Growth of Small Particles in Nonequilibrium Plasmas

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Growth of Small Particles in Nonequilibrium Plasmas

by

Necip Berker Üner

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

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List of Abbreviations

ATR: Attenuated total reflectance
CEM: Collision enhanced model
CM: Collisional model
DLS: Dynamic light scattering
EP: Equilibrium plasma
EDXS: Energy-dispersive X-ray spectrometry
FDP: Fluorescence decay probe
FTIR: Fourier transform infrared
HRTEM: High-resolution transmission electron microscopy
OES: Optical emission spectroscopy
OML: Orbital motion limited
NC: Nanocrystal
NEP: Nonequilibrium plasma
NPA: Nonequilibrium plasma aerotaxy
PL: Photoluminescence
SAED: Selective-area electron diffraction
SEM: Scanning electron microscope
TEM: Transmission electron microscopy
TGA: Thermogravimetric analysis
UV-VIS-NIR: Ultraviolet-visible-near-infrared
XRD: X-ray diffraction
XRF: X-ray fluorescence
XPS: X-ray photoelectron spectroscopy
Acknowledgments

It is funny that preparing this dissertation took five years, which is 1/6 of my entire life. More importantly, this period is half of my, let’s say, “conscious” life. For some people, spending such an effort might seem ridiculous, and some might think that the work presented in this dissertation is not enough for a five-year-long study. But I know that I have learned so much more than what is written in the next 200 pages. I believe that I have evolved and matured significantly in all aspects of life, especially as a researcher, and this was made possible by my advisor Prof. Elijah Thimsen. When I joined WashU, I didn’t even have the slightest idea about what plasmas were. I had no experience with doing experiments. I didn’t know how to communicate my ideas. This is not the case anymore. Prof. Thimsen has been a great mentor, and thanks to him, I will be moving on in my career as an independent researcher. I consider myself very lucky that I was a student of his.

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ABSTRACT OF THE DISSERTATION

Growth of Small Particles in Nonequilibrium Plasmas

by

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Doctor of Philosophy in Energy, Environmental & Chemical Engineering

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Nonequilibrium plasma (NEP) is an extraordinary environment for material synthesis. NEP is comprised of hot electrons with temperatures greater than 10000 K and of cold ions and neutrals that are usually at few hundred kelvins above room temperature. Due to this large difference in species’ temperatures, the assumption of local thermal equilibrium does not hold in NEP. Therefore, NEP can act as a unique processor of mass, and it can transform materials along pathways that are not accessible by methods wherein local thermal equilibrium is valid. For decades, NEPs have been employed in the semiconductor industry to manufacture many thin film electronic devices. In the last 15 years, NEPs have been translated to the synthesis of free-standing semiconductor nanocrystals (NCs) with success. It was shown that in low-pressure NEPs NCs could be made monodisperse with tunable size and optical properties, which is the level of control required for the synthesis of functional nanomaterials. Although successful synthesis of group IV and metal oxide semiconductor NCs has been reported in literature, the mechanisms responsible for the growth of high-quality nanocrystals are currently unknown. Furthermore, the lack of reports on the characterization of NEP reactors makes it difficult to determine the operating parameters that are necessary for synthesizing materials with desired properties. In order to move away from empiricisms in the design of NEP reactors and processes, and to develop new
approaches for synthesizing broader classes of semiconductors, experiments and measurements that elucidate the fundamentals of plasma-aerosol interactions are needed.

The first aim of this dissertation is to shed light on the growth dynamics of NCs in NEP. A simple platform for investigating plasma-aerosol interactions was developed. The platform allowed for experiments in which a pre-made aerosol was sent into the plasma as a probe, and the plasma-treated aerosol was collected downstream to monitor the changes in the size and shape of the aerosol particles. During these experiments, a new mechanism of growth was discovered. It was found that the aerosol rapidly vaporizes in the plasma, despite the low background gas temperature. Aerosol dynamics that follow the vaporization process was observed to cause a significant size-focusing in the aerosol. A simplified scheme of dynamics for the experimentally observed growth was proposed, and the scheme was tested by setting up a sectional aerosol dynamics model. Computations were complemented by a thorough characterization of the tubular flow-through reactor, which revealed a characteristic zone with elevated ion density and gas temperature that can induce intense ion bombardment on the particles.

The second aim of this dissertation is to advance NEP synthesis by providing a means to produce compound semiconductor nanocrystals that currently do not have an established method of synthesis. A new method that works in a way that is similar to the platform described above was developed. The method, named nonequilibrium plasma aerotaxy, uses elemental aerosols as precursors, and it employs NEP as the reactor. With this method, free-standing nanocrystals of gallium nitride, indium nitride and gallium antimonide were synthesized in gas-phase for the first time. The optical properties of these materials and their growth mechanisms were investigated in detail.
Chapter 1

Introduction

1.1. Plasmas in Nature and Laboratory

Plasma is an ionized gas and it is considered the fourth state of matter. Flames and the air that we breathe also contain ions, and therefore it can be said that they are ionized as well. However, they are not considered as plasmas. Plasma distinguishes itself by having ions and electrons with high concentrations, so high that it displays collective effects, such as waves and instabilities. Plasma has a very high electrical conductivity, and it can shield itself from external electrical fields\(^1\). These properties of plasma are all unique, thus, plasma earns the distinction of being a different state of matter.

Based on the volume it occupies, plasma is the most abundant phase in the universe since the majority of interstellar space consists of plasma (Figure 1.1a and 1.1b). However, our exposure to plasmas is much less than that of other phases of matter. In our daily lives, plasmas appear either as fascinating natural phenomena or as important tools in industry and scientific research (Figure 1.1).
Plasma has a very rich terminology since it comes in a wide variety of types based on its shape, electronegativity, continuity, the source that generates it, and so on. The most common classification is based on temperature, and it divides the plasma into two categories: equilibrium and nonequilibrium plasma. Equilibrium plasmas (EPs) are characterized by their very high temperatures. Their temperatures are most likely above a few thousand Kelvin; therefore, they are also called thermal plasmas. In an EP, all the species, i.e. electrons, ions and neutrals, have the same temperature. EP is characterized by a high concentration of ionized species, which is usually between $10^{23}$-$10^{28}$ m$^{-3}$. An example of an EP from nature is the lightning bolt (Figure 1.1c), which reaches up to temperatures of 28000 K. In the industry, EPs are used primarily in metallurgy and machining. They are generated in arc furnaces, plasma torches (Figure 1.1d) and electrical discharge machining instruments. They are also being used to synthesize powders of
Figure 1.2. Parameters of a nonequilibrium argon plasma. Measurements were done in a tubular, capacitively-coupled, radio frequency-driven reactor (13.56 MHz) at 1 Torr. There is a striking two-orders of magnitude difference between the background gas temperature and the electron temperature. The power shown is the amount that is generated at the power supply. Note that all three parameters simultaneously increase with power.

very hard materials, such as TiC\textsuperscript{11} and diamond\textsuperscript{12}.

From theoretical and applied perspectives, nonequilibrium plasmas (NEPs) are certainly more interesting than EPs. NEP is comprised of electrons that are very hot (10\textsuperscript{4}-10\textsuperscript{5} K) and of neutrals and ions that are substantially colder (300-1200 K). This unique mixture forms an environment in which the local thermal equilibrium assumption does not hold\textsuperscript{1} (Figure 1.2). The translational temperature of neutrals, ions and excited species are usually similar, and these temperatures are generally lumped into a single average value called the background gas temperature\textsuperscript{13}. Due to the coexistence of hot electrons with cold ions and neutrals, NEP is also named a two-temperature, nonthermal or low-temperature plasma. The discrepancy between the temperatures is due to the fact that energy transfer between hot electrons and cold heavy species during an elastic collision is highly inefficient due to the disparity in masses, whereas collisions between ions and neutrals lead to significant energy transfer and thermalization. Therefore, electrons are energized more by
electric fields, and they reach ionization energies to sustain the plasma. Although the percentage of ionized species in a NEP is quite low, usually between 0.001-0.1 %, the presence of hot electrons causes a large number of excited species to be generated, which can lead to rapid chemical reactions\textsuperscript{14}. NEP can be generated either at low or at atmospheric pressures.

Due to their low background temperature, NEPs are usually easier to generate and contain when compared to EPs. Therefore, most of the laboratory-generated plasmas are NEPs, and they are currently being used for a wide range of applications spanning from water disinfection\textsuperscript{15}, wound healing\textsuperscript{16}, fluorescent light bulbs\textsuperscript{17} (Figure 1.1e) and space propulsion\textsuperscript{18}. Amongst all of its applications, the use of NEPs in the semiconductor industry (Figure 1.1f) is the most essential for our everyday life. NEPs are being used to manufacture a large portion of the devices on integrated circuits, thus enabling almost all of the modern electronic conveniences that we enjoy like computers and mobile phones\textsuperscript{19}. An important NEP-based process in the semiconductor industry is dry etching, which is also called reactive ion etching\textsuperscript{20}. In dry etching, a halide gas, such as Cl\textsubscript{2}, BCl\textsubscript{3}, SF\textsubscript{6}, CF\textsubscript{4}, etc., is mixed with argon and a plasma is generated from this mixture on top of a masked substrate. Dry etching provides features that are etched directionally below the mask (a.k.a. anisotropic etching)\textsuperscript{21}, a task that must be accomplished for three dimensional layout and packaging of electronic components. The etching rate and profile are usually independent of the crystal structure of the substrate, which is a distinct advantage over wet etching in many of the applications\textsuperscript{22}. In addition to being used to remove a material, NEP can also be used as an additive tool, and it is vital in chemical vapor deposition (CVD) of semiconductor devices. In regular thermal CVD, appropriate vapor precursors, which are usually either metalorganic compounds, chalcogenides, or hydrides, are sent into a high-temperature reactor where the precursors decompose. The decomposed species land on a substrate placed in the same
reactor, leading to heterogeneous growth. Due to its inherent reactivity, NEP can decompose the precursors at background gas temperatures that are much lower than the temperatures used in thermal CVD. Therefore, conducting CVD in the presence of a NEP allows the use of temperature sensitive substrates, and thereby enables the manufacturing of new materials and technologies. The plasma-enhanced chemical vapor deposition (PECVD) method has become a capable tool in depositing metal contacts and dielectrics, which are commonly used for packaging various semiconductors.23

Although NEPs bring distinct advantages in materials processing, their physical complexity that stems from the nonequilibrium state, the presence of electric and magnetic fields, and the extensive radical chemistry within brings difficulties in terms of their modeling, measurement and control. In the semiconductor industry, processes that involve dry etching and PECVD have generated many problems in the last 20 years of the millennium, and those problems initially hindered successful use of NEPs. However, some of the problems led to significant developments in plasma science and engineering, and a prime example of this is the observation made in IBM laboratories in 1989. During measurements of laser-induced fluorescence to assess the concentrations of reactive species during dry etching, Gary Selwyn and co-workers detected significant light scattering coming from the plasma.24 The scattered light was shown to arise from suspended particles. The presence of particles in semiconductor processing plasmas was received with utmost interest by the plasma physics community, since these particle-loaded plasmas brought the field of dusty plasmas, which was essentially focused on astrophysical phenomena (e.g. Figure 1.1a), to the laboratory. The interaction between micron-sized particles and process plasmas was studied in depth, leading to advances in the understanding of particle charging, plasma dust crystals and
Figure 1.3. Trapping of dust in plasmas. In the plasma, micron-sized melamine formaldehyde particles acquire charges, and consequently, are suspended on top of a planar electrode due to electrostatic levitation. They form either a crystal with well-defined interparticle distances, or an amorphous layer as seen above25.

particle trapping mechanisms26 (Figure 1.3). Meanwhile in the semiconductor industry, particles generated and trapped in NEPs were largely unwelcome. Some of these particles were found to land on the substrate. When the size of a particle that lands on the substrate was larger than the half-width of an etched feature, the particle was found to create a killer defect, leading to a significant decrease in material quality and performance26. Therefore, efforts were concentrated on preventing the creation and deposition of these killer particles on substrates that were being processed27,28.

Sixteen years after the observation of dust in semiconductor processing plasmas, researchers had a change in perspective. It was shown that by feeding silane (SiH₄) into a tubular, flow-through NEP reactor, the propensity of the NEP for the creation of particles can be put to use for high-yield and continuous synthesis of silicon nanoparticles29 (Figure 1.4a). The particles were shown to be crystalline and monodisperse with an adjustable size between 3-7 nm. Accordingly, these Si nanocrystals (NCs) demonstrated tunable photoluminescence (PL) between 700-850 nm due to a native oxide layer on their surface. Upon functionalizing the surface of the Si NCs with halides in the gas phase, air-stable NCs were produced30. These NCs exhibited PL across the entire
Figure 1.4. The flow-through NEP reactor and the synthesis of photoluminescent Si NCs. (a) Schematic of NEP synthesis of monodisperse and free-standing Si NCs with an archetypal tubular, flow-through and capacitively coupled radio-frequency plasma reactor operating at 13.56 MHz. The aluminum shaft collars that are wrapped around the fused silica tube are electrodes. The powered electrode is the collar on the left, and the ground electrode is the collar on the right. Si NCs are 5 nm in diameter. The scale bar is 10 nm in width. (b) Emission at different wavelengths from Si NCs of different sizes when excited with 365 nm light.

visible spectrum with quantum yields of approximately 20% (Figure 1.4b). The intriguing capability of NEPs in synthesizing monodisperse NCs of Si gave rise to NEP as a promising environment for gas-phase synthesis of nanomaterials. In order to fully reveal the uniqueness of NEP and its potential for gas-phase synthesis, a brief survey on nanomaterials and their common methods of synthesis should be presented first.

1.2. NEPs for Gas Phase Synthesis of Nanomaterials

Materials having dimensions between fractions of a nanometer and a few hundred nanometer have attracted significant interest due to the new physics and applications inherent in their small size. The most obvious example is semiconductor nanomaterials, which are known to exhibit different electronic and optical properties due to an increase in their bandgap when the size of the
material is decreased\textsuperscript{32,33}. Accordingly, semiconductor nanomaterials are being studied for the purpose of developing new generation electronic devices that involve solar cells\textsuperscript{34}, transparent conductors\textsuperscript{35}, field effect transistors\textsuperscript{36} and light emitting diodes (LEDs)\textsuperscript{37,38}.

To be able to make a societal impact, nanomaterials require efficient synthesis routes which can provide control on size and structural properties. Nanoparticles usually constitute the most desired family of nanomaterials, and they have two main routes of production: colloidal synthesis and gas-phase synthesis. Colloidal synthesis involves liquid phase routes, during which solid precursors are dissolved in a liquid solvent. Upon letting the precursors decompose in a temperature controlled batch reactor, particles can be made to nucleate and grow in a controllable manner. Growth of particles is usually slow, but particles can be made to have uniform size and shape. Colloidal synthesis can be conducted with very good size control and monodisperse nanoparticles can be produced. However, making crystalline materials of refractory compounds is often difficult since high temperatures and consequent high pressures are required to prevent boiling of the solvent. Furthermore, particles produced with colloidal methods usually have organic ligands bound to them, which are mostly undesirable in electronic device applications\textsuperscript{39,40}. Therefore, additional synthesis steps such as drying and purification are often needed. Despite these disadvantages, colloidal synthesis stands as the main route for synthesizing many functional nanomaterials, due to a large number of materials that can be produced by colloidal routes with controlled size and shape.

When compared to colloidal synthesis, gas-phase synthesis methods have clear advantages, as well as disadvantages. Gas-phase methods can provide continuous and high-throughput production of various nanomaterials, including oxides, metals and metal alloys\textsuperscript{41-43}. They are usually employed to produce small particles suspended in gas phase; therefore, the term aerosol synthesis
is also used. These methods involve feeding a liquid or vapor precursor into a high temperature environment, for example, a flame, a hot wall reactor or an EP, which thermally activates particle growth. Particles produced in gas-phase synthesis are not covered with ligands. However, the difficulties in controlling size and monodispersity stand out as the drawbacks of many gas-phase methods. Nevertheless, since materials produced by these methods often have high surface areas, gas-phase synthesis is industrially used for producing materials that act as additives, such as fumed silica and carbon black.

To provide a comparison of the materials synthesized by the colloidal and gas-phase methods, electron microscope images of anatase TiO$_2$ particles are given in Figure 1.5. The colloidally synthesized TiO$_2$ particles (Figure 1.5a) have a much narrower size distribution, and they are freestanding. On the other hand, gas-phase-synthesized particles (Figure 1.5b) are comprised of very large aggregates and polydisperse primary particles. To understand why the particles are polydisperse and aggregated in gas-phase synthesis, one needs to look into the dynamics of aerosol growth.
The growth of nanoparticles from vapor precursors in a thermal environment is well understood. A schematic displaying the mechanisms of aerosol growth that prevail during gas-phase synthesis is given in Figure 1.6. A high-temperature environment provides rapid precursor decomposition and subsequent particle nucleation. Following nucleation, the growth of these particles proceed through two competing mechanisms. The first is the condensation mechanism, during which the vapor-phase species of the material condenses on fresh clusters generated by nucleation. A physically analogous mechanism is surface growth by heterogeneous reaction of vapor-phase species. Condensation and surface growth often lead to the formation of spherical particles. The alternative growth mechanism is aggregation. Since particles follow random paths due to diffusion, they frequently collide with each other. Collisions occur between particles of all sizes. Upon collision, particles may stick together and form an aggregate. The aggregate can grow further by scavenging other particles, eventually forming aggregates with fractal geometry if sintering is slow. Coagulation is a simplified view of this process where it assumes that particles immediately sinter into a spherical particle upon collision. This assumption is strictly valid for liquid droplets only. Independent of whether sintering occurs or not, aggregation broadens the particle size distribution. The size distribution of an aerosol is usually described with single or multiple lognormal distributions, whereas the breadth of a lognormal size distribution is
characterized with the geometric standard deviation $\sigma_g$. A perfectly monodisperse aerosol, which is extremely difficult to generate, has a $\sigma_g$ of 1. As the size distribution broadens, $\sigma_g$ increases.

In a high-temperature environment, equilibrium favors growth by aggregation, thereby it is common to form polydisperse aggregates in gas-phase synthesis$^{46,48,49}$. As growth by aggregation proceeds, $\sigma_g$ increases up to a point after which it stays approximately constant. The size distribution when $\sigma_g$ becomes constant is self-similar, and it is called the self-preserving size distribution$^{50}$. $\sigma_g$ usually approaches the self-preserving value of 1.46$^4$ in gas-phase synthesis if sintering is rapid$^{48,51}$.

The trends in the evolution of particle size distribution under growth by condensation and aggregation are opposites. Representative trends for the size distribution of an initially monodisperse aerosol during condensational or coagulational growth are plotted in Figure 1.7a.

![Figure 1.7. Comparison of growth by condensation and coagulation.](image)

This $\sigma_g$ value corresponds to that of the self-preserving number distribution of spherical particles in the free molecular regime. For the mass distribution in the same regime, the self-preserving value of $\sigma_g$ is 1.33$^{50}$. 

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$^a$ This $\sigma_g$ value corresponds to that of the self-preserving number distribution of spherical particles in the free molecular regime. For the mass distribution in the same regime, the self-preserving value of $\sigma_g$ is 1.33$^{50}$. 

11
and Figure 1.7b, respectively. \( N_\infty \) is the total particle number concentration, \( dN_\infty/d\log(d_p) \) is the number distribution function (also symbolized as \( n_p \)) and \( d_p \) is the particle diameter. During condensational growth, the aerosol maintains its initial spread in size, but on a logarithmic size scale, the distribution gets narrower as particles grow (Figure 1.7a), leading to a decrease in \( \sigma_g \) until it becomes equal to 1. In contrast, coagulation broadens the distribution (Figure 1.7b). The growth during colloidal synthesis is analogous to the trend given in Figure 1.7a, although the physical mechanism is different\(^{52} \). In gas-phase synthesis, however, usually a trend in growth that is very similar to the one shown in Figure 1.7b is observed, indicating that collisional growth usually dominates over condensational growth.

