dissertation the unique nanocrystal synthesis capabilities of nonthermal plasmas were leveraged to produce crystalline nanoparticles of high melting point metal-oxides with narrow size distributions. Additionally, the need to intentionally consolidate these nanocrystals for technologically relevant applications while maintaining the nanocrystalline morphology was addressed. Finally, characterization of the crystallization and mechanical properties of consolidated nanocomposites demonstrated the capabilities of the synthesis and fabrication platform detailed as a means to probe structure-property relationships at the nanoscale. In this chapter, a summary of the key findings from the previous chapters are presented in addition to a brief outlook of where this line of research could lead.
7.1 Summary of Key Findings

Chapter 3 presented a synthesis approach to producing Al₂O₃ nanocrystals of well-defined size and crystallinity. The advancement produced by the work is the illustration of a predictive modeling framework surrounding the heating of nanoparticles in a nonthermal plasma. Specifically, the capability to use only the external plasma parameters: pressure, discharge volume, gas composition, and applied power to predict particle temperatures in the plasma. As a means of validation, Al₂O₃ nanocrystals were shown to be amorphous at low powers and crystalline at high powers where the predicted temperatures exceeded the crystallization temperature.

Chapter 4 presented a consolidation strategy for plasma-produced nanocrystals. The strategy involves first producing a network of nanocrystals by inertial impaction of the plasma generated aerosol followed by ALD to infill the interstices. The chapter presents a complete set of design considerations necessary to ensure densification of the nanocomposites produced in this way. The predictive models were validated using two material systems and at least two independent measurement techniques for each criterion.

Chapter 5 describes the observed seeding effect of nanocrystals in the ALD deposited matrix. The presence of γ-Al₂O₃ nanocrystals was shown to promote the crystallization of the ALD matrix into the preferred γ-phase under conditions where a planar ALD film of similar mass showed no signs of crystallization. Furthermore, the presence of α-Cr₂O₃ nanocrystals synthesized in the nonthermal plasma in the ALD Al₂O₃ matrix caused the suppression of the γ-phase and resulted in α-Al₂O₃. This clearly demonstrates the capability of the plasma-synthesized nanocrystals to be utilized as a structure directing agent for dense nanocomposites.
Chapter 6 summarizes the mechanical properties of nanocomposites produced via this platform. Nanoindentation was used to characterize composites prior to and after thermal annealing post treatments. Size-controlled Al$_2$O$_3$ nanocrystals were also utilized to study the size-dependent hardness of the composites. Interestingly, an optimal nanocrystal grain size for the γ-Al$_2$O$_3$ composites was reported of ~10 nm. Additionally, the presence of α-Al$_2$O$_3$ in the composites showed a dramatic increase in the hardness when compared to the γ-Al$_2$O$_3$ composites with similar nanocrystal size.

7.2 Outlook

Nonthermal plasma synthesis of nanocrystals has already proven to be a useful tool in achieving nanocrystals of materials that are difficult to achieve by other means, such as nitrides. However there is still a wide range of materials that plasmas could prove beneficial in realizing in nanocrystal morphologies. One outstanding challenge in extending the material library is selecting the appropriate reactor and process for producing a given material. For example, should N$_2$ or NH$_3$ be used as a nitrogen source for my synthesis process? These questions have historically been answered through trial and error but I believe approaches similar to that taken in Chapter 3 could greatly reduce the empirical development of some of these processes. The synthesis of Cr$_2$O$_3$ presented in Chapter 5 is a great example of the potential benefits of this approach, in that the particle heating models presented in Chapter 3 were used as a starting point for the conditions used in synthesis. As a result, the amount of experimental fine-tuning required to achieve the desired α-Cr$_2$O$_3$ nanocrystals was minimized.

Towards the efforts around consolidation of the nanocrystals, this fabrication technique presents a number of opportunities for potential applications of nanocrystal thin films. The models
described in this dissertation can be used for any ALD coating process required for thin films comprised of randomly packed nanocrystal networks, regardless of the need for complete densification. However, the scaling of the models presented is untested and for applications seeking film thicknesses of larger than ~10 μm and it remains unclear whether the criteria presented here will hold. Regardless, this methodology has proven useful in testing nanoscale properties that have been elusive even for historically well-investigated materials such as Al₂O₃. Additionally, the capability of the synthesized crystals to direct the structure of the ultimate nanocomposite could prove useful for many applications where a high-surface area to volume ratio of costly materials is necessary, such as catalysis.
References


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Appendix I

Solid State NMR – Czjzek Model Fitting

The experimental NMR data were processed by the GSim program using the Baseline Corrector application\textsuperscript{171} to generate the frequency domain spectra. Preliminary fitting of the $^{27}$Al lineshapes corresponding to the central transitions were fit from the 1-dimensional spectra using Dmfit\textsuperscript{74} using the CzjzekSimple model. The contributions to the central transition intensity from satellite transitions were included by fitting the spinning sidebands (of those satellite transitions) underlying the central transitions. In Figure A1-1, the 100 W Al$_2$O$_3$ nanocrystal sample deconvolution is shown. The model extracts both the isotropic chemical shift ($\delta_{\text{iso}}$) and quadrupolar coupling constant ($C_Q$) values for 4-, 5- and 6-coordinate aluminum sites. The values are shown in Table S1 below.
Figure A1-1. $^{27}$Al SSNMR (with MAS) spectrum for Al$_2$O$_3$ nanocrystals synthesized at 100 W, deconvoluted into separate resonances using DMfit. The Czjzek peak fitting for the 4- (blue), 5- (green), and 6-coordinate (purple) aluminum sites is shown. The small resonances with very low intensity are spinning sidebands from the satellite transitions.

TABLE A1.1. Parameters extracted from the preliminary Czjzek fitting of the $^{27}$Al resonances for the “100 W” synthesized sample of Al$_2$O$_3$ nanoclusters. (Note: the isotropic resonance values, $\delta_{iso}$, extracted for the Czjzek-broadened lineshapes differ from the appearance of the most intense peaks in the 1-dimensional spectrum.)

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<td>5.4 MHz</td>
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</tr>
</tbody>
</table>
Appendix 2

X-Ray Fluorescence Calibration

The intensity of an XRF signal, $I$, is proportional to the thickness of the film in the thin film limit as,

$$I = k \rho_f A_{\text{beam}} t_f$$

(S1)

where $\rho_f$ and $t_f$ are the film mass density and thickness, respectively. The parameters $k$ and $A_{\text{beam}}$ are the proportionality constant for the spectral line and the beam cross-section at the sample, respectively. For films of a given material with varying thickness, the XRF intensity is then directly proportional to the film thickness (i.e. $I = k_{\text{eff dense}} t_f$). For a porous material of the same thickness, the density of the film is simply given as the product of the bulk density and the volume fraction of solid material. This means that the XRF intensity for a porous film is given by,

$$I = k_{\text{eff dense}} t_f \phi_{\text{solid}}$$

(S2)
Thus, dense thin film standards can be used to calibrate the XRF peak intensity for quantification of porosity in NC films of known thickness.

Figure A2-1. Sample XRF spectrum of GaN NC film (a) and the result of the custom peak fitting algorithm utilized in MATLAB (b) for quantification of peak intensity.