Among the environments used for gas-phase synthesis, NEPs are exceptional since growth in a NEP resembles Figure 1.7a rather than Figure 1.7b. In a NEP, particles are bombarded by mobile and energetic electrons, and most of the particles become negatively charged. The Coulombic repulsion that arises between the unipolarly charged particles suppresses aggregation\(^{53,54} \), and has been used to explain the resultant monodisperse size distribution for NEP synthesis of nanoparticles. With aggregation suppressed, particles are expected grow mainly by surface growth via heterogeneous reactions between the precursor fragments and particles\(^{53} \). The ability to synthesize monodisperse and free-standing particles in NEP is the major reason that makes NEP a promising environment for nanomaterial synthesis.

Another intriguing property of NEPs relevant to synthesis is their capability of producing crystalline materials. For Si particles that are 10 nm, crystallinity requires a temperature of approximately 1273 K\(^{55} \). With background gas temperatures close to room temperature, the ability of NEP for synthesizing Si NCs particles is puzzling. In literature, the aptitude for producing Si NCs in NEP is attributed to the selective heating of small particles in NEP due to
ion bombardment. It is argued that Si particles smaller than 10 nm experience stochastic spikes in their temperature whenever ions recombine on their surface. Ion recombination releases energies usually on the order of 10 eV, which is comparable with the internal energy of small particles. Therefore, particle temperatures can be momentarily raised above 1000 K. As a result, a NEP with particles, a.k.a. dusty NEP, can be said to be a three-temperature system in which electrons, the background gas and particles are at different temperatures.

The unique properties of NEP for nanomaterial synthesis led to many studies within the last 15 years. Studies primarily focused on continuous synthesis of nanocrystals by using tubular flow-through reactors (Figure 1.4a). This reactor stands out among other reactor designs due to its simplicity, uniform particle residence times and high production rates. The reactor is usually operated at low pressures, between 1-50 Torr, thus it provides a voluminous plasma. It often has two rings that act as electrodes, for power and ground, wrapped around a glass tube. Power is sent to one of these electrodes by using a radio frequency (RF) electric signal at 13.56 MHz. The high frequency signal causes an oscillating displacement current in the glass wall and power can be coupled capacitively to the plasma. With this configuration, all contact between the plasma and electrodes is removed, therefore the reactor operates with relatively little contamination from wetted surfaces. The flow-through reactor has already been the workhorse of NEP synthesis of nanomaterials, and it is being used by an increasing number of groups worldwide.

1.3. Problems in using NEPs for Nanomaterial Synthesis

With the flow-through reactor, semiconductor nanocrystals of high quality Si, Ge, ZnO, Cu$_2$S, InP and InGaP were produced as monodisperse and free-standing NCs, some with tunable size and optical properties. However, the synthesis of metal particles and semiconducting carbides and nitrides were less successful, since aggregates were present, and
the control on size and optical properties was poor. Furthermore, reports on the synthesis of non-refractory metals and semi-metals have been absent in literature.

Based on the studies reported, it appears that the guidelines for choosing the right vapor precursor that yields a good material through NEP synthesis are unclear. Hydrides, chlorides and fluorides are the purest vapor precursors as they only lead to hydrogen or halogen impurities, but their availability is limited to Si (e.g. SiH₄, SiCl₄), Ge (e.g. GeCl₄, GeF₄) and a few other elements. Furthermore, their practical use is often quite laborious since many of them, especially the pnictogens (e.g. PH₃, SbH₃), are extremely toxic. Metalorganic precursors are largely available for almost every element (e.g. diethylzinc for Zn, trimethylgallium for Ga), but they often lead to significant carbon contamination in the final product⁷⁶,⁷⁷. In addition, when metalorganic compounds that have large amounts of organic groups are used as precursors, aggregated particles are commonly observed⁷³,⁷⁵. Moreover, the material yield varies for different precursors of the same element⁷⁸. Even in the case where the same precursors are used, the lack of reports on the measurement of plasma parameters make the comparison of results obtained by different groups of researchers difficult. Overall, the choice of a precursor and plasma parameters that would result in the production of high-quality NCs with good yield is not known. Most importantly, this ambiguity is further complimented by the unknown requirements dictated by the physical properties of the desired material, such as vapor pressure, melting point, surface tension, etc., in terms of plasma parameters necessary for obtaining a final product with good quality.

Investigation of the fundamental mechanisms of aerosol growth in NEP can shed light on the unknowns of NEP synthesis of NCs and unravel the true potential NEP as a synthesis environment. However, elucidating the dominant mechanisms of growth in NEP is largely hindered by the chemical complexity that arises upon the decomposition of vapor precursors used to synthesize the
material. Most of the experimental and modeling work on aerosol dynamics in NEP is done on the synthesis and growth of Si particles from SiH$_4^{79,80}$. Even though SiH$_4$ is one of the chemically simplest precursors, growth of silicon particles from SiH$_4$ involves a chemical clustering mechanism comprised of more than 2000 reactions$^{80}$. Such a chemical reaction network can be solved, but to amass an overall knowledge on the fundamentals of aerosol dynamics in such a case is difficult, and some of the important physical growth mechanisms may be overlooked. It can be said that the synthesis of high-quality Si NCs from SiH$_4$ in NEP has been empirically established in the last 15 years, but translation of this knowledge for well-defined synthesis of other materials is currently unclear.

1.4. The Aim and Scope of the Dissertation

The promise of synthesizing monodisperse, free-standing and size-controlled nanomaterials in the gas-phase makes NEP a unique synthesis environment. NEP has the potential to combine the advantages of colloidal and equilibrium gas-phase synthesis. However, understanding of the aerosol dynamics inside NEPs is far from complete. There is a need for the fundamental investigation of plasma-aerosol interactions, which can reveal the important growth mechanisms and the operational parameters that are responsible for producing a material with desired properties. This dissertation aims to extend the understanding of dusty NEPs and their use in nanomaterial synthesis.

The primary goal of this dissertation is to develop a simple framework for studying the interaction between NEP and aerosols composed of small particles (<500 nm). The study employs archetypal tubular flow-through reactors operated at low pressure, as many researchers have done previously. The novelty of the approach lies in the type of the precursors used for studying plasma-
Figure 1.8. Methodology employed in this dissertation. Solid red arrows depict the flow of aerosols. Dotted orange arrows denote the feedback loop that involves the measurement and adjustment of plasma parameters. Dashed blue lines represent aerosol modeling, which takes measured plasma parameters as input and replicates experimental results.

In the first part of this work, pre-made elemental aerosols are sent into a NEP as probes for investigating plasma-aerosol interactions. The change in aerosol size distribution and morphology upon passing through a NEP of argon is studied primarily by electron microscopy. Using elemental precursors as probes removes the chemical complexity that is encountered when vapor precursors are used, so that the barebones of physical growth mechanisms can be observed. Experimental results are complemented by the measurement of plasma parameters and modeling of aerosol dynamics. The methodology is summarized in Figure 1.8, and it depicts the general conception of NEP acting as a processor of mass.

In the second part of this work, knowledge obtained from the combined experimental-modeling approach employed in the first part of the dissertation is translated into the design and characterization of a new NEP-based synthesis method. This method, termed as nonequilibrium plasma aerotaxy (NPA), uses elemental aerosols as precursors. Accordingly, studies on NPA were also conducted by following the methodology shown in Figure 1.8. The precursor aerosols are sent into a reactive plasma for the purpose of producing compound semiconductor NCs that
currently do not have an established method of synthesis. The materials studied are gallium nitride (GaN), indium nitride (InN) and gallium antimonide (GaSb).

The structure of the text is as follows. Chapter 2 provides a brief summary of the most important aspects of dusty plasmas, namely, the characteristic length scales, charging and particle heating. Chapters 3-6 form the first part of the dissertation, where fundamental studies on plasma-aerosol interactions are reported. Chapter 3 presents the results obtained by sending pre-made bismuth aerosols into NEP, where a new aerosol growth mechanism is revealed. Chapter 4 is on a simple model of aerosol dynamics that describes the results obtained in Chapter 3. Results of chapters 3 and 4 were published in the following paper:


Identifiers, such as the one given in brackets above, are used to cite the papers published during the course of this study. Chapter 5 presents the results of plasma diagnostics conducted on the flow-through reactor. Chapter 6 uses the data presented in Chapter 5 in a model that calculates the temperature history of particles as they travel through the flow-through reactor. Based on the modeling results, the vaporization mechanism detailed in Chapter 3 is re-evaluated. Results of Chapters 5 and 6 were published as:


Chapters 7-10 form the second part of the dissertation, and they focus on synthesis of compound semiconductors by employing the fundamental knowledge obtained in the first part. Chapter 7 introduces NPA for the synthesis of GaN NCs. Chapter 8 presents the observations
relevant to the mechanism of GaN growth during NPA. The majority of these results was published in:


Chapter 9 is on the extension of NPA to another nitride, InN. Chapter 10 further extends NPA to the synthesis of GaSb, in which two precursor aerosols are employed. These studies were published as separate papers:


Finally, Chapter 11 concludes the dissertation and presents an outlook on future experiments and relevant applications.
Chapter 2

Fundamental Processes in Dusty Nonequilibrium Plasmas

This chapter provides a brief introduction to the two of the most important processes in dusty nonequilibrium plasmas: particle charging and particle heating. The presentation of a complete survey of the physics behind these processes would be intractable. Therefore, first, the characteristic length scales in dusty NEP are described. Afterwards, by using the hierarchy between these length scales under conditions that are relevant to this work, simplified models of particle charging and heating are presented. More advanced theories and relevant literature are mentioned and described in the following chapters.

2.1. Characteristic Length Scales in Dusty NEP

Five characteristic length scales and their hierarchy allow the categorization of numerous physical phenomena in dusty NEP. These scales are:

i) The characteristic size of the reactor: $L$. 
ii) Particle diameter: $d_p$. The term “particle size” is also used interchangeably.

iii) Mean interparticle spacing: $\ell$.

iv) Mean free path of the neutrals, ions and electrons: $\lambda_g$, $\lambda_i$ and $\lambda_e$ respectively.

v) Debye length: $\lambda_D$.

In this work, only tubular flow-through reactors were used. Therefore, the characteristic size of the reactor was the inner radius of the tube. Tube radii were between 0.35-2.3 cm. Particle sizes, that were either employed in calculations or observed in experiments, spanned from the size of a dimer (<1nm) to 500 nm. Mean interparticle spacing can be calculated by assuming a simple cubic arrangement of aerosol particles,

$$\ell = N_\infty^{-1/3}, \quad (2.1)$$

where $N_\infty$ is the total number concentration.

For the mean free path of the neutrals and ions, the expression derived from simple kinetic theory can be used:\n
$$\lambda = \frac{k_B T_g}{\sqrt{2\sigma p}}. \quad (2.2)$$

In equation 2.2, $k_B$ is the Boltzmann constant, $T_g$ is the background gas temperature, $\sigma$ is the collision cross-section and $p$ is the total pressure. For $\lambda_g$, the cross-section for neutral-neutral collisions, $\sigma_n$, is used in equation 2.2. Similarly, for $\lambda_i$, the cross-section for ion-neutral collisions, $\sigma_i$, is used. In general, $\sigma_n < \sigma_i$. The only neutral-neutral collision cross section of interest in this

\footnote{Throughout the text, the word “particle” is only used for the particles of the aerosol, and not for electrons or for molecules as in many textbooks of plasma physics.}

\footnote{The constant factor $1/\sqrt{2} = 0.707$ may differ in different approaches involving kinetic theory. For example, in Mason and MacDaniel\cite{82}, it is $2/\sqrt{(3\pi)} = 0.651$.}
study is the one of argon\textsuperscript{83}, which can be taken as $3.8 \times 10^{-19}$ m\textsuperscript{2}, independent of temperature\textsuperscript{e}. However, for $\sigma_i$, the dependence on temperature should be accounted for, since $\sigma_i$ affects the rates of ion bombardment significantly (Chapter 6). $\sigma_i$ depends on an effective ion temperature\textsuperscript{82}, which has both thermal and field-related components,

$$T_{\text{eff}} = T_i + \frac{m_i}{3k_B} \left( \mu_i E \right)^2,$$

(2.3)

where $T_i$ is the ion temperature, $m_i$ is the ion mass, $E$ is the local electric field and $\mu_i$ is the mobility of the ion. Throughout the text, it is assumed that the ion temperature is equal to the background gas temperature, i.e. $T_i = T_g$. Furthermore, only the “bulk” plasma, which is the plasma far away from walls, is considered for the evaluation of plasma parameters and related variables. In the tubular flow-through reactor, bulk plasma corresponds to the region nearby the centerline. Around the centerline, the plasma has a flat potential due to axial symmetry\textsuperscript{79}, and thus the local field has a relatively small magnitude. Using the published values of $\mu_i$ for argon\textsuperscript{85}, the drift-related component is found to be small, therefore $T_{\text{eff}} \approx T_i$ in this work. The temperature-dependent cross sections of the monovalent argon ion are given in Table 2.1.

**Table 2.1. Ar-Ar\textsuperscript{+} cross section\textsuperscript{85}.**

<table>
<thead>
<tr>
<th>$T_{\text{eff}}$ (K)</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_i \left(10^{-19} \text{ m}^2\right)$\textsuperscript{d}</td>
<td>15.7</td>
<td>15.7</td>
<td>15.3</td>
<td>14.8</td>
<td>14.5</td>
<td>13.7</td>
<td>13.2</td>
<td>12.9</td>
</tr>
</tbody>
</table>

The mean free path of electrons is given with a slightly different convention:

$$\lambda_e = \frac{k_B T_g}{\sigma_e p}.$$

(2.4)

\textsuperscript{e} Neutral-neutral cross-sections usually have a weak dependence on temperature\textsuperscript{84}.

\textsuperscript{d} This cross section is rigorously described by the momentum-transfer collision integral\textsuperscript{85}, generally shown as $\Omega^{(1,1)}$. 
\( \sigma_e \) is the electron-neutral total cross section, and it is highly dependent on electron temperature\(^{86}\).

The remaining parameter, the Debye length, is an important parameter that characterizes the length over which electrostatic force is screened from the rest of the plasma. It is derived from the linearized Poisson-Boltzmann equation, and it has the general form\(^ {87}\)

\[
\lambda_D = \sqrt{\frac{\varepsilon_0 k_B}{e^2 n_0} \left( \frac{1}{T_e} + \frac{1}{T_i} \right)^{-1}},
\]

which simplifies into \( \lambda_D \approx (\varepsilon_0 k_B T_i / e^2 n_0)^{1/2} \) since \( T_e >> T_i \) in this work. In equation 2.5, \( \varepsilon_0 \) is the permittivity of free space, \( e \) is the elementary charge and \( n_0 \) is the plasma density. Pristine plasmas, i.e. plasmas that do not contain any particles, are quasineutral as long as they are sufficiently far away from the walls, and plasma density is equal to the density of ions and electrons: \( n_0 = n_e = n_i \). The screening zone that surrounds an ion, a charged particle or a charged surface is on the order of few \( \lambda_D \)\(^ {88}\). This zone is called as the sheath. Throughout the text, Debye lengths that are specific to ions and electrons, \( \lambda_{Di} = (\varepsilon_0 k_B T_i / e^2 n_0)^{1/2} \) and \( \lambda_{De} = (\varepsilon_0 k_B T_e / e^2 n_0)^{1/2} \) respectively, are also mentioned.

Calculated values of \( \lambda, \lambda_D \) and \( \ell \) are given in Figure 2.1. In this work, plasma densities were between \( 10^{17} \text{-} 10^{19} \text{ m}^{-3} \), and pressures were between 1.5-6 Torr (200-800 Pa), whereas particle concentration spanned the entire axis given in Figure 2.1. The most basic criterion that was satisfied in this work is \( L \) having the largest value amongst all characteristic lengths. The relation between the remaining four lengths are discussed in the next section.
Figure 2.1. Representative values of mean free paths, Debye length and mean interparticle spacing in dusty NEP. Calculations were done for an Ar plasma at 400 K background gas temperature and with an electron temperature of 2 eV for determining the electron-neutral cross section\(^6\). The vertical axes have identical span.

2.2. Particle Charging

Particle charging is the most important process in a dusty plasma. It can affect the motion of a particle due to charge-associated drift or electrostatic trapping, as mentioned in the Introduction (Figure 1.3). It also causes particles to be bombarded intensely by ions, which can lead to many surface processes, such as growth, etching and sputtering.

In the plasma, particles are negatively charged. This can be immediately recognized based on the orders of magnitude difference between the fluxes of ions and electrons onto an uncharged particle. To an uncharged particle, ions and electrons arrive with their thermal fluxes\(^7\)

---
\(^6\) Energy units for electron temperature, i.e. \(k_B T_e\), are used throughout the text. 1 eV \(\approx 11600 \text{ K}\).
\(^7\) The drift component of velocities caused by gas flow and local fields is usually insignificant when compared to thermal velocities in bulk RF plasmas.
\[ J_{i,th} = \frac{1}{4} n_i \beta_i, \quad J_{e,th} = \frac{1}{4} n_e \beta_e, \quad (2.6) \]

where \( \beta_{i,e} = (8k_B T_{i,e}/\pi m_{i,e})^{1/2} \) is the mean thermal speed of ions and electrons, respectively. \( m_e \) is the free electron mass. Electrons have thermal velocities of roughly \( 10^6 \) m/s, whereas ions generally have velocities on the order of few hundreds of m/s.

The initial arrival of an electron to a particle builds up a potential that repels other surrounding electrons. This potential rejects a major portion of the electrons that have low energy. At the same time, it attracts ions, and the particle starts receiving ions with much greater flux than the thermal flux given in equation 2.6. The majority of the ions that enter the sheath eventually hit the particle. In this dissertation, all electrons that collide with a particle are assumed to be absorbed, and similarly, all ions that collide with the particle recombine, extracting an electron from the particle. Eventually, the fluxes of electrons and ions balance on the surface of the particle:

---

\( \Phi_p \) is the particle potential (vide infra). At steady state, the ion current density on to a particle, \( I_i \), is usually few A/cm².

---

\( \Phi_p < 0 \)

---

\( \langle J \rangle = \langle J_e \rangle, \quad I_i \sim \text{few A/cm}^2 \)

---

\( \Phi_p = 0 \)

---

\( J_i = J_{i,th} \ll J_e = J_{e,th} \)

---

\( t \sim \text{few } \tau_C \)

---

**Figure 2.2. Particle charging in NEP.** Charging of a conducting particle placed in NEP is pictured. The width of the solid arrows depict the magnitude of the fluxes. \( \Phi_p \) is the particle potential (vide infra). At steady state, the ion current density on to a particle, \( I_i \), is usually few A/cm².

---

\( \Phi_p \) is the particle potential (vide infra). At steady state, the ion current density on to a particle, \( I_i \), is usually few A/cm².

---

\( \Phi_p < 0 \)

---

\( \langle J \rangle = \langle J_e \rangle, \quad I_i \sim \text{few A/cm}^2 \)

---

\( \Phi_p = 0 \)

---

\( J_i = J_{i,th} \ll J_e = J_{e,th} \)

---

\( t \sim \text{few } \tau_C \)
\[ \langle J_i \rangle = \langle J_e \rangle. \]  
(2.7)

The process of particle charging is summarized in Figure 2.2. The angle brackets in equation 2.7 stand for the time-average of the fluxes. They are used for completeness, since charging is a stochastic phenomenon, and it involves the addition and subtraction of discrete charges. Therefore, charge of a particle usually oscillates around a mean charge with some frequency, and a charge distribution exists across particles that have the same diameter\(^89\).

The accumulation of negative charge on the particle leads to the creation of a sheath around the particle. In the Introduction, it was mentioned that the ability to shield itself against electric fields is one of the major properties of the plasma phase. The creation of the sheath is a manifestation of this property. Since a negatively charged particle creates a field, the sheath surrounding the particle ends up having a positive space charge to shield this field from the plasma. The perturbed density of ions and electrons and the resulting potential profile are given in Figure 2.3. Resolving the distribution of the potential together with the concentration profile of ions and electrons is not straightforward\(^88,90,91\). However, if the hierarchy between the characteristic lengths allows, simple expressions for the fluxes of electrons and ions can be obtained without solving complete problem. The first simplification made is based on the criterion \( \ell \gg \lambda_D \), which was always satisfied in this work (Figure 2.1). This criterion means that the charging of a particle is independent of the charges carried by neighboring particles. Furthermore, if \( \lambda_i \gg \lambda_D \) and \( \lambda_e \gg \lambda_D \), ions and electrons do not collide with neutrals as they travel within the sheath. Electrons easily satisfy this criterion, though ions satisfy it barely. Under these conditions, electrons and ions can be considered collisionless, and one can use the orbital motion limited (OML) theory\(^92\), which is the simplest and the most commonly used charging model for low pressure plasmas. The model derives capture cross-sections based on the conservation of energy and momentum of the ions and
Figure 2.3. Schematics of the sheath around a charged particle. Region I is the bulk plasma with plasma density \( n_0 \), which is equal to ion and electron densities, \( n_i \) and \( n_e \) respectively. Region II is usually called as the pre-sheath. This region has perturbed densities of charged species, but quasineutrality is retained. Regions III and IV constitute the sheath, which is few \( \lambda_D \) wide. \( \Phi_0 \) is the plasma potential and \( \Phi_s \) is the potential on the surface of the particle, whereas \( r_p \) is the radius of the particle. In reality, the edge of the sheath is not well defined in terms of the potential distribution. Quasineutrality does not hold in the sheath. Region IV is sometimes called as the ion-sheath, or the Child-Langmuir sheath. In region IV, electron density is negligible, and a strong positive space charge exists.

Electrons upon hitting the particle. Assuming Maxwellian energy distributions for both the ions and electrons, the following expressions of fluxes for ions and electrons onto a negatively charged spherical particle can be derived using the OML theory:

\[
J_i = \frac{1}{4} n_i \beta_i \left( 1 - e^{\Phi_p / k_B T_i} \right),
\]

(2.8)

---

1 The electron energy distribution function (EEDF) is most of the time non-Maxwellian. However, the choice of the EEDF for deriving the OML electron flux expression has negligible effect on the resulting particle potentials in general.

2 For a positively charged particle: \( J_i = (1/4)n_i \beta_i \exp(-e\Phi_p/k_B T_i) \), and \( J_e = (1/4)n_e \beta_e \exp(1 + e\Phi_p/k_B T_e) \). That is, fluxes are piecewise continuous with respect to charge, or equivalently, with respect to potential (Equation 2.10).
\[ J_e = \frac{1}{4} n_e \beta_e \exp \left( \frac{e \Phi_p}{k_B T_e} \right). \]  

(2.9)

These expressions assume the presence of monovalent ions only, and most importantly, they are valid for \( d_p << \lambda_D \). Therefore, the overall criterion for the OML model to be valid in a dusty NEP is \( d_p << \lambda_D << \lambda_i \). By using equations 2.7, 2.8 and 2.9, one can estimate the particle potential, \( \Phi_p \).

A small particle can be modeled as a spherical capacitor, therefore \( \Phi_p \) can be given as:

\[ \Phi_p = \frac{eZ}{2\pi \epsilon_0 d_p}, \]

which depends linearly on charge, \( Z \). \( \Phi_p \) is defined with respect to the plasma potential \( \Phi_0 \),

\[ \Phi_p = \Phi_s - \Phi_0, \]

with \( \Phi_s \) being the potential on the surface of the particle. Although there is no exact solution for the time-averaged, mean particle charge when \( T_i \neq T_e \) in OML theory, a highly accurate approximate solution is available:

\[ \langle \bar{Z} \rangle \approx 0.73 \frac{2\pi \epsilon_0 d_p k_B T_e}{e^2} \ln \left( \frac{n_i}{n_e} \frac{m_e T_e}{m_i T_i} \right). \]

(2.12)

Equation 2.12 indicates that the mean particle charge is linearly dependent on particle size and electron temperature. Substituting equation 2.12 in equation 2.10 gives the mean particle potential:

\[ \langle \bar{\Phi}_p \rangle \approx 0.73 \frac{k_B T_e}{e} \ln \left( \frac{n_i}{n_e} \frac{m_e T_e}{m_i T_i} \right). \]

(2.13)

---

\( ^k \) When \( \lambda_D << \lambda_i \) and \( \lambda_D << d_p \) (a.k.a. thin sheath limit), Bohm theory applies for the ion flux. This case is observed during the charging of large particles and walls when the plasma density is relatively high. Due to the thin sheath, Bohm ion flux is independent of geometry, and so is the OML electron flux given by equation 2.9, unless the collecting surface has a concave shape. Thus, equation 2.9 is valid for any spheroidal particle size as long as \( \lambda_{De} << \lambda_\epsilon \).
which is independent of particle size.

Since the particles acquire a net negative charge, they act as sinks for electrons. The quasineutrality is disturbed within the sheath (Figure 2.3), but in the bulk plasma, it is retained. However, particles can cause a drop in electron density of the bulk plasma. The condition of quasineutrality has to be modified accordingly when particles are present,

\[ n_e = n_i + \int_{d_p^*}^{\infty} \langle Z \rangle n_p \, d_d \, d_p, \]

where \( n_p \) is the size distribution and \( d_p^* \) is the critical nucleus size. The integral computes the number of charges on all particles of all sizes within the aerosol. This modified quasineutrality criterion is expected to be valid as long as the particles do not deplete electrons. Thus, the criterion for unipolar charging is presented as a comparison between the total charge on particles and the positive ion density, which is usually the value measured in a pristine plasma:\(^{54}\)

\[ n_i \gg \int_{d_p^*}^{\infty} \langle Z \rangle n_p \, d_d \, d_p. \]  

When the inequality given by equation 2.15 is violated, bipolar charging and coagulation is expected to occur due to low electron density in the bulk plasma\(^ {54}\).

2.3. Particle Heating

A particle suspended in NEP is constantly involved in a plethora of heat transfer processes. Electrons and ions that reach the surface of the particle carry significant kinetic energy, and some of this energy is transferred to the particle. When ions recombine on the surface of the particle, a heat of recombination is released. Excited neutrals can quench on the surface of the particle,
releasing energies in a way that is similar to the ions that recombine. Neutrals can cool the particle down by conduction. A particle can lose heat by thermal radiation or via thermionic emission. UV light emitted by the plasma can be absorbed by a particle in the form of heat. Condensation or vaporization of species from the surface of the particle can lead to the absorption or release of heat respectively. These processes are depicted in Figure 2.4. In terms of energy influx, it is generally argued that the energy transferred to a particle by ion and electron bombardment dominates\textsuperscript{97}, and at few Torr pressure, the main cooling channel is conduction\textsuperscript{98,99}. Therefore, in this chapter only the major mechanisms of heat transfer are reviewed. Some of the other relevant mechanisms are discussed in Chapter 6.

Assuming that the continuum description of heat transfer holds within a particle, a lumped-in-space formalism appears to be valid since Biot numbers\textsuperscript{100} are orders of magnitude lower than 1, primarily due to the small sizes of the particles. With all temperature gradients in the particle neglected, the transient energy balance for a particle in NEP can be written as

![Figure 2.4. Heat transfer mechanisms on a particle suspended in NEP\textsuperscript{97,98}.](image-url)
\[
\frac{dT_p}{dt} = \frac{6}{d_p\rho_p C_p} \left( q_{ie} - q_{Kn} \right),
\]  
(2.16)

where \( t \) is time, \( T_p \) is particle temperature, \( \rho_p \) is particle density and \( C_p \) is particle heat capacity. \( q_{ie} \) and \( q_{Kn} \) denote the heat flux terms due to ion-electron bombardment and Knudsen conduction cooling, respectively. \( q_{ie} \) includes the heat of recombination of ions and the transfer of kinetic energy by ion and electron bombardment:

\[
q_{ie} = J_i \left( \Delta H_{rec} - W + f e \Phi_p \right) + 2k_B T_e.
\]  
(2.17)

\( \Delta H_{rec} \) is the heat of recombination (-15.76 eV for argon), \( W \) is the work function, and \( f \) is the efficiency for kinetic energy transfer upon ion impact. The first two terms in the parentheses stand for the heat released upon ion-electron recombination on the surface. It is assumed that \( \Delta H_{rec} \) is completely absorbed by the particle, and an amount specified by \( W \) is spent for the detachment of an electron. The third term in the parentheses denote the kinetic energy of an impacting ion, which is approximately equal to the particle potential since the energy of a cold ion in the bulk plasma is low. The final term describes the kinetic energy of collected electrons. This term is obtained by using the OML capture cross-section, and by averaging the energy of the arriving electrons over the Maxwell-Boltzmann energy distribution. It is interesting that the particle potential does not play a role in the mean energy of the captured electrons. Particle potential only affects the number of captured electrons. In equation 2.17, it is implicitly assumed that \( J_i = J_e \).

For a monoatomic gas, Knudsen conduction flux, \( q_{Kn} \), is expressed as:

\[
q_{Kn} = \frac{1}{2} \beta_g \frac{P}{T_g} \alpha_H \left( T_p - T_g \right).
\]  
(2.18)
$\alpha_H$ is the thermal accommodation coefficient (~0.9 is suggested for Ar$^{102,103}$). In this work, the use of this kinetic theory expression is justified by the fact that the Knudsen numbers$^{48}$,

$$Kn = \frac{2\lambda_g}{d_p}, \quad (2.19)$$

are larger than 10 for the sizes of the particles employed.

In Chapter 1, it was mentioned that small particles are argued to experience spikes in temperature upon collecting an ion. This effect can be realized when the internal energy of a particle is of the same magnitude when compared to the energy released due to ion-electron recombination. When temperature spikes are present, the continuous time formulation given by equation 2.16 loses its validity. It is important to come up with a criterion that determines when equation 2.16 is valid. The following inequality provides a suitable criterion:

$$O\left(mC_p T_g\right) > O\left(\left|\Delta H_{rec}\right| - W + fe\left|\Phi_p\right|\right), \quad (2.20)$$

where $O$ denotes order of magnitude, and $m$ is the mass of a particle: $m = (\pi/6)\rho_p d_p^3$. Equation 2.19 holds for particles that have diameters larger than 10 nm. Results from detailed calculations support this criterion$^{56}$. With equation 2.16 valid, one can solve for the steady-state temperature of a particle$^{99}$:

$$T_p = T_g \left[1 + \frac{2J_i}{\alpha_H \beta_g} \left(\left|\Delta H_{rec}\right| - W + fe\left|\Phi_p\right| + 2k_B T_e\right)\right]. \quad (2.21)$$

Steady-state particle temperature is independent on size. It is linearly proportional to ion flux, but inversely proportional to pressure.
Particle heating theory is somewhat controversial due to the ambiguities in the heat transfer mechanisms, especially in ion recombination. The partitioning of $\Delta H_{\text{rec}}$ between the produced neutral molecule and the particle is unknown. Furthermore, it is also unknown whether the amount of heat that is absorbed by the particle is localized\textsuperscript{104}. In other words, the validity of thermal equilibration across the particle after each input of energy via recombination is unclear. Despite these ambiguities, particle heating models are used in literature to explain experimental results with a reasonable amount of success. Examples from published studies are given in Chapter 6.
Chapter 3

Vaporization of Aerosols in Nonequilibrium Plasma

The first and the most fundamental inquiry that involves the use of the methodology given at the end of the Introduction (Figure 1.8) is presented in this chapter. In a simple experiment, the change in the size distribution of a pre-made aerosol after it passes through a NEP was investigated. The environment was made to be chemically pure; it only contained argon as the plasma and the material of the aerosol, which was chosen to be metallic bismuth. As summarized in Chapter 1 and 2, the current conception of growth in NEP suggests that the pre-made aerosol would get negatively charged in the plasma if its number concentration is significantly lower than the ion density. Coagulation would be suppressed, and the aerosol is expected to leave the plasma with a size distribution that is similar to that of its initial state.

To realize the experimental methodology that relies on pre-made aerosols for probing growth dynamics in NEP, submicron aerosols of metallic bismuth with a polydisperse size distribution were produced upstream by a thermal route using an evaporation-condensation generator. These aerosols were subsequently passed through a tubular flow-through NEP reactor downstream. It
was found that the plasma can convert a polydisperse size distribution into a size distribution with geometric standard deviation less than or equal to 1.1, which is an accepted indicator of monodispersity for gas-phase synthesized particulate materials\textsuperscript{105}. The observed transformation in size distribution requires a new mechanism in the growth dynamics of particulate materials in NEP, namely vaporization at low background gas temperature by a nonequilibrium process. The observation of such a vaporization mechanism presented here is previously unreported. The mechanism operates in a highly nonequilibrium environment, and it is expected to assist a wide range of chemical transformations during synthesis of materials in NEP. Furthermore, it may be a major reason for the production of monodispersed particles in NEP.

3.1. Using Test Aerosols as Probes

3.1.1. Generation of Test Aerosols and the NEP Reactor

The test aerosol was generated by an evaporation-condensation process. In this method, a thermal medium evaporates the material. The produced vapor is carried by an inert gas and the vapor-gas mixture is then rapidly quenched, leading to aerosol growth. By adjusting the temperature of the evaporating medium and the quenching rate, it is possible to generate aerosols having different size distributions and mass concentrations. The method allows preparation of materials without using metal-organic vapor precursors. Precursors were avoided to study plasma-particle interaction in a well-defined environment that contains no chemicals other than the particle material and the plasma gas.

The feasibility of creating an aerosol with an evaporation-condensation generator depends on the vapor pressure and the purity of the source material that is to be evaporated, as well as the stability of the material against oxidation in presence of trace oxygen and water vapor. Low purity
can lead to accumulation of impurities on the surface where evaporation occurs. A layer of accumulated impurities can hinder evaporation if the vapor pressure of the impurities are lower than that of the source material. The stability, which is usually described by the use of an Ellingham diagram\textsuperscript{106,107}, is required to prevent the formation of an oxide layer, which usually has a lower vapor pressure in comparison to that of the pure element. In the experimental setups employed in this work, trace oxygen and water vapor usually stem from the gas cylinders used. As an example, early experiments conducted with 99.99% pure zinc shots to generate a zinc aerosol under ultra-high purity argon atmosphere (impurity concentrations: 2 ppm O\textsubscript{2}, ~3 ppm H\textsubscript{2}O) failed due to the formation of a tarnished oxide layer on the surface of metallic zinc.

Bismuth was found to be a suitable material for generating an aerosol of it by evaporation-condensation (Figure 3.1). It is a semi-metal with a vapor pressure significantly lower than that of zinc. Pellets of Bi (99.999\% purity, Sigma-Aldrich), weighing approximately 33 g were placed into an alumina boat (Coors Z561738, Millipore Sigma). The boat rested in a fused silica tube of 1.9 cm outer diameter and the tube was placed into a furnace (CM Furnaces Inc.). The carrier gas was ultra-high purity argon (UHP 5.0, Praxair) and it flowed through the tube at a rate of 5000

![Aerosol generator diagram](image)

**Figure 3.1.** Setup for aerosol probe experiments.
standard cubic centimeters per minute (sccm), which was controlled using a mass flow controller (G-Series, MKS). By operating the furnace at 1173 and 1273 K, two different aerosols were produced upon subsequent quenching. These aerosols had different mass concentrations. The aerosol generated using a furnace temperature of 1173 K had a mass concentration of 0.54 mg/m$^3$ and is termed low concentration. The aerosol generated at 1273 K had a mass concentration of 2.69 mg/m$^3$ and is termed high concentration. Over the course of a single experiment, approximately 10% of the Bi evaporated from the boat. Quenching of the vapor was accomplished using an electric fan to increase the cooling rate by forced convection. The test aerosols were found to be reproducible for runs on different days for the same process parameters (Figure 3.2). The test aerosols had a bimodal size distribution. A possible reason for the formation of a bimodal size distribution is the occurrence of two subsequent nucleation events, which can be caused due to a residence time distribution under laminar flow as the metal vapor leaves the furnace.

![Figure 3.2. Frequency distributions of primary particle size for high concentration Bi test aerosols produced in three different experiments.](image)

The distributions were obtained via transmission electron microscopy (*vide infra*).
Downstream from the evaporation/condensation generator, a portion of the aerosol was sampled through a 150 μm tube orifice (optically measured 1/4” SS, Lenox Laser) into a low-pressure section, wherein the plasma was generated. The formation of bimodal test aerosols might also be caused due to partial agglomeration as the aerosol passes through the orifice. The flow rate in the low-pressure section was estimated to be 165 sccm. Pressure was maintained at 1.5 Torr using a diaphragm valve upstream of a rotary vane vacuum pump (RV12, Edwards) and measured using a pressure transducer (Baratron 722B, MKS). At the inlet to the vacuum section, the temperature was measured by a K-type thermocouple and found to be approximately 295 K. The gas velocity in the vacuum portion of the apparatus was approximately 7.4 m s⁻¹. The plasma was generated in a fused silica tube of 1.9 cm outer diameter and 1.5 mm wall thickness by capacitively coupling RF power through two aluminum ring electrodes (The reactor used is shown in Figure 1.4a). The powered electrode was upstream of the ground electrode. The position of the electrodes was kept fixed in all experiments. A 13.56 MHz RF power supply (AG0613, T&C Power Conversion) was used in conjunction with a matching network (AIT600, T&C Power Conversion) to minimize the reflected power. For all RF powers used (10-120 W), the plasma filled the entire silica tube (Figure 3.3).

![Image of plasma reactor](image)

**Figure 3.3. Complete view of the fused silica tube containing the plasma.** The left ring was the powered electrode, and the right ring was the ground electrode. Gas flow was from left to right. The reactor shown was operated at 1.5 Torr with argon plasma ignited in it.
3.1.2. **Electron Microscopy**

Particles were collected upstream of the diaphragm valve for imaging with a transmission electron microscope (TEM). The particles were dispersed on an ultrathin carbon film, which was supported on lacey carbon, which in turn was supported on a copper grid (01824, Ted Pella). The TEM grids were suspended vertically on a 400 mesh steel filter using adhesive tape. Particles were found to deposit on the center of the filter at low input plasma powers, up to 40 W. Thus, the TEM grids were placed in the center of the filter for experiments conducted with low RF power inputs. At higher powers the deposition pattern was observed to expand on the filter in the form of a concentric ring. Experiments were conducted wherein TEM grids were placed at different radial positions on the filter, and it was found that there was negligible particle deposition outside of the observed rings. For subsequent experiments at higher RF power inputs, the grid was placed in the ring wherein the particles deposited. The collected particles were imaged with a TEM having a 120 kV LaB$_6$ filament (Tecnai G2 Spirit, FEI). Primary particle sizes were extracted by processing the images with ImageJ software. A minimum of 260 particles were measured from the images obtained from each grid. Histograms were created for the frequency distribution of the logarithm of primary particle diameter. Normal distributions were fitted to these histograms. The corresponding geometric standard deviations of a lognormal distribution was obtained with the formula $\sigma_g = e^{2.303 \sigma}$ where $\sigma$ is the standard deviation for the normal distribution fitted to the histogram of the logarithm of particle diameter. Monodispersed is defined as $\sigma_g \leq 1.1^{105}$.

3.1.3. **Plasma Treatment of Aerosols**

Test aerosols were treated with the plasma at different input powers. For the low concentration aerosol, the upper limit was 40 W. For the high concentration aerosol, the maximum power
explored was 120 W. Powers lower than 10 W were not investigated since it was not possible to generate a stable and voluminous plasma as shown in Figure 3.3.

Mass yield of the plasma treatment was assessed by collecting particles on filters upstream of the diaphragm valve. 400 mesh stainless steel filters were used. These stainless steel mesh filters were found to have high collection efficiency. A quartz-crystal microbalance with 0.1 mg precision (Entris 124-1S, Sartorius) was used for weighing the filters. For mass measurements, only the high concentration aerosol was used, in order to collect more material and make the measurements more accurate.

3.1.4. Optical Emission Spectroscopy (OES)

Light emitted from the plasma was collected by a fiber optic cable connected to a plano-convex lens. Intensities over the spectrum between 200-1025 nm were measured using a miniature spectrometer (USB2000+XR1-ES, Ocean Insight). Light was collected using two different configurations. In the first configuration, the lens was placed below the fused silica tube. The emission spectra were recorded at different axial positions along the plasma. In the second configuration, the lens was placed at the diagnostic port at the end of the straight tubular path and aligned with the axis of the plasma tube (Figure 3.1). The spectrometer was used without any calibration. Therefore, it detected light around 450 nm with maximum sensitivity, due to the peak internal quantum efficiency of its linear array CCD sensor (Sony ILX511) at that wavelength.

3.2. In-flight size tuning

Electron microscopy revealed that the size distribution of the test aerosols became narrower after they passed through the plasma (Figure 3.4). Initially polydisperse aerosols (Figure 3.4a and
Figure 3.4. In-flight size tuning of Bi aerosols. (a, b) Bi test aerosols at different mass concentrations, termed respectively as low concentration and high concentration in the text. (c, d) Plasma treated forms of the aerosols given in (a) and (b) at 10 and 20 W of applied RF power, respectively. (e, f) Frequency distribution of primary particle size for aerosols of low and high concentration, with plasma off and on. Fitted curves represent log-normal distributions and corresponding geometric standard deviations are given.

3.4d) became monodisperse after plasma treatment, if the power was sufficiently low, 10 and 20 W respectively for the low and high concentration aerosols (Figure 3.4b and 3.4e). For both test aerosols, which had different mass concentrations and frequency distributions, the geometric standard deviation reached 1.1. The mean sizes of the particles were seen to be larger after plasma treatment (Figure 3.4c and 3.4f). Monodisperse Bi aerosols were found to have hexagonal-like facets (Figure 3.5), similar to previous observations on the Bi nanoparticles generated by evaporation-condensation\textsuperscript{108}.
Figure 3.5. Overview TEM image of plasma-treated high concentration Bi aerosol at 20W. Most particles were found to be faceted, with some secondary triangular grain growth on a hexagonal structure.

As input powers increased, the monodispersed peak started to vanish while its mean size increased and the fine mode reappeared (Figures 3.6 and 3.7). When input powers were high enough, an aerosol similar to the test aerosol was observed, however its mass concentration was
Figure 3.6. Frequency distributions of primary particle size obtained from TEM images for the low concentration Bi aerosol when the plasma is off and on (10 to 40 W). The applied RF power and $\sigma_g$ values are indicated in each of the panels.

much less when compared to the test aerosol. The mass yield decreased rapidly as input powers increased, presumably as a result of wall losses. A metallic film downstream of the powered
Figure 3.7. Frequency distributions of primary particle size obtained from TEM images for the high concentration Bi aerosol when the plasma is off and on (20-100 W). The applied RF power and $\sigma_g$ values extracted from lognormal fits are indicated in each of the panels.

electrode was quickly deposited at high power inputs and observed after sufficiently long experiments at lower power (Figure 3.8).
Figure 3.8. Metallic film formed in the vicinity of the powered electrode. Such films were formed more rapidly at higher applied RF powers and with higher aerosol mass concentration in the plasma. The collar seen in the photo is the powered electrode pushed to left. Its original location is marked by the two white dashed lines. The lens of the fiber used for OES (vide infra) can be seen at the bottom right.

At the plasma conditions that produced the monodispersed size distribution, a fiber optic probe was inserted into the center of the powered electrode to estimate the gas temperature. As discussed in Chapter 2, surfaces immersed in the plasma get hotter than the ambient gas primarily due to electron and ion bombardment. Nevertheless, it can be safely asserted that the temperatures measured with the probe indicate a maximum for the gas temperature\(^a\). The temperature measured by the sensor in the vicinity of the powered electrode was 354 K and 408 K for 10 and 20 W input power, respectively. These measurements indicated that the plasma was far from thermalization.

Unipolar negative charging of the aerosol particles in the LTP cannot fully explain the observation that the plasma causes the polydispersed aerosol to become monodispersed, since the

\(^a\) The measurement of gas temperature with fiber optic probes is discussed in detail in Chapter 5.
size distribution is modified after the plasma treatment, and the morphology of the plasma-treated aerosol is clearly different. However, if a new mechanism is included whereby particles can vaporize to generate a highly supersaturated vapor despite the low background gas temperature, then it would be possible to generate a monodispersed size distribution by condensation onto nuclei and remaining fragments. Such a mechanism has previously not been considered for dusty NEP. If vaporization of the Bi were occurring in the low temperature plasma, then photoemission from excited electronic transitions in those free Bi atoms is expected to occur.

### 3.3. Vaporization of the Bi Aerosol

Optical emission spectroscopy (OES) revealed that the Bi particles did indeed vaporize in the plasma, despite the low background gas temperature. Figure 3.9a shows emission spectra for a representative plasma with and without Bi particles present. The highest Bi peak observed at 306.0 nm belonged to the documented $6p^2(3P_0)7s \rightarrow 6p^3$ transition at 306.77 nm. At all power inputs, there was clear emission from atomic Bi (Bi I emission) when the particles were sent into the

![Figure 3.9. Plasma emission in the presence of Bi aerosol.](image)

(a) Emission spectra gathered downstream of the powered electrode with and without particles. The upper spectrum is offset for clarity. (b) A pale blue emission arises in the vicinity of the powered electrode when the Bi aerosol is present.
plasma, which resulted in the emission of a pale blue light (Figure 3.9b). The observation of blue light is rather curious since human eye cannot see the dominant Bi I emission at 306.77 nm. However, there are other Bi I lines between 400-500 nm with detectable emission intensity\textsuperscript{109}, which can cause this pale blue emission. Another explanation is the intensification of Ar II line emission, i.e. increased emission from excited ions\textsuperscript{109}. From an axial scan on the reactor, it was seen that mainly Ar I lines were present in the plasma, however, Ar II lines with significant intensity was detected in the vicinity of the powered electrode even when no aerosol was present in the plasma. A possible mechanism for the generation of additional Ar ions in the presence of excited Bi vapor is Penning ionization. An example reaction would be: Bi\textsuperscript{*} + Ar\textsuperscript{*} → Bi + Ar\textsuperscript{+}, where superscript \textsuperscript{*} stands for excited states.

It is possible to obtain the relative distribution of the Bi vapor along the reactor by doing actinometry\textsuperscript{110} as a function of position. Actinometry was performed by taking the ratio of the main Bi emission line to a neutral Ar emission line. The Ar I line at 751.4 nm was selected (3s\textsuperscript{2}3p\textsuperscript{5}(2P\textsuperscript{0}_{3/2})4p → 3s\textsuperscript{2}3p\textsuperscript{5}(2P\textsuperscript{0}_{3/2})4s)\textsuperscript{109}. The change in the magnitude of the Ar I line used for actinometry was found to be small (~10\%) in the presence of particles. However, in the presence of particles, measurements at different axial positions suffered from film build up on the walls. Therefore, the low concentration aerosol was used only. To minimize film build-up, the plasma was ignited only when taking a measurement. The lines were seen to be stabilized in 2-3 seconds after turning the plasma on. To obtain the vapor distribution profile, the following formula was used\textsuperscript{110}:

\[
P_{Bi} \propto \left[ \frac{I_{306}}{I_{751}} \right]_{wp} \left[ \frac{I_{306}}{I_{751}} \right]_{wop}.
\] (3.1)
Figure 3.10. Axially resolved actinometry. The data was obtained as a function of position along the cylindrical axis of the plasma with the low concentration test aerosol. For each data point, the axial spot width recorded by the spectrometer was approximately 3 mm.

$p_{Bi}$ is the partial pressure of Bi vapor and $I$ is the emission intensity at a fixed wavelength. Numbered subscripts stand for the wavelengths of the lines, and subscripts $wp$ and $wop$ denote “with particles” and “without particles”, respectively. The measurement of the intensity “without particles” is the background that is subtracted in equation 3.1.

Actinometry revealed that Bi vapor was produced and lost in the vicinity of the powered electrode (Figure 3.10). The vapor appeared upstream of the powered electrode and vapor content increased as particles approached this electrode. Just downstream of the powered electrode, the vapor content reached a maximum but then it rapidly vanished at positions further downstream, even though the plasma still occupied that space (Figure 3.3). At 10 W, the power which resulted in the monodispersed output for the low concentration aerosol, vaporization was gradual and reached a plateau inside the powered electrode. At 40W, vaporization was much more intense. The observation of Bi vapor by OES, which must be highly supersaturated given the low gas
temperature, is consistent with the rapid deposition of the metal film on the wall of the plasma tube (Figure 3.8).

The Bi vapor detected by OES resulted from particle vaporization and was not residual vapor from the evaporation-condensation particle generator. To test whether there was residual Bi vapor coming from the particle generator, electrodes were placed in a position further away from the orifice. At positions sufficiently upstream of the powered electrode, no bismuth lines were detected. This demonstrated that there was no Bi vapor left after expansion through the orifice, and that any Bi vapor observed by OES was a result of particle vaporization.

The rate of film deposition on the walls of the plasma tube was very fast with the high concentration aerosol. Therefore, the lens was placed at the diagnostic port downstream, and oriented such that light was integrated along the cylindrical axis of the system (Figure 3.1). Using this configuration, information about the distribution of Bi vapor along the cylindrical axis of the

![Graph](image)

**Figure 3.11. Axially integrated actinometry.** Data was acquired at different powers with the high concentration test aerosol present.
plasma was lost, however it was possible to estimate the total relative Bi vapor content within the plasma, since the integrated intensities of the selected lines for Bi and Ar were obtained. As shown in Figure 3.11, the total vapor content increased with increasing power input. At approximately 70 W, the total vapor content did not increase with further increases in applied RF power, indicating complete vaporization. At higher powers, the vapor content decreased slightly, which can be explained by increased losses to the walls. The errors in the axial measurements largely resulted from poor precision in the alignment of the lens at the centerline of the reactor. Nevertheless, OES results indicated the particles were clearly being vaporized in the plasma despite the low gas temperature, and the amount of the generated vapor was dependent on plasma power.

The mass yield of the process decreased with increasing power (Figure 3.12). For the high concentration case at 20 W, which was the power that resulted in the monodispersed size

![Graph](image_url)

**Figure 3.12.** Mass yield as a function of applied RF power for the high concentration Bi aerosol.
distribution in Figure 3.5, the mass yield was found to be 65%. Mass losses increased with increasing power and for powers larger than 60 W very little mass was collected.

By assuming the primary particles were spherical, the mass measurements allow quantitative number and mass distributions to be obtained. First, the total mass concentration of the aerosol, $M_\infty$, has to be calculated:

$$M_\infty = \frac{\dot{m}_f}{V \eta_{\text{eff}}},$$  \hspace{1cm} (3.2)

where $\dot{m}_f$ is the aerosol mass flow rate as measured on the filters, $\eta_{\text{eff}}$ is the overall mass-based filter capture efficiency, which is assumed to be 1 for all particle sizes investigated here; and $V$ is the volumetric flow rate of argon, which is obtained from the ideal gas equation of state and the conservation of mass as follows:

$$V = \dot{V}_{\text{sccm}} \left( \frac{p_{\text{ref}}}{p} \right) \left( \frac{T}{T_{\text{ref}}} \right) \left( \frac{10^{-6}}{60} \right).$$  \hspace{1cm} (3.3)

$p$ and $T$ are the operating pressure and temperature, which are 1.5 Torr and 294 K when the plasma is off respectively. Similarly, $p_{\text{ref}}$ and $T_{\text{ref}}$ are the reference pressure and temperature set at 760 Torr and at 273.15 K. The final brackets in equation 3.3 is to convert the flowrate from the units of sccm, as given by $\dot{V}_{\text{sccm}}$, to the units of m$^3$/s. With the size distributions obtained from TEM images in hand, one can calculate the total number concentration $N_\infty$:

$$N_\infty = \frac{M_\infty}{\sum_i \frac{\pi}{6} \rho_p d_{p,i}^3 \eta_{p,i}^*}.$$  \hspace{1cm} (3.4)
$d_{p,i}$ is the particle size for bin $i$ and $n_{p,i}^*$ is the frequency of particles in that bin. Each term of the summation in the denominator of equation 3.4 was multiplied by $N_\alpha$ to obtain the mass distribution $dM_\alpha/d\log(d_p)$. The quantitative distributions are given in Figure 3.13, and the properties of these distributions are provided in Table 3.1. Number distributions in Figure 3.13a clearly show that small particles completely disappeared when the plasma was on, and the number of particles that were larger than 200 nm increased. It is important to remind that all size distributions given in this chapter are for primary particles, whereas the calculation outlined above works the best for free-standing particles. Since the test aerosol was highly aggregated (Figure 3.4d), the number concentration of the aggregates was overestimated.

In comparison to the number frequency distributions given in Figure 3.4, mass distributions in Figure 3.13b clearly show the transport of mass from both sides of the size spectrum. For the monodispersed case at 20 W with the high concentration aerosol, it can be seen from Figure 3.13b that the amount of mass in the size range of the monodispersed peak after plasma treatment was greater than the amount of mass in that size range for the test aerosol. Accordingly, this mass

![Figure 3.13. Quantitative (a) number and (b) mass distributions for the high concentration Bi aerosol with and without plasma treatment at different applied RF powers.](image)
Table 3.1. Properties of the low concentration (LC) and high concentration (HC) Bi test aerosols, along with the plasma treated forms of the high concentration Bi aerosol. The variable $<d_p>_1$ is the mean size of the finer mode, $<d_p>_2$ is the mean size of the coarse mode, $\dot{m}_f$ is the mass flow rate of particles, $N_\infty$ is the total number concentration and $M_\infty$ is the total mass concentration.

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<th>$&lt;d_p&gt;_2$ / nm</th>
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<th>$N_\infty$ / m$^3$</th>
<th>$M_\infty$ / mg m$^3$</th>
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</tbody>
</table>

transport lead to the disappearance of particles that were larger and smaller than the final size. This type of a transformation indicates that all particles vaporize. The final result of this transformation is the in-flight tuning of size, which is a new emergent phenomenon in dusty NEP.

The process of in-flight size tuning is intriguing from the perspective of thermodynamics. NEP allows one to put work into the system, which can lead to a transformation resulting in monodispersed size distribution. It is important to note that this work input is different than filtering out certain portions of the size distribution. NEP takes mass from across the size distribution and transports it into the final monodispersed size. Thus, NEP has a much higher throughput of mass compared to other approaches for obtaining monodispersed size such as electrostatic classification$^{111-113}$. It is interesting to note that such a transformation in the size distribution cannot occur spontaneously. It is well known that particulate media tend to decrease surface energy by means of coagulation in the case of aerosols, or via Ostwald ripening in the case of colloids. The decrease in surface area and surface energy is accompanied by an increase in entropy until equilibrium has been reached. Coagulation (Figure 1.7) and Ostwald ripening lead to a broadening of the size distribution$^{52,114}$. 

52
A more quantitative way to look at the thermodynamics of the size-focusing process is investigating the width of the size distribution since it is a measure of the specific entropy of an aerosol\textsuperscript{115}. The size distributions of all aerosols produced in this work were constructed in discrete fashion. An aerosol with a discrete number distribution carries an information $H$ quantified as\textsuperscript{115,116}:

$$H = -\sum \Omega P_i \ln P_i.$$  \hspace{1cm} (3.5)

$\Omega$ stands for all the size bins, i.e. all states; and $P_i$ is the probability of a particle being in a bin of particle size $i$, which is equal to $n^*_p,i$. It can be shown that $H = \hat{S}/k_B$, where $\hat{S}$ is the specific entropy of the aerosol associated with size dispersion\textsuperscript{117}. $\hat{S}$ is obtained by normalizing the entropy of the aerosol by the total particle number density, $N_a$. $\hat{S}$ decreases according to equation 3.5 as the width of the size distribution decreases and eventually becomes zero for exactly monodisperse particles. In our experiments, $\hat{S}$ can decrease after plasma treatment due to size-focusing. On the other hand, it can be shown that $\hat{S}$ increases monotonously during coagulation due to the continuous increase in the width of the distribution.

### 3.4. Conclusions and Comments

It is shown that the Bi aerosol vaporizes in NEP despite the low background gas temperature, which is a previously unreported mechanism in dusty NEP. Vaporization appears to occur in the vicinity of the powered electrode. Downstream of this zone of vaporization, which is called as the intense zone in the rest of this dissertation, the size distribution of the aerosol changes significantly. It is shown that if properly tuned, NEP can act as a unique processor of mass, and it can convert
polydisperse aerosols into monodisperse aerosols with high mass yield (~65%). The in-flight size tuning of the aerosol can be a major mechanism that provides NEP the capability to synthesize monodisperse and free-standing particles.

The vaporization process has to involve a highly nonequilibrium mechanism since the background gas temperature is low. The Bi vapor created in the intense zone should be highly supersaturated, and it is expected to lead to nucleation or to condensation on the remaining particles and reactor walls, and the latter was clearly observed. The formation of the metallic film on the wall is most likely the reason for the decrease in mass yield when the plasma is on.

The results presented in this chapter motivate all of the upcoming chapters in this dissertation. The following questions deserve to be answered:

1) Is the phenomenon of in-flight size tuning general? Would it be observed with other materials?

2) What is the physical mechanism that causes the in-flight tuning of size?

3) How can this process be put to practical use?

Throughout this dissertation, qualitative answers to 1 and 2 are provided. Question 3, however, is investigated in detail.
Chapter 4

A Sectional Model of Aerosol Dynamics for Vaporization And In-Flight Tuning of Size

A way to elucidate the mechanism responsible for in-flight size tuning presented in the previous chapter is proposing a scheme of aerosol growth and then implementing it in a simulation of aerosol dynamics. Comparison of model predictions with experimental results can provide insight on the validity of the selected growth mechanisms. Furthermore, such a model can point out experiments which can be used to test hypotheses on the physics underlying the observed polydisperse-to-monodisperse transformation. The goal of this chapter is to develop the simplest model of aerosol dynamics that can predict the evolution of the entire size distribution. It is shown that a sectional model that accounts for charging, nonequilibrium vaporization, nucleation and condensation can match experimental results presented in the previous chapter qualitatively.
4.1. The Simplified Picture of Aerosol Dynamics in NEP

The suppression of aggregation in dusty NEP, along with the existence of the vaporization process demonstrated in the previous chapter, leads to a modified set of aerosol growth mechanisms when compared to the set that applies in a thermal environment. Growth mechanisms in dusty NEP is pictured in Figure 4.1, which is a modified version of Figure 1.6.

The unique aspect of Figure 4.1 is that growth in NEP can either proceed in forward direction due to condensation and/or surface growth, or in backward direction due to nonequilibrium vaporization. Description of the condensation process appears to be simple, but the physics behind vaporization is unknown. The vaporization mechanism must allow the removal of material from the surface of the particles amidst a gaseous atmosphere close to room temperature. Two possible mechanisms are thermal evaporation due to particle heating and ion bombardment-induced surface erosion, i.e. sputtering. First, thermal evaporation is examined, and then sputtering is addressed.

4.2. Thermal Evaporation vs. Sputtering

A simple way of assessing whether thermal evaporation is important for a particle in NEP is to estimate the temperature of a particle under experimental conditions. Equation 2.21 is tailo-
made for this purpose, but the use of that equation requires plasma parameters to be known in order to evaluate $J_i$ and $\Phi_p$. At 20 W, which was the power that resulted in the formation of monodisperse particles for the high concentration Bi aerosol, preliminary double Langmuir probe measurements revealed that the ion density was $2.7 \times 10^{17}$ m$^{-3}$ and the electron temperature was roughly 2.7 eV nearby the intense zone [VAP]. By using these values, $\Phi_p$ was found to be -6.4 V using OML theory when the background gas temperature was assumed to be equal to room temperature, 294 K. For Bi, $W = 4.25$ eV and $f = 0.6$ 118. Thus, with these parameters in hand and with the potential calculated, one can evaluate $J_i$. Accordingly, equation 2.21 predicts a particle temperature approximately equal to 480 K at 20W and at 1.5 Torr pressure. At such temperatures, Bi has negligible vapor pressure119, therefore thermal evaporation is ruled out.

Sputtering by ion bombardment is an alternative means by which particles could be vaporized in the NEP at room temperature, but its quantitative description presents some difficulties. The ion bombardment energy, $E_{ion}$, which is approximately equal to $e|\Phi_p| = 6.4$ eV for collisionless ions, is significantly larger than the surface binding energy of Bi, abbreviated as $U_0$, which is 1.9 eV when calculated from the enthalpy of sublimation120. In the classical theory of sputtering, yields for such ion energies are very low121, but as long as $E_{ion} > U_0$, the yield is non-zero. It is important to mention that sputtering theories and empiricisms are mostly developed for large planar surfaces, not for charged particles with a curved surface. Such particles are expected to have lower surface binding energies and increased sputtering yields122,123. Furthermore, in nanoparticles, $U_0$ becomes size-dependent and can be much smaller than the bulk value due to the surface energy and charging124,125. Therefore, the sputtering yields can be significantly higher than what is predicted by the available empirical formulae.

In general, the rate of vaporization by sputtering can be expressed as120
\[ SR = \frac{J_i Y}{en_{at}}, \]  
\[ (4.1) \]

where \( J_i \) is the ion flux predicted by OML theory, \( Y \) is the sputtering yield and \( n_{at} = \rho_{\rho}/MW \) is the atomic density with \( MW \) being the molecular weight. \( SR \) has the units of length per time. The sputtering yield \( Y \) can be estimated by various semi-empirical formulae for the near-threshold regime\textsuperscript{121,126}. We use the following expression\textsuperscript{126}:

\[ Y \approx \frac{3}{4\pi^2} \alpha \gamma \frac{E_{ion}}{U_0}. \]  
\[ (4.2) \]

\( \alpha \) and \( \gamma \) are functions that depend only on the mass of the ion and atomic mass, \( m_s \), of the material comprising the particles\textsuperscript{127}:

\[ \alpha = 0.08 + 0.164 \left( \frac{m_s}{m_i} \right)^{0.4} + 0.0145 \left( \frac{m_s}{m_i} \right)^{1.29}, \]  
\[ (4.3) \]

\[ \gamma = \frac{4m_s m_i}{(m_s + m_i)^2}. \]  
\[ (4.4) \]

4.3. Development of a Sectional Model

Preliminary Langmuir probe measurements indicated that the ion density was lower downstream of the intense zone [VAP]. Therefore, the system was conceived as having two zones, the first being the intense zone where the majority of the vaporization happened, which is consistent with the observations made by OES (Figure 3.9 and 3.10). The second zone is the weak zone with lower ion density. In both zones, the ion density is much larger than the nanoparticle number concentration, so coagulation is neglected (Equation 2.15). Nanoparticles are vaporized
in the intense zone due to sputtering. At the end of that zone, the aerosol consists of a supersaturated vapor and fragments left over from the test aerosol, as well as some nuclei that have been born out of the supersaturated vapor. In the second zone, which is weaker but still a plasma, the supersaturated vapor condenses back onto the fragments and nuclei coming out of the first zone. Once all of the vapor has been consumed by condensation in the weak zone, the process is finished. Both zones are modeled in the same way, the only difference is the value of the ion density. A schematic of the proposed mechanism is given in Figure 4.2.

To realize the dynamics described above, a sectional aerosol dynamics model is developed. Sectional models can calculate the evolution of the entire size distribution without any *a priori* assumptions on the shape of the distribution. In a sectional model, the particle size dimension is discretized, and the population in every size bin is tracked. The aerosol model presented here considers charging, sputtering, condensation and nucleation of particles inside the plasma. All particles are assumed to be spherical. The evolution of the size distribution was tracked as a function of time and the amount of supersaturated vapor surrounding the particles was calculated. The first step was to calculate the particle charge as a function of size. The mean charge on an individual particle was found by flux-balancing, akin to equation 2.7:
\[ J_i + J_{e,FE} = J_e \]  \hspace{1cm} (4.5)

\( J_i \) and \( J_e \) were calculated from the OML expressions (Equations 2.8 and 2.9). \( J_{e,FE} \) is the field emission flux of electrons, which places a limit on the charge that can be carried by a particle. The electron density was calculated from quasineutrality (Equation 2.14). The ion temperature was assumed to be equal to room temperature, and the electron temperature was again taken from preliminary measurements, as 2.7 eV [VAP]. In our simulations, the particles usually did not reach the field emission limit\(^{128}\) and thus \( J_{e,FE} \) in equation 4.5 dropped out. Equation 4.5 was solved for the particle potential. The algebraic nature of this balance comes from the fact that charging processes are 2-3 orders of magnitude faster than the timescales of vaporization, condensation and nucleation considered here (Chapter 6). By using the calculated value of the potential, which was -6.4 V, the particle charge \( Z \) was calculated from equation 2.10 for all particle sizes considered. Once the charge was known as a function of size, equation 2.14 was used to ensure that the system was charge neutral. In addition, the condition given by equation 2.15 was checked to ensure that the assumption on the suppression of coagulation had not been violated. Provided condition 2.15 is true, \( n_i \approx n_e \), and coagulation can be neglected because of unipolar negative charging and consequent electrostatic repulsion.

The evolution of the particle size distribution was evaluated by solving the Liouville equation\(^{48}\). The Liouville equation describes the transport of mass along the size spectrum due to surface growth. In this equation, the change in the mass distribution, \( m_p \), with respect to time, can be written as
\[
\frac{\partial m_p}{\partial t} = -\frac{\partial I_m}{\partial d_p}, \tag{4.6}
\]

where the right side is the change in the mass current \(I_m\) with respect to particle size. Time in equation 4.6 is equivalent to residence time when plug flow is assumed. The mass current \(I_m\) has the following form:

\[
I_m = m_p \frac{d d_p}{d t}. \tag{4.7}
\]

In equation 4.7, the change in particle diameter causes a transport of mass into a particle size either smaller or larger. In this model, the direction of this transport depends on the competition between the rates of vaporization and condensation. Specifically:

\[
\frac{d d_p}{d t} = CR - SR, \tag{4.8}
\]

where \(CR\) is the condensation rate, and \(SR\) is the sputtering rate given by equation 4.1. Since the particle Knudsen numbers were large, \(CR\) was written from kinetic theory of gases:

\[
CR = \frac{4\alpha_M (p_{Bi} - p_s)}{\pi \rho_p \beta_v}, \tag{4.9}
\]

where \(\alpha_M\) is the mass accommodation coefficient, which was taken as 1, \(p_{Bi}\) is the partial pressure of Bi vapor far away from the particle, \(p_s\) is the vapor pressure at the particle surface calculated from the Kelvin relation considering the surface curvature, and \(\beta_v\) is the mean thermal speed of the vapor molecules. Finally, equation 4.6 can be closed with a mass balance that determines the vapor pressure:
where \( m_v \) is the mass of the vapor molecules, and \( I_0 \) is the nucleation current from classical nucleation theory\(^{48} \). In equation 4.10 it was assumed that the critical nucleus is a dimer of Bi, which is the smallest cluster size that is larger than a vapor molecule, and compound forms of Bi vapor\(^{129} \) were ignored (i.e. \( m_v = m_s \)).

Equation 4.6 is a hyperbolic partial differential equation, also called an advection equation. It presents difficulties to many numerical solvers, two of the most important being numerical diffusion and the Gibbs phenomenon that leads to non-physical oscillations\(^{130} \). To solve equation 4.6, MacCormack’s method of discretization was used since it is simple to implement and free of numerical diffusion. However, it produces spurious oscillations\(^{131} \). These oscillations were suppressed by a mass-conserving smoothing algorithm while keeping the incorporated diffusion as small as possible. The size coordinate in equation 4.6 was meshed into 200 logarithmically spaced bins, and constant time steps of 1 \( \mu \)s were used for marching in time.

The inputs to the model were as follows. The initial particle size distribution was set to the measured quantitative primary particle size distribution of the test aerosol for the case of initial mass concentration of 2.69 mg m\(^{-3} \), but a finer histogram was utilized in accord with the size mesh. The gas temperature and ion temperatures were 300 K and particle temperatures were kept at 450K. The simulation was divided into two zones to simulate the experimental system. The electron temperature was set to 2.7 eV [VAP]. The ion density in the first zone was \( 1.7 \times 10^{18} \) m\(^{-3} \) [VAP], and in the second zone it was set to 0. The ion energy was set equal to the particle potential of 6.4 eV. To compensate for the uncertainties in the sputtering yield, the model was run for sufficient
time in the intense zone until the vapor pressure reached a nominally steady state value. The resulting size distribution and vapor pressure from the first zone were then passed into the second zone, which was also run for enough time to nominally reach steady state. The solver was checked against various other models, such as the lognormal and monodispersed models, as well as the analytical solution to the evolution of the size distribution due to condensation from an infinite vapor reservoir\textsuperscript{132}.

### 4.4. Evolution of the Particle Size Distribution

The calculated partial pressure of Bi vapor in both zones is given in Figure 4.3. In the intense zone where vaporization dominates, partial pressure of Bi reached a limiting value. After this step, both the vapor and the remaining particles enter the weak zone with reduced ion density. In the weak zone, due to the large supersaturation of Bi vapor that was developed in the intense zone, a

![Figure 4.3. Bi partial pressure calculated by the model as residence time progresses. The intense zone (Zone 1), where vaporization dominates, is shown with red background and the weak zone (Zone 2), where condensation dominates, is shown with blue.](image)
nucleation burst occurred, and then Bi vapor began to condense. Since the nuclei were of similar size, the size distribution remained nominally monodispersed as the vapor condensed onto the particles. As the particles moved further downstream, condensation proceeded to completion. This trend is depicted in Figure 4.4a and 4.4b, where the size distribution of the aerosol is plotted as a function of time in the two zones of different ion density. It should be noted that the size distribution broadens during vaporization. Therefore, to obtain a final distribution that is narrower than the initial distribution by re-condensation, the majority of the aerosol has to be vaporized.

Figure 4.4. Evolution of the size distribution. (a,b) Size distributions during vaporization and condensation. (c) Experimental (solid) and model (dotted) results of the mass distribution before and after plasma treatment. The solid curves are lognormal fits to the data presented in Figure 3.13.
The resulting mass distribution was closely captured by the model (Figure 4.4c). The overpredicted amount of mass in the monodispersed size is due to the omission of vapor losses to the walls.

Although the model presents a viable overall mechanism for in-flight size tuning, its kinetics is orders of magnitude slower than what the plasma provided, as can be seen from Figures 4.3, 4.4a and 4.4b. The total residence time in the plasma was approximately 20 ms. The residence time in the intense zone was even shorter, it was only a few ms. On the opposite, it takes approximately 6 seconds for the aerosol to vaporize by sputtering in the model, and roughly 100 seconds for the vapor to re-condense on the small clusters.

The mismatch between calculated and experimentally observed time scales of growth indicates that the dominant mechanism for surface growth is not the condensation of neutral vapor molecules. An expression for the characteristic time of condensation supports this argument. Such an expression was derived in Appendix II (equation AII.8):

\[ \tau_{cond} = \frac{1}{\alpha_M N_x d_{pf}^2 \beta_v} \]  

(4.11)

\( d_{pf} \) is the final size of the particles at the end of the condensation process (obtained from Equation AII.16). The characteristic time for condensation given in Equation 4.11 predicts that at least few seconds are required for the growth to cease (Figure AII.1). A mechanism that can provide rapid growth could be the condensation of Bi ions, also called as ionized vapor deposition. It has been previously argued that ionized vapor deposition can enhance growth rates by two orders of magnitude when compared to the condensation of neutrals in a low pressure NEP. Simple calculations show that the rate of growth can be significantly enhanced in the presence of ionized
metal vapor (Appendix III). Considering that the ionization energy of Bi (7.29 eV) is much lower than that of Ar (15.76 eV), ionized vapor deposition is expected to occur to some extent. The presence of ionized vapor deposition can be experimentally confirmed by monitoring Bi II emission. However, such a measurement requires a high resolution spectrometer with a very low noise level.

Even though the model is off in terms of the kinetics of the process, an interesting observation can made by looking at the steady-state reached at the end on the intense zone. In Figure 4.5, the steady-state partial pressure of Bi vapor computed by the model is compared with the axially integrated OES measurements (Figure 3.11), which represent the total relative partial pressure of Bi in the reactor. Instead of using power for the values of x-axis, preliminary measurements of ion density, which were made as a function of power in the vicinity of the powered electrode, were used [VAP]. The trends match surprisingly well, indicating that the steady-state solutions for $P_{Bi}$
predicted by the model replicates what is experimentally observed by OES. Since the kinetics in the model is slow, this result means that the rates of both vaporization and condensation in the model are slower than their experimentally observed rates by approximately the same order of magnitude.

4.5. Conclusions and Comments

A simple model for aerosol dynamics that captures the evolution of the entire size distribution was described for the vaporization of Bi aerosols and subsequent in-flight size tuning in NEP. Qualitatively, the model presents a route for the experimentally observed polydisperse-to-monodisperse transformation, which was described in the previous chapter. The route involves near-complete vaporization of all particles in the intense zone, which only leaves small clusters and a highly supersaturated Bi vapor at the exit of that zone. Near-complete vaporization reduces size dispersion to a minimum, and consequently, this small size dispersion is preserved as growth occurs due to nucleation and condensation in the weak zone, leading to the formation of the monodisperse aerosol.

An alternative route for a polydisperse-to-monodisperse transformation may exist if the vaporization mechanism has some dependence on particle size. If all particles vaporize, but if the smaller particles vaporize faster or more than bigger particles, then it should be possible to transfer the mass of smaller particles onto bigger particles by vaporization and re-condensation. However, the sputtering rate expression used in the model (Equation 4.1) had no dependency on size, which stems from the size-independence of sputtering yield and particle potential. The possible causes that can induce a size-dependency in the vaporization mechanism are re-evaluated in Chapter 6.
An important task in understanding plasma-aerosol interactions is elucidating the role and extent of nucleation. Independent of the mechanism that causes vaporization, the nucleation rate is expected to be important since it determines the number concentration of the particles and the final size. For a given amount of supersaturated vapor, a faster nucleation rate would result in smaller particles, while a slower nucleation rate would give larger particles. The vapor generated from refractory materials is anticipated to yield smaller particles due to faster nucleation, since refractory materials have lower equilibrium vapor pressures. Adjustment of input aerosol concentrations, operating power, optimization of plasma geometry and manipulating the vapor amounts can make NEPs an effective size processing tool for gas-phase synthesized nanomaterials.

In the rest of this dissertation, emphasis is put on the vaporization mechanism, rather than condensation. If sputtering is actually responsible for vaporization, and if its description given by equation 4.1 is adequate, then to match the experimental time scales of vaporization, either the ion density or the sputtering yield has to be at least two orders of magnitude greater. The uncertainties in estimating the sputtering yield makes it difficult to assess whether such an increase is feasible. However, detailed and careful measurement of the plasma parameters as a function of axial position in the reactor, especially in and nearby the intense zone, can answer whether ion density is a possible reason for the discrepancy. In the next chapter, a detailed set of measurements of the distribution of ion density and electron temperature, along with background gas temperature and wall temperature, is presented.
Chapter 5

Characterization of The Tubular Flow-Through Reactor

Modeling results given in the previous chapter indicated that the overall ion and electron bombardment experienced by a particle is dependent on not only the magnitude of the plasma parameters, but also on the distribution of these parameters along the reactor. The goal of this chapter is to spatially characterize the plasma, and especially the intense zone where most of the vaporization occurs.

Although the tubular flow-through reactor has been used in many studies, reports on its characterization are rare. Existing studies only contain measurements of the plasma parameters at fixed position, which are usually done far away from the powered electrode\textsuperscript{29,135}. For the characterization work reported in this chapter, probe based methods were employed. A double Langmuir probe\textsuperscript{136} was used to measure ion density and electron temperature; and background gas temperature was measured using fiber optic temperature probes. The validity of the gas temperature measurements was discussed in detail. In addition, measurement of the reactor wall
temperature was done via infrared thermometry. All methods of measurements indicate the presence of an intense zone with elevated ion densities and gas temperatures in the vicinity of the powered electrode.

5.1. Characterization Setup

The setup presented in Chapter 3 was simplified considerably by removing the evaporation-condensation generator. The plasma reactor was reconfigured in such a way that it was possible to insert probes from both ends of the reactor (Figure 5.1). Argon gas flow rate was maintained at 150 sccm and pressure was varied between 1.5 and 10 Torr. The existing circuitry for RF power delivery was complemented with a power meter (VI Probe, Bird), which was placed in between the reactor and the matching network to measure and monitor the power that was transmitted to the reactor. The meter revealed that the ground electrode did not serve as the dedicated ground during probe insertion. In order to have a well-defined ground, metal parts both upstream and downstream of the silica tube were grounded. Values of the ion density, $n_i$, measured with the new ground configuration were higher than the values mentioned in the Chapters 3 and 4 (vide infra). It is presumed that inappropriate grounding was the reason for this discrepancy. Unless otherwise noted, power values reported in this section are the set point values on the power supply.

![Figure 5.1. Setup for plasma characterization. PWR: powered electrode. GND: Ground electrode.](image-url)
5.2. Double Langmuir Probe Measurements

Values of $k_B T_e$ and $n_i$ were measured using an RF-compensated double Langmuir probe (Impedans LTD). The probe was inserted through one of the diagnostic ports (Figure 5.1), and the cylindrical axis of the probe was positioned on the centerline of the fused silica tube. Port-I was only used for measurements performed at axial positions upstream of the powered electrode, and similarly, port-II was only used for measurements performed at axial positions downstream of the powered electrode. Tips of the probe were platinum, and they were 5 mm in length and 0.36 mm in diameter. $k_B T_e$ and $n_i$ were extracted from I-V curves (Figure 5.2) as reported in literature\textsuperscript{137}, by assuming that the electron energy distribution function was Maxwellian.

At 1.5 Torr, axial scans conducted with the double Langmuir probe at power set points of 10 W and 20 W showed that the electron temperature was nominally independent of axial position and power (Figure 5.2a). However, ion density reached a maximum at the center of the zone surrounded by the powered electrode (Figure 5.2b). At 20 W, the ion densities measured in this intense zone were approximately 5 times higher than the densities measured in the low-intensity plasma at positions further away. The maximum in ion density at the center of the intense zone became greater with power increasing from 10 to 20 W, whereas ion densities in the low-intensity plasma did not change significantly. Plasma emission spectra collected at different locations showed that Ar II emission lines were detectable only near the powered electrode, providing further evidence for the existence of the intense zone (Figure 5.3).
Figure 5.2. **Axial profile of plasma parameters.** (a) Electron temperature and (b) ion density along the central axis of the reactor measured at 1.5 Torr for different power set points.

![Graph showing electron temperature and ion density profiles along the central axis of the reactor](image)

Figure 5.3. **Plasma emission in the vicinity of the powered electrode.** Plasma power was set at 20 W and the pressure was 1.5 Torr. Spectra were collected with the miniature spectrometer described in Chapter 3 and normalized with the Ar I peak at 811.8 nm.

![Spectra showing plasma emission](image)
Since changing the applied power primarily affected the ion density in the zone surrounded by the powered electrode while the low-intensity plasma remained approximately constant, further measurements focused on the plasma parameters at the peak position as a function of external process parameters. Plotted in Figure 5.4 are the electron temperature and ion density as a function of the applied RF power for two different pressures: 1.5 Torr and 10 Torr. At 1.5 Torr, the electron temperature increased slightly from 1.9 to 3.2 eV with applied power in the range from 10 to 60 W (Figure 5.4a). Higher powers were not explored, due to extensive contamination of the double Langmuir probe, which caused the IV curves to become increasingly skewed, leading to an erroneous increase in the apparent electron temperature\textsuperscript{138}. At a pressure of 10 Torr, the electron

![Figure 5.4](image-url)  

**Figure 5.4.** Plasma parameters measured at the center of the zone surrounded by the powered electrode. (a) Electron temperature and (b) ion density as a function of applied RF power.
temperature was nominally independent of applied power, and slightly greater than 2 eV. At both pressures, the ion density increased with applied power in the range from $10^{17}$ to $10^{18}$ m$^{-3}$ (Figure 5.4b); and the measured ion density at 1.5 Torr was greater than at 10 Torr. The ion density measured at 60 W and at 1.5 Torr is about an order of magnitude higher when compared to the values presented in literature for reactors having similar geometry and operating at similar set powers.

5.3. Measurement of Reactor Wall Temperature

The reactor wall temperature was measured by infrared thermometry. Thermal images were acquired using an infrared camera (Compact LW-AAA, Seek Thermal) with a spectral range of 7.5-14 μm. In this wavelength range, the fused silica tube is opaque, therefore the wall temperature of the reactor can be measured. The camera was calibrated for measurements conducted on the tube and on the black oxide coated screw of electrodes. The calibration procedure is illustrated in Figures 5.5a and 5.5b. For measurements on the tube, the temperature inside the tube was measured by a thermocouple. The temperature difference across the tube wall (1.5 mm thickness) was estimated to be below 5 K. The obtained calibration data is given in Figure 5.5c, where the red dotted line depicts the ideal case when IR measurements are equal to thermocouple measurements.

The temperature of the reactor wall, as measured from infrared thermal images, obtained a maximum value in the vicinity of the powered electrode. A hot spot was observed around the powered electrode at all powers and pressures (Figure 5.6a and 5.6b). RF power measurements revealed that the matching network transmitted approximately 2/3 of the power sent by the power supply (vide infra). This power was coupled to the plasma and appeared to be dissipated primarily
in the intense zone. Measurements showed that the wall temperature approached 650 K at a set power of 70 W (Figure 5.6c). Wall temperature is an important piece of information that is required to determine the radiative heat exchanged by fiber optic probes and particles with the walls. In addition, since wall temperature is clearly related to the temperature of the gas flowing through the reactor, it is expected to serve as a rough estimate to the background gas temperature.
Figure 5.6. Reactor wall temperature. (a) Photograph of the reactor and the Ar plasma with 20 W power and at 1.5 Torr\(^{13}\). (b) Thermal image taken at the same conditions given in (a)\(^{13}\). The scale bar represents the calibration done on glass. (c) Wall temperature measurements at 1.5 Torr as a function of power and position. The temperature of the black screw was assumed to be equal to the electrode temperature and to the temperature of the tube wall inside the electrode.
5.4. Measurement of Background Gas Temperature

Background gas temperature measurements were performed by fiber optic thermometry. Thermocouples are susceptible to electromagnetic interference, due to field-induced currents and induction heating, when inserted into high-frequency plasmas\textsuperscript{140,141}. As an alternative, one can use the temperature-dependent florescence decay of a fluorophore crystal as a fundamentally different measurement principle that does not require any electrical conductors to be immersed in the plasma\textsuperscript{142,143}. When configured as a probe, these thermometers are called as fluorescence decay probes (FDP). They operate by sending pulsed light from a narrow-band light emitting diode through an optical fiber to the fluorophore crystal. The fluorophore, which is located at the tip of the fiber, absorbs a portion of this light, and after a time delay, the absorbed light is emitted across a time span of tens of milliseconds\textsuperscript{144}. The rate of decay in the intensity of the emitted light is detected and correlated to the temperature of the fluorophore crystal. Two different commercially-available FDPs, which were calibrated for different temperature ranges were used: 288-673 K and 423-1173 K (OptoTemp 2000, Micromaterials Inc). Both probes were comprised of a composite structure of nested cylinders, which consisted of an outer alumina sheath (3.1 mm OD, 0.7 mm wall thickness) and an inner alumina sheath (0.9 mm OD, wall thickness of 0.2 mm). The inner alumina sheath surrounded the optical fiber at the core. The tip of the high temperature probe only had the inner sheath. Images of the probes are presented below.

Like any surface in contact with the plasma, it can be argued that the tip of the FDP gets hotter than the surrounding gas due to ion-electron bombardment. Therefore, the reading of the FDP was corrected by a heat transfer model to ascertain the background gas temperature. It will be shown that this correction, which calculates the difference between the temperature of the gas and that of the FDP, is expected to be relatively small at the powers and pressures investigated in this chapter.
Thus, the probe temperature is a good approximation of the background gas temperature. To calculate the heating of the tip of the probe, the charging of the probe should be analyzed, in a way that is similar to the framework detailed in Chapter 2.

The charging regime that applies to the probe is different than the one that applies to a submicron particle. This difference is caused by the relatively large size of the probe. The radius of the probe, \( r_{pr} \) was equal to 0.45 or 1.55 mm. For the probe, the hierarchy of the characteristic lengths is as follows\textsuperscript{137}: \( \lambda_e \approx r_{pr} \approx R \gg \lambda_i \approx \lambda_D \), where \( R \) is the width of the zone with perturbed ion and electron densities (Figure 2.3). In words, this hierarchy suggests that ions are highly collisional in their approach to the probe, but electrons are not. Under such conditions, the ion and electron fluxes to the tip of the probe can be described by the following equations\textsuperscript{137,145}:

\[
J_i = \frac{\pi}{8} n_i \beta_i \frac{\lambda_i}{r_{pr}} \left( 1 + \frac{T_e}{T_i} \right), \tag{5.1}
\]

\[
J_e = \frac{1}{4} n_e \beta_e \exp \left( \frac{e\phi}{k_B T_e} \right). \tag{5.2}
\]

Equation 5.2 is analogous to the OML electron flux to a particle since electrons are still collisionless, however, \( \phi \) in equation 5.2 is the probe potential. Since the probe is not conductive, the net current flowing onto the probe is zero. Therefore, flux-balancing can be used to determine the probe potential:

\[
J_i = J_e. \tag{2.7}
\]

The probe potential and the corresponding ion fluxes enter into the energy balance of the probe, which at steady state can be written as:
\begin{align*}
q_{ie} &= q_{\text{conv}} + q_{\text{rad}} + q_{\text{cond}}. 
\end{align*}
\number{5.3}

Similar to a particle, the probe absorbs heat from ion-electron recombination and from the transfer of kinetic energy of bombarding electrons and ions. Hence, the total heat flux to the probe due to ion and electron bombardment can be expressed as:

\begin{align*}
q_{ie} &= J_i \left( \Delta H_{\text{rec}} + KE \right) = J_i \left( \Delta H_{\text{rec}} + e|\phi| + 2k_B T_e \right). 
\end{align*}
\number{5.4}

The only difference between equation 5.4 and 2.17 is the omission of the work function in equation 5.4 (For alumina, \( W = 1.5-2.4 \text{ eV}^{146} \)). On the right-hand side of equation 5.3, fluxes representing heat loss due to convection, radiation exchange with the walls and conduction losses through the cross-section of the probe are given. The conduction term is omitted in this work. The convection and radiation terms can be expressed as:

\begin{align*}
q_{\text{conv}} &= h \left( T_{\text{pr}} - T_g \right), 
\end{align*}
\number{5.5}

\begin{align*}
q_{\text{rad}} &= \varepsilon \sigma_{\text{SB}} \left( T_{\text{pr}}^4 - T_w^4 \right), 
\end{align*}
\number{5.6}

where \( h \) is the convective heat transfer coefficient, \( T_{\text{pr}} \) is the probe temperature, \( T_w \) is the wall temperature, \( \varepsilon \) is the emissivity of the alumina probe surface and \( \sigma_{\text{SB}} \) is the Stefan-Boltzmann constant. The view factor corresponding to the probe tip and the reactor walls is neglected in equation 5.6, which leads to a slight underestimate in the magnitude of radiative cooling.

Numerical solutions of equation 5.3 were used to correct the probe measurement to determine the background gas temperature. First, the probe potential was solved for. For \( n_i = n_e \) and \( T_i = T_g \):

\begin{align*}
\phi &= \ln \left[ \frac{\pi}{2} \frac{T_g m_e}{T_e m_i} \left( \frac{\lambda_i}{r_{pr}} \right) \left( 1 + \frac{T_e}{T_g} \right) \right] \frac{k_B T_e}{e}. 
\end{align*}
\number{5.7}
The expanded form of equation 5.3 can be written as:

\[ J_i \left( |\Delta H_{rec}| + e \phi + 2k_B T_e \right) = h \left( T_{pr} - T_g \right) + \varepsilon(T_{pr}) \sigma_{SB} \left( T_{pr}^4 - T_w^4 \right). \] (5.8)

With the plasma parameters and wall temperatures in hand, equation 5.8 can be solved numerically for the gas temperature by utilizing equation 5.6. The emissivity of probe was estimated from tabulated values in literature. Both the raw measurement of the probe and the corrected values, termed the background gas temperature, are reported (vide infra).

As an aside, if one wishes to make a short-cut estimate of the expected difference between gas and probe temperatures, \( \Delta T \), the kinetic energy contribution to equation 5.4 can be obtained by solving for the probe potential in equations 5.1, 5.2 and 2.7:

\[ KE = \left\{ \ln \left[ \frac{\pi}{2} \frac{T_i m_e}{T_e m_i} \left( \frac{\lambda_i}{r_{pr}} \right) \left( 1 + \frac{T_e}{T_i} \right) \right] + 2 \right\} k_B T_e. \] (5.9)

The contribution of heat input to the probe due to kinetic energy transfer is expected to be 15-30 eV, depending on \( r_{pr}, \lambda_i, T_e \) and \( T_i \). By substituting the maximum value predicted by equation 5.9 into equation 5.4, equations 5.3, and 5.5-5.7 yield the maximum difference between gas and probe temperature:

\[ \Delta T \approx \frac{3 J_i |\Delta H_{rec}| - \varepsilon \sigma_{SB} \left( T_{pr}^4 - T_w^4 \right)}{h}, \] (5.10)

where \( J_i \) is to be calculated from equation 5.1. For the low and high temperature probe, conservative estimates for the heat transfer coefficient, which are independent of pressure, are found to be 35 and 72 W/m²K from tabulated data, respectively.
Similar to the measurements of ion density and wall temperature, FDP measurements also revealed an intense zone in the vicinity of the powered electrode, specifically a maximum in the background gas temperature. A photo of the low temperature probe inserted in the zone surrounded by the powered electrode is presented in Figure 5.7a, and a photo of the high temperature probe outside the reactor in Figure 5.7b. FDP measurements were made as a function of axial position. Measurements were corrected with the heat transfer model described above, using the experimentally determined plasma parameters and wall temperature as inputs. As

![Figure 5.7. Measurements of background gas temperature.](image)

(a) Low temperature probe (288-673 K) inserted into the reactor. (b) High temperature probe (423-1173 K). (c) Probe temperature ($T_{pr}$) and calculated gas temperatures ($T_g$) as a function of position at 1.5 Torr. (d) Probe temperatures and calculated gas temperatures in the zone surrounded by the powered electrode as a function of power and pressure.
discussed when deriving equation 5.10, the difference between the probe temperature and the calculated gas temperature was found to be small. Probe and background gas temperatures were found to be approximately equal at 10 Torr. Both the raw and corrected values are presented in Figure 5.7c as a function of axial position for 10 and 20 W of applied RF power. For 20 W, the background gas temperature peaked at approximately 410 K.

Since the peak temperature was observed in the zone surrounded by the powered electrode, the effect of applied power and total gas pressure was studied only at that axial location (Figure 5.7d). The probe temperature increased with applied power, apparently reaching values of nearly 1000 K at applied power set point of 80 W. In our experiments, at a given applied power, increasing the pressure from 1.5 to 10 Torr generally had the effect of lowering the background gas temperature, which can be explained by increased cooling rate and lower ion density (Figure 5.4b). These results clearly emphasize the need to experimentally characterize the background gas temperature, since it appears to be well above room temperature at commonly used applied RF powers. By using measured values of \( n_i, T_e \) and \( T_w, \Delta T \) can be calculated to check whether probe temperature is representative of the gas temperature.

A summary of all parameters measured in the intense zone at 1.5 Torr as a function of applied power is given in Table 5.1.

5.5. Conclusions and Comments

As inferred from the vaporization experiments and preliminary Langmuir probe measurements presented in the previous chapters, the existence of the intense zone was shown clearly via detailed characterization of the flow-through reactor in this chapter. In the vicinity of the powered electrode, the ion density and background gas temperature were substantially elevated, whereas
Table 5.1. Summary of characterization data obtained in the intense zone. Power, temperature and plasma density measurements conducted at 1.5 Torr pressure. The variation in the measured plasma parameters indicates three standard deviation bounds.

<table>
<thead>
<tr>
<th>$\hat{P}_{\text{set}}$ (W)(^a)</th>
<th>$\hat{P}_m$ (W)(^b)</th>
<th>$T_{w,\text{max}}$ (K)(^c)</th>
<th>$T_{pr}$ (K)</th>
<th>$k_B T_e$ (eV)</th>
<th>$n_i \times 10^{18}$ (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7</td>
<td>334</td>
<td>367</td>
<td>1.93 ± 1.33</td>
<td>0.53 ± 0.11</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
<td>390</td>
<td>413</td>
<td>1.57 ± 0.02</td>
<td>1.03 ± 0.02</td>
</tr>
<tr>
<td>30</td>
<td>19</td>
<td>444</td>
<td>483</td>
<td>2.04 ± 0.54</td>
<td>1.32 ± 0.18</td>
</tr>
<tr>
<td>40</td>
<td>25</td>
<td>507</td>
<td>578</td>
<td>2.40 ± 0.52</td>
<td>1.79 ± 0.14</td>
</tr>
<tr>
<td>50</td>
<td>31</td>
<td>556</td>
<td>668</td>
<td>3.00 ± 0.06</td>
<td>2.45 ± 0.06</td>
</tr>
<tr>
<td>60</td>
<td>38</td>
<td>592</td>
<td>753</td>
<td>3.18 ± 0.21</td>
<td>2.86 ± 0.15</td>
</tr>
<tr>
<td>70</td>
<td>44</td>
<td>630</td>
<td>863</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>80</td>
<td>52</td>
<td>&gt; 650</td>
<td>963</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\) $\hat{P}_{\text{set}}$ is the power set point on the RF power supply.
\(^b\) $\hat{P}_m$ is the measured power delivered to the electrodes. All measurements had a maximum variability of ± 1W. $\hat{P}_m$ was found to be approximately equal to 2/3 $\hat{P}_{\text{set}}$.
\(^c\) $T_{w,\text{max}}$ is the maximum wall temperature recorded at each applied power, which was measured in the vicinity of the powered electrode.

electron temperature was found to be approximately constant throughout the reactor. The measurements presented in this chapter are supported by a computational study on a similar reactor, which found similar profiles of elevated ion density and gas temperature near the powered electrode\(^{79}\). Thus, the results presented below are expected to be qualitatively general to the tubular flow-through NEP reactors, while the quantitative details will of course depend on pressure, applied power, reactor size, and etc.

It is important to remind that the extraction of plasma parameters from Langmuir probe measurements is rather simplistic, and it is subject to many assumptions. Therefore, unless verified by other diagnostic methods, the absolute values measured by the Langmuir probe should be
treated as order-of-magnitude estimates. Emphasis should be placed on trends and distributions, rather than the absolute values of $n_i$ and $k_B T_e$.

A detailed analysis suggested that the temperature detected by fiber optic probes once inserted into NEP can be representative of the background gas temperature. The accuracy of the measurements are expected to increase at higher pressures. Furthermore, wall temperature, which is simple to measure, was found to be a good estimate of the gas temperature at low plasma powers.

The ion densities measured in this chapter are larger than the preliminary values used in the sectional aerosol dynamics model of Chapter 4, especially at the center of the intense zone. Going back to the vaporization mechanisms and their rates, higher values of ion density presented in this chapter would make the sputtering rate faster, but not fast enough to match the experimental time scales given in Chapter 3. However, this increase in ion density can lead to a significant increase in particle temperatures. Therefore, calculations of particle temperature are revisited along with newer theories of particle charging in the next chapter, where thermal evaporation is re-examined as the potential vaporization mechanism.
Chapter 6

Temperature History of Particles in The Tubular Flow-Through Reactor

In this chapter, with relatively high values of ion densities measured in the intense zone and the spatial distribution of plasma parameters in hand, particle temperatures are calculated along the reactor. These calculations are done for the purpose of re-assessing the candidacy of thermal evaporation as the vaporization mechanism observed during the experiments with Bi aerosols. Furthermore, more recent charging theories that account for weakly-collisional ions, which are expected to be present in the plasmas used in this work, are utilized. The size-dependency of thermal evaporation is also re-examined, albeit qualitatively.

6.1. Weakly-Collisional Charging

In Chapters 1 and 2, without providing any experimental evidence, it was argued that particles in NEP are heated above the surrounding gas temperature primarily due to ion-electron bombardment. Between 1990-2010, several direct measurements of the temperature of
micrometer-sized particles in RF argon plasmas have been made\textsuperscript{149–151}. At pressures between 0.1 to 0.4 Torr, measurements demonstrated that particle temperatures in the plasma can be approximately 100 K higher than the background gas temperature. In those studies, the framework based on OML theory for predicting the particle temperature replicated the experimentally measured temperatures relatively well. However, in NEPs for synthesis, higher pressures are typically employed (> 1 Torr). At these higher pressures, the relation between the length scales that are important for charging is usually $\lambda_i \gtrsim \lambda_D >> d_p$. In words, the ion mean free path $\lambda_i$ can become smaller than $10 \lambda_D$, and ions can experience rare collisions within the sheath\textsuperscript{152}. Interestingly, experiments showed that these rare collisions can increase the ion flux to the particle significantly\textsuperscript{153}. Due to increased ion flux particles have a smaller electrostatic potential. Thus, at the pressures where most synthesis reactors operate, OML theory is expected to be inadequate for calculating ion fluxes and particle potential because of ion transport becoming weakly-collisional within the sheath. Since the heat flux to a particle is mainly driven by ion bombardment and subsequent recombination at the surface, OML is expected to significantly underestimate the particle temperature in the weakly-collisional regime\textsuperscript{99}.

6.2. Charge Distribution

It was mentioned in Chapter 2 that charging is a dynamic process, and a charge distribution exists. For a monodisperse aerosol, most of the particles acquire a potential that is close to the mean potential, which was found by flux-balancing in the previous chapters. However, the charge distribution leads to a fraction of particles with potentials significantly different than the mean potential. Since a change in potential results in different electron and ion fluxes reaching the surface of a particle, a temperature distribution develops across a monodisperse aerosol.
A single-step Markov process describes the charge distribution on a monodisperse aerosol:\(^{96}\):

\[
\frac{1}{\pi d_p^2} \frac{dF_Z}{dt} = (J_i + J_{TE})_Z - (J_e)_Z F_Z + (J_e)_Z F_{Z+1}.
\]  

(6.1)

\(F_Z\) is the fraction of particles having charge \(Z\) and \(t\) is time. Subscript \(Z\) used with the brackets stands for the charge that the fluxes are evaluated at. In this chapter, charging and heat transfer phenomena related to thermionic emission are taken into account. In equation 6.1, \(J_{TE}\) is the electron flux due to thermionic emission.

To allow for collisional ions, the following expression for ion flux is used:\(^{154}\):

\[
J_i = \left[ \frac{1}{J_{i,CEM}} + \frac{1}{J_{i,HYD}} \right]^{-1}.
\]  

(6.2)

\(J_{i,CEM}\) represents the ion flux in the collision-enhanced model (CEM) of ion collection in the weakly-collisional regime, \(\lambda_i \gtrsim \lambda_D\):\(^{152,153}\):

\[
J_{i,CEM} = \frac{1}{4} n_i \beta_i \left[ 1 - \frac{e \Phi_p}{k_B T_i} + 0.1 \left( \frac{\lambda_D}{\lambda_i} \right) \left( \frac{e \Phi_p}{k_B T_i} \right)^2 \right].
\]  

(6.3)

In this chapter, the following expression is used for particle potential\(^{9}\):

\[
\Phi_p = \frac{eZ}{2\pi\epsilon_0 d_p} e^{-d_p/\lambda_D}.\]  

(6.4)

The first two terms inside the square brackets of equation 6.3 arise from the OML theory. The third term is an approximate correction factor for single collisions between ions and neutrals in the sheath of the particle. In equation 6.2, \(J_{i,HYD}\) is the ion flux according to the hydrodynamic

---

\(^{a}\) The potential given in equation 6.4 has many names, some of them are Debye-Hückel, Yukawa, and screened Coulomb potential. It is more complete and accurate than equation 2.10 for large \(d_p\) and \(n_i\).
description in the continuum regime\textsuperscript{155}. $J_{i, HYD}$ is the dominant ion collection mechanism when the sheath is highly collisional\textsuperscript{b}:

$$J_{i, HYD} = \sqrt{\frac{\pi}{2}} n_i \beta_i \left( \frac{\lambda_i}{d_p} \right) \left| e \Phi_p / k_B T_i \right|.$$  \hspace{1cm} \text{(6.5)}

Equation 6.5 is valid when $\lambda_i \ll \lambda_D$ (i.e. fully collisional ions), and when two additional criteria are satisfied: $d_p \ll \lambda_D e$ and $d_p \ll 0.1 \lambda_e$. These criteria are stem from the assumptions employed when solving the coupled Poisson and Nernst-Planck equations\textsuperscript{155}. The bracket of equation 6.2 is an interpolation formula that bridges different charging regimes, and it has a common mathematical form that is used to cover transport phenomena occurring on free molecular, transition and continuum regimes\textsuperscript{159}. $\lambda_i$ is the parameter that defines the collisionality. As pressure increases, $\lambda_i$ decreases, thus equation 6.3 overpredicts fluxes when the pressure is high. A similar overprediction in ion fluxes is obtained from equation 6.5 when the pressure is too low. Therefore, equation 6.2 allows the determination of the appropriate ion flux expression at a given pressure.

With all charging terms included, equation 6.2 is termed the collisional model (CM). If the model is described as OML, then only the OML terms are considered (i.e. $J_{i, HYD}$ is ignored and the third term inside the square brackets of equation 6.3 is ignored). At the pressures investigated in this work, the hydrodynamic charging term has a minor effect on particle charge. Since $\lambda_e$ is large, the OML expression given by equation 2.9 for $J_e$ can be used in equation 6.1.

\textsuperscript{b} The prefactor in equation 6.5 is often given as a different constant in literature. The original form of equation 6.5 is: $J_i = 2 n_i (D / d_p) [e \Phi_p / k_B T_i]$. The differences come from the expression of ionic diffusivity, $D_i$, as a function of $\lambda_i$ and $\beta_i$: $D_i = C \lambda_i \beta_i$, where $C$ is a constant. In equation 6.5, $C = (\pi/8)^{1/2} = 0.627$. In some papers\textsuperscript{154,156}, $C = 1$. In Raizer’s book\textsuperscript{137}, $C$ is occasionally taken as $\pi/8 = 0.393$ (e.g. equation 5.1), whereas simple kinetic theory\textsuperscript{157} suggests $C = 1/3 = 0.333$. The best approach would most likely be utilizing the Einstein relation and expressing ion flux as a function of ionic mobility\textsuperscript{158} $\mu_i$, $J_i = 2 n_i (\mu_i / d_p) [\Phi_p]$, so that tabulated data on ion mobilities\textsuperscript{85} can be used directly.
The thermionic flux is given by the Richardson-Dushman equation:

\[ J_{TE} = bA_0 T_p^2 \exp \left( -\frac{W}{k_B T_p} \right), \]  

(6.6)

where \( T_p \) is the particle temperature, \( W \) is the work function for the particle, \( A_0 \) is the Richardson-Dushman constant (= 1.202\times10^6 \text{ A/m}^2\text{K}^2) and \( b \) is a material dependent correction factor. The lowering of work function due to the field on the surface of a negatively charged particle is incorporated via the Schottky expression:\n
\[ W = W_0 - \frac{e^2 |Z|^{1/2}}{2\pi\varepsilon_0 d_p}. \]  

(6.7)

\( W_0 \) is the work function of the uncharged, bulk material.

6.3. Particle Temperature - Revisited

It takes a finite amount of time for a particle to reach elevated temperatures once it enters the plasma. In this section, it is shown that both the rate of heating and the steady-state temperature can be affected by the size of the particle as it travels through regions with different ion density. A monodisperse aerosol travelling through the reactor satisfies the following energy balance equation:

\[ \frac{d(\dot{m}H_p)}{dx} = \pi d_p^2 \dot{N}_\infty \left( q_{ie} - q_{Kn} - q_{rad} - q_{TE} \right), \]  

(6.8)

where \( x \) represents the axial coordinate in the reactor, \( \dot{m} \) is the mass flux of the aerosol and it is equal to \( \nu_p N_0 (\pi/6) \rho_p d_p^3 \), and \( \nu_p \) is the particle velocity. \( H_p = C_p T_p \) denotes the mass specific enthalpy of the particles. The parentheses on the right-hand side of equation 6.8 is similar to the
ones in 2.16 as they contain various heat fluxes. However, two new terms are present here, which are the fluxes due to radiative cooling, \( q_{\text{rad}} \), and thermionic emission, \( q_{\text{TE}} \). Equation 6.8 can be rearranged for a particle with fixed size as:

\[
\frac{dT_p}{dx} = \frac{1}{v_p} \left[ \frac{6}{\rho_p C_p d_p} \left( q_{\text{ie}} - q_{\text{Kn}} - q_{\text{rad}} - q_{\text{TE}} \right) - T_p \frac{dv_p}{dx} \right]. \tag{6.9}
\]

The second term in the brackets of equation 6.9 incorporates the effect of particle acceleration on particle temperature (*vide infra*). The heating term \( q_{\text{ie}} \) is very similar to the versions used in the preceding chapters, but, since the charge distribution is now calculated, \( J_i \neq J_e \) in general. Hence:

\[
q_{\text{ie}} = J_i \left( [\Delta H_{\text{rec}}] - W + f e \left| \Phi_p \right| \right) + 2 J_e k_B T_e. \tag{6.10}
\]

Knudsen cooling is described by equation 2.19, and the radiation cooling term is given by equation 5.6. Emissivities of small particles can be calculated by the Rayleigh-Penndorf approximation [TEMP]. The cooling due to thermionic emission is written as:

\[
q_{\text{TE}} = J_{\text{TE}} W. \tag{6.11}
\]

Before investigating the dynamic problem, it is informative to solve for the steady-state temperature distribution of a stationary aerosol. In such a case, the left hand sides of equation 6.1 and 6.8 are set to zero. An example solution for the steady-state charge and temperature distributions on a monodisperse aerosol with 50 nm particles is shown in Figure 6.1. Distributions are plotted for two different charging models: CM and OML theory. Parameters used to solve for the charge and temperature distributions were taken from values given in Table 5.1. OML theory predicts a higher particle charge and lower temperatures. On the other hand, CM leads to decreased particle charge due to a higher ion flux, which eventually results in higher temperatures. Although
Figure 6.1. **Particle charge and temperature distributions with different charging models in NEP of argon.** Particles were monodispersed and they had 50 nm diameter. The following parameters were used: $n_i = 5 \times 10^{17} \text{ m}^{-3}$, $k_B T_e = 2 \text{ eV}$, $T_g = 370 \text{ K}$, $T_w = 335 \text{ K}$, $p = 1.5 \text{ Torr}$. These parameters are representative of the case with 10 W set power in Table 5.1

A slight increase in particle temperature according to CM when compared to OML theory has been previously discussed in literature\(^{99,156}\), in our case, the discrepancy is much more dramatic. The difference in mean temperatures predicted by different charging models is approximately 250 K. In both models, the particle temperature increases with increasing charge, and thus, few percent of the particles reach to 1000 K temperature according to the CM. The very high particle temperatures predicted by the CM can provide a means by which to vaporize the particles in the plasma.

### 6.4. Particle Temperature History – Model Setup

Solving the stationary version of equation 6.8 is informative, but the main purpose of this chapter is to fully solve equation 6.9. In order to close this equation, one needs to come up with a description of particle kinematics to evaluate the term $d\nu_p/dx$. In the previous chapter, gas
temperatures in the intense zone were found to be significantly higher than the temperatures measured upstream and downstream. Since the gas flow accelerates due to elevated temperature in the intense zone, particles also accelerate and adapt to the changes in gas velocity. Acceleration causes particles to spend less time in the locations where gas temperature is elevated. In our case, the particle Reynolds numbers, $Re_p = d_p v_g \rho_g / \mu$ are much lower than 1, and thus, the Stokes regime applies. The velocity of the particle as a function of position in the reactor is given as:\(^{48}\):

$$\frac{d v_p}{dx} = -\frac{18 \mu}{\rho_p d_p ^2 C_c \left(1 - \frac{v_g}{v_p}\right)}, \quad (6.12)$$

$\mu$ is the viscosity of argon, and it can be expressed as a function of temperature by using Sutherland’s equation:

$$\mu = \mu_0 \left(\frac{T_0 + C_S}{T_g + C_S \left(\frac{T_g}{T_0}\right)}\right)^{1.5}, \quad (6.13)$$

where $\mu_0 = 2.125 \times 10^{-5}$ Pa s, $T_0 = 291.15$ K and $C_S = 144.4$ K\(^c\). $C_c$ in equation 6.12 is the Cunningham slip correction factor:

$$C_c = 1 + Kn \left(1.257 + 0.4e^{-1.1Kn}\right). \quad (6.14)$$

The gas velocity, $v_g$, in equation 6.12 can be calculated from continuity and the ideal gas law:

$$v_g = v_{g0} \frac{T_g}{T_0}, \quad (6.15)$$

where $T_0$ is the ambient temperature equal to 294 K, and $v_{g0}$ is the average gas velocity at $T_0$.\(^{161}\)

\(^{c}\) These parameters provide a good fit to published data, especially for $T_g < 500$ K.
Now it is possible to solve non-stationary versions of equation 6.1 and equation 6.9. However, before attempting a complete solution, the characteristic times for charging, heating and the residence time within a region with constant ion density will be reviewed. The charging process is expected to be rapid when compared to other processes that a particle experiences in the plasma. In Appendix IV, the time required for a particle to obtain the mean charge is derived as:

\[ \tau_C = \left[ \frac{1}{\tau_{OML}} + \frac{1}{\tau_{CEM}} \right]^{-1}. \]  

(6.16)

The term \( \tau_{OML} \) describes the charging time for the OML theory and \( \tau_{CEM} \) is the contribution due to the collision-enhanced mechanism:

\[ \tau_{OML} = \frac{8\lambda_D^2}{\beta_i d_p}, \]  

(6.17)

\[ \tau_{CEM} = 40\frac{\lambda_D^2}{\beta_i d_p} \left( \frac{e |\Phi_p|}{k_B T_i} \right)^{-1}. \]  

(6.18)

The time \( \tau_C \) can be compared to the time required for a particle to move a distance over which a significant change in ion density occurs. Let \( x_m \) be the axial distance over which there is a change in ion density, which is approximately 1 mm (Figure 5.2b). When \( x_m \) is divided by the gas velocity, an estimate can be made for the time it takes the ion density to change, \( \tau_R = x_m/v_g \), which is less than or equal to 100 \( \mu s \). The charging times for the cases investigated in this study are few \( \mu s \), as determined from equation 6.16. Since the charging time is much smaller than the time during which a particle experiences a difference in the surrounding ion density, the solution to equation 6.1 can be simplified by assuming quasi steady-state\(^{96}\). From the steady-state charge distribution, the average charge and the standard deviation can be calculated. For particle temperatures below
2000 K, equation 6.1 can be further simplified due to the fact that the effect of the thermionic emission on the particle charge is negligible (*vide infra*). For low particle temperatures, the thermionic emission terms in equation 6.1 are dropped out, unless otherwise noted. Without the thermionic emission terms, charging and heating are decoupled.

The particles are expected to thermally equilibrate at a rate depending on their size and the overall heat transfer coefficient inside the plasma. This equilibration time can be given as

\[ \tau_H = \frac{d_p \rho_p C_p}{6U}, \]  

(6.19)

where \( U \) is an approximate form of the overall heat transfer coefficient:

\[ U = \sigma_{SB} \varepsilon \left( T_{p\infty}^3 + T_w^3 \right) + \frac{1}{2} \alpha_H \beta_g \frac{p}{T_g}. \]  

(6.20)

\( T_{p\infty} \) stands for the temperature that a particle obtains at the end of a heating process. At 1.5 Torr, the equilibration time of a 20 nm particle is less than 100 \( \mu \)s within the particle temperatures explored, that is \( \tau_H \approx \tau_R \). Therefore, the 20 nm particle is expected to be at near steady-state temperature inside the plasma. However, larger particles will experience a lag in heating, and this lag can create a size dependence in vaporization.

The final piece of physics that is implemented in this section is melting. Melting can absorb significant amounts of energy; thus, it can delay vaporization. Melting is taken into account in a classical way, and any pre-melting phenomena and size effects are neglected. Size effects, if they were included, would cause the nanoparticles to melt at a temperature less than \( T_m \), which is the bulk melting temperature. At \( T_p = T_m \), the evolution of the melt fraction \( y_\ell \) can be described with the following equation:
\[
\frac{d y_\ell}{d x} = \frac{1}{v_p} \left[ \frac{6}{\rho_p d_p L_m} (q_{in} - q_{Kn} - q_{rad} - q_{TE}) - y_\ell \frac{d v_p}{d x} \right],
\] (6.21)

which is similar to equation 6.9. \( L_m \) is the enthalpy of melting. The few percent change in particle size upon complete melting is omitted.

In the model, an aerosol-based process similar to the experiments with Bi aerosols (Chapter 3), wherein particles are fed into the reactor, is simulated. Using the theoretical framework described above, the temperature history of the particles is calculated by using the experimentally measured profiles of electron temperature, ion density, background gas temperature and wall temperature as inputs (Chapter 5). Equation 6.9 is the main equation to be solved. The charge distribution and the particle velocity were calculated to evaluate equation 6.9. The gas mass flow rate was the set point on the flow controller and the \( v_{g0} \) corresponds to the average gas velocity at the inlet temperature, which was 6.8 m/s. Spherical particles that have a diameter of 20 nm or larger were considered. These particles were assumed to have a monodisperse size distribution with sufficiently low particle concentrations (\( \pi n_p d_p^2 < 0.01 \text{ m}^{-1} \)), such that \( n_i = n_e \) and the electron temperature of the pristine plasma is unperturbed\(^{163} \). The particles maintain a unipolar negative charge throughout the entire process, and thus, coagulation can be suppressed.

The characterization data of the previous chapter is utilized as follows. Constant extrapolation of the measured ion densities at the ends of the axial data sets were used for regions far away from the powered electrode. For calculations at 10 W, \( 1.50 \times 10^{17} \) and \( 1.07 \times 10^{17} \text{ m}^{-3} \) were used to extrapolate to upstream and downstream respectively. For calculations at 20 W, \( 1.46 \times 10^{17} \) and \( 1.38 \times 10^{17} \) are taken as the extrapolated values. A similar extrapolation was used for the wall temperature, since some parts of the glass upstream of the powered electrode were beneath the steel parts, and therefore were optically inaccessible. For these parts, 305 and 309 K were used as
the extrapolated values at 10 and 20 W power, respectively. For the calculation of temperature histories at these powers, electron temperature was kept fixed at 2 eV along the reactor. A multistep differential equation solver (ode113 in MATLAB®)\textsuperscript{164} was utilized to solve equations 6.9, 6.12 and 6.21. An event locator switches between equations 6.9 and 6.21 to model melting.

As for the particle material, copper zirconium (CuZr) alloy was selected. One of the reasons of choosing this material is its negligible vapor pressure for most of the temperatures calculated below. Therefore, evaporation can be neglected, and the particle sizes are fixed. This conforms with how equation 6.9 was derived. Another important reason for selecting CuZr as the test aerosol

<table>
<thead>
<tr>
<th>Parameter/Property</th>
<th>Value</th>
<th>Unit</th>
<th>Definition</th>
<th>Reference</th>
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<td>$C_{pCu}$</td>
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<td>J/kgK</td>
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</tr>
<tr>
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<td>J/kgK</td>
<td>Heat capacity of Zr at 300 K\textsuperscript{*}</td>
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<tr>
<td>$\rho_{pCu}$</td>
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<td>kg/m$^3$</td>
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<tr>
<td>$\rho_{pZr}$</td>
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<td>kg/m$^3$</td>
<td>Density of Zr\textsuperscript{*}</td>
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</tr>
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<td>$L_{mCu}$</td>
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<td>kJ/mol</td>
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</tr>
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<td>$W_{0Cu}$</td>
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<tr>
<td>$\alpha_H$</td>
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<tr>
<td>$f$</td>
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<td>Fraction of ion kinetic energy transferred upon bombardment\textsuperscript{§}</td>
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<tr>
<td>$b$</td>
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<td>-</td>
<td>Correction factor to the Richardson constant\textsuperscript{**}</td>
<td>169</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Taken to be independent of temperature.
\textsuperscript{†}Value for polycrystalline material.
\textsuperscript{‡}Average value.
\textsuperscript{§}An approximate value measured for Cu is assumed to be valid for the CuZr particle.
\textsuperscript{**}Value for Cu, assumed to be valid for the CuZr particle. The value of $b$ for Zr was argued to be close to 1 in an early report\textsuperscript{170}.
is provided in the next section. For the CuZr alloy, phase-averaged properties were used, except for the melting temperature:

\[ \theta_{CuZr} = y_{Zr} \theta_{Zr} + (1 - y_{Zr}) \theta_{Cu}, \]  

(6.22)

where \( \theta \) stands for a material property, which can be \( C_p, \rho_p, L_m, W_0 \) or \( \varepsilon \). \( y_{Zr} \) is the atomic fraction of Zr in the alloy. \( T_m \) of the alloy was taken from literature\(^{171} \). The material properties and parameters used in the model are given in Table 6.1.

6.5. Particle Temperature History – Results

The calculated NP temperature reaches a maximum in the intense zone and then rapidly drops in the low-intensity plasma downstream. Temperature histories of 50 nm diameter particles at 1.5 Torr are given in 6.2. The temperatures of particles having the mean charge are plotted for two

![Figure 6.2. Nanoparticle temperature histories for different applied powers and charging models. The nanoparticles were monodisperse 50 nm diameter Cu\(_{58}\)Zr\(_{42}\). Temperatures of the particles with a charge that is the average of the distribution were plotted. The red curves are for a power set point of 20 W and the black curves are for 10 W. The dashed lines are for charging described by OML theory and the solid lines are for charging described by CM.](image)

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different applied powers, 10 and 20 W. At 10 W, the difference between the particle temperature predicted by the OML and CM is approximately 100 K in the regions sufficiently far away from the electrode. However, the difference in predicted temperatures increases to 300 K at the center of powered electrode. The discrepancy between the theories increases further to 500 K at the center of the electrode when the power is set to 20 W. The divergence in the predictions of NP temperature for CM and OML is quite sensitive to ion density. The plateau in the particle temperature history modeled with CM at 20 W is due to melting, which is an isothermal process\(^d\).

Particle size plays a major role in the peak particle temperature reached in the intense zone. Smaller particles reach a higher temperature, whereas larger particles experience lower temperatures and they take longer to heat up and cool down (Equation 6.19). Particle temperature as a function of axial position and particle size is plotted in Figure 6.3a, for CuZr particles of 20, 200 and 500 nm in diameter. As the NP diameter increases, the peak temperature decreases and the axial position at which the maximum occurs shifts to positions further downstream. The distribution in NP temperature, which is described by the shaded region in Figure 6.3a, corresponds to the temperature of particles having ±1 standard deviation of the NP charge distribution. Smaller particles have a wider temperature distribution, and they experience temperature fluctuations as wide as ±150 K around the mean temperature. Since the measured ion densities are nearly symmetric around the electrode (Figure 3b), the heating and cooling rates in the vicinity of the powered electrode are approximately equal for particles that are smaller than few hundred nanometers. All particles carry a unipolar negative charge in both the high-intensity and low-intensity zones of the plasma. The average charge is plotted in Figure 6.3b, where the shaded

---

\(^d\) Section 6.6 deals with the reason why melting is modeled as a one-way process.
Figure 6.3. Effect of particle size on temperature history. (a) Temperature histories of Cu$_{58}$Zr$_{42}$ particles of different sizes as a function of axial position, predicted by the CM charging model at an applied power set point of 20 W and a total pressure of 1.5 Torr. The bands correspond to the distribution in nanoparticle temperatures due to the charge distribution. (b) Evolution of particle charge for particles simulated in (a). The bands correspond to the ±1 standard deviation limits.

region corresponds to ±1 standard deviation of the distribution. Although $T_e$ is constant across the reactor, particle charge becomes more negative inside the intense zone. This effect is caused by a decrease in ion collisionality, since $\lambda_D$ decreases and $\lambda_i$ increases in the intense zone.

For smaller particles, the peak temperature in the intense zone exceeds the melting point of CuZr. However, particles start melting at different times and their melting periods are different
due to the temperature distribution. Larger NPs are more difficult to heat up and would most likely require higher powers to reach the requisite ion densities to achieve similar temperatures with smaller particles (Figure 6.3a). Another possibility for increasing the temperature of larger NPs would be increasing the residence time spent in the intense zone.

With sufficiently long residence times inside the intense zone, or with higher applied power, the maximum particle temperatures can be increased above 2000 K. Figure 6.4 shows the mean values of particle temperature distribution inside the intense zone obtained by solving equation 6.9 at steady state. It was found that at temperatures above 2000 K, the thermionic emission terms in equations 6.1 and 6.9 can become comparable in magnitude to other charging and cooling mechanisms. Thermionic emission shifts the particle charge distribution to a less negative mean charge, and this shift is accompanied by a decrease in particle temperature. Accordingly, thermionic emission terms were retained in these steady-state calculations. For the 20 nm particle,

Figure 6.4. Steady-state mean temperatures of particles inside the intense zone. Particles were Cu_{52}Zr_{48}.
which is already at steady-state as it travels through the intense zone, particle temperatures can reach 2000 K at 1.5 Torr for powers above 40 W. At temperatures greater than 2000 K, thermionic emission is seen to limit the particle temperature. Evaporation, which was neglected in these calculations, is expected to be an important cooling mechanism at such temperatures as well. At steady state, the 200 nm particle is seen to reach a temperature that is higher than its melting point at 20 W, which is approximately 150 K higher than the maximum value given in Figure 6.3a. We estimate that the width of the intense zone should be a centimeter broader than its original width (1.3 cm) for a 200 nm particle to melt at 20W as it passes through the intense zone. It was observed that thermionic emission does not limit the temperature of the 200 nm particle within range of plasma parameters investigated, since the mean temperatures calculated by accounting for thermionic emission turned out to be very close to the values calculated when thermionic emission was neglected. The reason stems from the fact that the Schottky effect is size dependent, and the electric field on a smaller charged particle is usually higher. Furthermore, increasing the pressure is accompanied by increased Knudsen cooling rates and decreased ion density (Figure 5.4b). Therefore, particle temperatures were much lower at 10 Torr, and the maximum mean temperature of a 20 nm particle stayed below 1000 K.

6.6. Nonequilibrium Materials

A curious aspect of the temperature histories is that they involve stages of very fast heating and cooling. An immediate question that comes to mind is the possibility of forming of materials with nonequilibrium atomic structure due to rapid thermal treatment in NEP. In the context of solids, a material is in nonequilibrium (or metastable) state whenever it has a free energy that is higher than that of the same mass in its equilibrium state at given temperature and pressure.

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Since the calculated particle temperatures appear to be high enough to melt many materials, the most relevant process for forming a nonequilibrium material in NEP would be melt quenching.

Melt quenching is a well-established method for synthesizing amorphous metals. At solid state, metals are typically crystalline, and thus amorphous metals have a nonequilibrium atomic structure. Amorphous metals and amorphous metal alloys can be formed by rapid quenching that starts from either a vapor or a liquid melt. The amorphous state is imagined as a highly viscous, super-cooled liquid. The difference in free energy between the super-cooled liquid and the crystalline equilibrium state increases as temperature decreases below the melting point. Quenching allows the amorphous state to be arrested and re-crystallization is extremely slow at low temperatures due to very low self-diffusion coefficients in the material. In other words, the strong thermodynamic driving force for crystallization is counteracted by slow crystallization kinetics at low temperature. Depending on the composition of the starting material, quenching rates between $10^4$-$10^7$ K/s are usually required to obtain amorphous binary alloys\textsuperscript{173}. When amorphous alloys are made as nanoparticles, they acquire unique material properties and can be used as magnets with low coercivity\textsuperscript{174}, as metal gates with uniform work function\textsuperscript{175,176}, and as highly active catalysts\textsuperscript{177}.

The possibility of forming amorphous metal alloys in NEP is another reason why CuZr was selected as the particle material in the calculations presented above. CuZr is a well-established marginal glass former\textsuperscript{178}. Amorphous CuZr is a proven catalyst for various isomerization and hydrogenation reactions\textsuperscript{179,180}, and a candidate for low-temperature electrocatalysis. It is shown below that quenching rates in NEP can easily exceed $10^5$ K/s, which is an order of magnitude higher than the experimentally measured cooling rates required to prepare amorphous CuZr by melt quenching\textsuperscript{181}. A schematic of the key idea explored in this section is presented in Figure 6.5.
Figure 6.5. Schematic of the hypothesis for amorphization of crystalline metal alloy particles. The initially crystalline nanoparticles are melted in the intense zone, which has elevated ion density and gas temperature in the vicinity of the powered (PWR) electrode, and then rapidly quenched to arrest the amorphous state in the low-intensity plasma downstream; all while maintaining a unipolar negative charge.

The quenching rate of particles is expected to be sufficiently fast to arrest an amorphous state from the liquid melt that forms in the intense zone. The residence time in the intense zone is very short, approximately 1 ms due to high flow velocities, which range from 6 to 10 m/s at 1.5 Torr depending on axial position due to gradients in background gas temperature (Figure 5.7c). The temperatures of 20 and 200 nm CuZr nanoparticles after they reach their peak temperature are plotted in Figure 6.6 as a function of time. The nanoparticles cool from their melting point to the glass transition temperature $T_{g^*}$, at a rate greater than $10^5$ K/s, which is sufficiently fast to arrest the amorphous state for CuZr $^{181}$. At positions further downstream, the temperature of the particles stay below $T_{g^*}$ (see Figure 6.3a). Therefore, it appears feasible to transform crystalline CuZr NPs into an amorphous state using the ion density profile naturally present in the archetypal tubular flow-through RF plasma reactor. This is the main reason why re-solidification was not considered in Figures 6.2 and 6.3. Based on the results given in Figure 6.4, melting larger particles would be
Figure 6.6. Quenching of 20 nm and 200 nm particles as they leave the intense zone. Particles were Cu_{45}Zr_{55}. Power was set at 20 W and pressure was 1.5 Torr.

feasible at higher powers. However, external cooling may be required to maintain the reactor temperature below the crystallization temperature of the metal.

Although the example presented herein was for CuZr alloy, other marginal metallic glasses could probably also be synthesized due to the similar requisite quenching rates, e.g. PdSi\textsuperscript{183} or NiZr\textsuperscript{182}. The possibility of forming amorphous particles should primarily depend on the maximum particle temperatures reached in the intense zone, which would dictate whether particles would melt or not. Therefore, the melting temperature is a threshold temperature of the process that needs to be surpassed. This threshold temperature is reminiscent of plasma synthesis of crystalline silicon particles, where crystallinity requires particles to reach temperatures above the crystallization temperature\textsuperscript{184}. In order to reach the threshold particle temperature in the NEP, ion densities should be high enough. As shown by the particle temperature histories and maximum steady-state temperatures in Figures 6.3 and 6.4, however, the maximum temperature achieved in the NEP also depends on the ion density distribution, gas temperature, particle residence time and
particle thermal inertia. For particles that melt in the intense zone, forming an amorphous phase is then primarily determined by the background gas temperature and by the ion densities in the low-intensity plasma downstream of the powered electrode. If the reactor can be tuned in such a way that the background gas temperature is kept sufficiently low while the ion density can be increased predominantly at the intense zone, then theory suggests that the quenching rates could be increased to orders even higher than $10^5$ K/s. As presented in Figure 6.3a, larger particles are more difficult to heat up due to their higher heat capacity. On the other hand, particles smaller than 10 nm are also expected to be difficult to make amorphous. In the case of smaller nanoparticles, the nonequilibrium acts against the formation of an amorphous phase since charging is stochastic and the low heat capacities of particles allow heat spikes to occur. Heat spikes continuously elevate nanoparticle temperature and then the particle gets quenched. Since heat spikes, which are of magnitude large enough to elevate very small nanoparticles above the glass transition temperature, can occur in a large region of the plasma, i.e. outside the intense zone; recrystallization is expected to be pronounced, and the formation of an amorphous phase might therefore be difficult.

The process discussed here can be experimentally accomplished with a configuration that is similar to the one described in Chapter 3. An aerosol generator can be used to generate the CuZr aerosol with particles of the sizes considered in the calculations. As nanopowder of CuZr is commercially available, a dust dispenser would be capable of providing a constant feed of the aerosol into the NEP.
6.7. Conclusions and Comments

The intense zone in flow-through tubular reactors can heat submicron particles up to temperatures of 1000 K and above if ion collisionality is taken into account. The maximum temperature obtained by a particle as it travels along the reactor can depend on its size. Larger particles experience a lag in their heating and cooling as they pass through the intense zone. Therefore, if particles reach the temperatures at which considerable evaporation occurs, thermal evaporation can be size dependent. Furthermore, even for a monodisperse aerosol, charge distribution can lead to a significant temperature distribution across the aerosol, leading to the random vaporization of some of the particles. As long as particle sizes are below 500 nm, heating and cooling rates of particles are rapid and on the order of $10^5$ K/s. Such heat transfer rates might render NEP as a processor that can cause nonequilibrium atomic transformations in small particles, and the unique axial distributions of ion density and gas temperature in the flow-through reactor play a major role in such transformations. The exact dynamics would depend on the absolute values of the plasma parameters, which are expected to be tunable through power and pressure (Chapter 5).

The particle temperatures calculated in this section are significantly higher than the values calculated in Chapter 4. For Bi particles, these temperatures are high enough to bring thermal evaporation back as a feasible vaporization mechanism in dusty NEP. In order to see whether experimental results in the size-tuning of the Bi aerosol can be modeled when thermal evaporation is considered, the model presented in Chapter 4 could be modified to include the particle temperature model presented in this chapter, and the plasma parameters presented in the previous chapter. However, such an attempt was not done during the course of this work. Instead of going back to the sectional model, a simple time constant-approach for evaporation is presented here.
Similar to the discussion on the characteristic time of condensation given at the end of chapter 4, the time constant of evaporation can indicate whether the rate of evaporation is on par with the experimentally observed vaporization rates. An expression for the time constant was derived in Appendix II:

$$\tau_{evap} = \frac{d_p \beta_p \rho_p}{\alpha_M (p_s - p_0)}.$$  \hspace{1cm} (6.23)

For the high concentration Bi aerosol of Chapter 3, $\tau_{evap}$ is approximately 30 ms if particle temperature is taken as 1050 K (Figure 6.3a). This time constant has the same order of magnitude with residence time in the reactor. Therefore, it is likely that thermal evaporation plays a significant role in nonequilibrium vaporization of aerosols in tubular flow-through NEP reactors.
Chapter 7

Nonequilibrium Plasma Aerotaxy (NPA) and the Synthesis of Size-Controlled GaN Nanocrystals

Up to this chapter, the following results on the growth dynamics of small particles in NEP have been obtained:

1) Particles vaporize in NEP. The vapor appears to have a very high supersaturation ratio. Therefore, it tends to condense on the walls and on the remaining particles, or it might lead to nucleation.

2) Vaporization-condensation dynamics can lead to formation of monodisperse particles.

3) The flow-through reactor has an intense zone in the vicinity of its powered electrode. This zone has elevated ion density and background gas temperature. It is capable of vaporizing an aerosol in a time scale of milliseconds.

4) Calculations indicate that at moderate powers, particle temperatures can be raised to 1000 K or above.
Based on these results, we ask the following questions that motivate the rest of this dissertation:

“What happens if we send an aerosol into a nonequilibrium plasma that has gaseous reactive species within? Would the aerosol still vaporize? Would a new compound material form after the feed aerosol vaporizes? Would we able to form the new compound material as monodisperse nanocrystals?”

Calculations of particle temperature suggest that it should be possible to vaporize materials that are less volatile than Bi in the intense zone. For example, if gallium can be vaporized, then the gallium vapor is expected to be highly reactive. If excited species of a gas phase element, such as nitrogen, are also present in the plasma, then it should be very much possible to generate gallium nitride particles upon growth downstream of the intense zone. In this chapter, these expectations are tested in an experiment during which a Ga aerosol is fed to an argon/nitrogen plasma for the purpose of making gallium nitride. It is shown that the answer to the last three of the questions given above is yes. We initially focus on material properties, and vaporization will be investigated in detail in the next chapter. The aerosol-based NEP synthesis method presented in this chapter, termed as nonequilibrium plasma aerotation, is studied in the rest of this dissertation. Synthesizing III-V semiconductor NCs is the goal, and studies start with gallium nitride. Before presenting the results, we discuss why gallium nitride was chosen as the test material.

7.1. Gallium Nitride (GaN)

III-V nitride semiconductors are an important family of materials for applications in optoelectronics due to their band gaps that span between 0.65 to 6 eV\textsuperscript{185,186}. Gallium nitride (GaN) is the most-studied binary compound of the III-V nitrides. An attractive feature of GaN is its large direct bandgap between 3.2 and 3.4 eV depending on the crystal structure, which allows LEDs and
laser diodes that operate at near ultraviolet wavelengths. Moreover, GaN has high thermal stability, high thermal conductivity, and relatively high charge carrier mobility and breakdown field strength. It is therefore seen as a promising material in power electronics\textsuperscript{187,188}. Furthermore, GaN is resistant to radiation-damage\textsuperscript{189}, it is chemically stable\textsuperscript{190} and non-toxic\textsuperscript{191}. Such favorable properties extend the use of GaN to biomedical materials\textsuperscript{192–195}. Due to the wide range of applications, an intense effort focused on developing methods of synthesizing GaN has been conducted over the last three decades. Hydride vapor phase epitaxy, chemical vapor deposition and molecular beam epitaxy have become the major methods of making thin films of GaN, which is the most common form of the material\textsuperscript{196,197}.

Synthesis of high quality GaN nanocrystals (NCs) would open up possibilities for additional applications of the semiconductor. First of all, quantum-confined crystals can extend the emission range of LEDs and laser diodes deeper into the UV, to wavelengths less than 400 nm. The estimated value of the exciton Bohr diameter of GaN is approximately 6-8 nm\textsuperscript{198–200}. The ability to make GaN NCs with similar or smaller sizes would allow manufacturing of UV phosphors with tunable emission by utilizing quantum confinement. Furthermore, deposition, self-assembly and printing of GaN NCs into solid GaN structures may allow smaller optoelectronic devices\textsuperscript{201–205}. On the other hand, particles that are larger than the exciton Bohr radius could be used for growing porous or randomly structured films comprised of GaN NCs. GaN NCs have a relatively high index of refraction (~2.4 across the visible spectrum\textsuperscript{206}) and are almost completely transparent to visible light when free of defects and impurities. Therefore, films comprised of high quality GaN NCs can have unique applications in photonics\textsuperscript{207}, lasing\textsuperscript{208} and photocatalysis\textsuperscript{209–211}.

The synthesis of GaN NCs is an active area of research. Previously, both liquid phase and gas phase methods of synthesis have been employed. Liquid phase methods generally rely on
metathesis or thermolysis reactions\textsuperscript{212}. Unlike II-VI compounds, early methods\textsuperscript{213–217} of GaN NC synthesis in the liquid phase suffered from either poor crystallinity, poor size control, highly polydisperse size distributions or low chemical purity. The major reasons for this contrast include the covalent nature of the nitrogen bonds, compared to the relatively ionic chalcogenide bonds. Moreover, the relatively high crystallization temperature of GaN requires liquid-phase methods to employ solvents with high boiling temperature. However, very recently Choi et al. succeeded in synthesizing size controlled GaN NCs with tunable optical properties\textsuperscript{218}. Their method of synthesis is inherently limited to particles that have PL emission at or below 3.9 eV. On the other hand, few gas-phase methods of GaN synthesis have been reported in the literature. These studies involved heating powders of Ga, Ga\textsubscript{2}O\textsubscript{3} or organometallic Ga precursors in the presence of ammonia\textsuperscript{219–222}, pulsed laser ablation from bulk GaN or Ga metal\textsuperscript{223–225}, and plasma synthesis from metallic Ga or organometallic Ga precursors\textsuperscript{75,226–228}. Some of the major drawbacks of these methods are the formation of large aggregates, poor size control and the necessity to use post-synthesis annealing to improve crystallinity and/or to tune stoichiometry. It is shown that with the process described here, producing free-standing, size-controlled, ligand-free and photoluminescent GaN NCs is possible.

7.2. The Concept of Nonequilibrium Plasma Aerotaxy

The general approach to nanomaterials synthesis in NEPs involves feeding the relevant organometallic precursors and hydrides (if available) into the NEP, wherein the precursors decompose and lead to the nucleation and growth of NCs. In contrast, the method described here employs a metallic Ga aerosol and gaseous N\textsubscript{2} as precursors, thus avoiding the need for pyrophoric and toxic chemicals. An aerosol of Ga, termed the precursor aerosol, is generated by evaporation-condensation and the NEP subsequently serves as the reaction environment, wherein the Ga
aerosol vaporizes and reacts with excited N\textsubscript{2} species in the plasma to form GaN. The method is continuous, and it can provide crystalline and stoichiometric particles with controlled size, demonstrated in this study in the range from 5 to 45 nm. The plasma only contains Ga, N\textsubscript{2} and an inert gas, in this case Ar. Therefore, the material produced does not contain significant quantities of impurities such as C or H, which are known contaminants if hydride or organometallic precursors are used\textsuperscript{76,77}. These pure GaN particles are photoluminescent, and they can be made to be quantum confined, leading to PL emission at energies greater than the bulk band gap. They can be deposited in the form of porous films within the same setup right after they have been synthesized, by using a supersonic impact deposition stage.

We term the method of synthesis as nonequilibrium plasma aerotaxy (NPA). The method is similar to the thermal aerotaxy method used for the synthesis of phosphide and arsenide NCs and nanowires by Deppert, Samuelson and coworkers\textsuperscript{229–231}. During the thermal aerotaxy method, a precursor aerosol of the group III element is generated by evaporation-condensation and a defined particle size is selected by a differential mobility analyzer. The selected portion of the aerosol is then made to react with the relevant pnictides, such as arsine or phosphine, in a high temperature environment to form the III-V semiconductor. In our system, NEP uses the whole precursor aerosol, and tunes the final particle size of the semiconductor NCs using the process parameters. Keeping the whole aerosol allows a throughput that is approximately 1000 times greater when compared to mobility-selected aerotaxy. Furthermore, employing a NEP reactor in place of a thermal environment has unique advantages due to the non-equilibrium features of the NEP. NCs obtain negative charges in the NEP, which prevent aggregation due to Coulombic repulsion\textsuperscript{53}. The absence of aggregation leads to the simplified scheme of aerosol growth dynamics which primarily involve nucleation and surface growth (Figure 4.1). As previously discussed, these mechanisms
can produce narrow size distributions, provided the particle size is sufficiently large. The NPA method can be used for the synthesis of many other compound semiconductors. Further examples of compound semiconductors that can be made with NPA are provided in Chapters 9 and 10.

7.3. Nonequilibrium Plasma Aerotaxy: The Setup

The setup is composed of three parts: the aerosol source, the plasma reactor and the collection section (Figure 7.1). The whole setup was under vacuum, with pressure typically in the range from 2 to 6 Torr.

For the Ga aerosol source, a hot-filament type evaporation-condensation generator was developed. A piece of Ga (99.999%, Sigma Aldrich), usually 1 to 2 grams, sat on an alumina-coated molybdenum filament (EVS9AAOMO, Kurt J. Lesker). The filament was resistively heated by a DC power supply (6011A, HP). The hot Ga blob (Figure 7.2) produced Ga vapor, and that vapor was swept by an UHP Ar (further purified through an alumina supported copper oxide O$_2$ scrubber, CeeKay, 6300-4SS) flow passed over the blob’s surface. Thus, immediate cooling of the vapor lead to the nucleation of the Ga precursor aerosol. The evaporator was similar to the

![Figure 7.1. Experimental setup for nonequilibrium plasma aerotaxy (NPA) of gallium nitride.](image-url)
Figure 7.2. **Hot-filament evaporator.** Liquid Ga on an alumina-coated Mo filament.

Figure 7.3. **Schematic of the hot-filament evaporator.**

evaporators used in thin film deposition. However, higher gas pressures allowed faster heat-up times (approximately 200 K/min) and favored nucleation of particles. Unlike thin film deposition,
each filament was used for more than 10 heating and cooling cycles, and fresh Ga was usually added after each experiment. A schematic of the hot-filament evaporator is given in Figure 7.3. Operation of the hot-filament evaporator is similar to a hot wire aerosol generator\textsuperscript{141,232}, but unlike the hot wire generator, the hot-filament evaporator can produce aerosols from molten metals.

The mass output of the evaporator is related to the temperature of the hot Ga blob on the filament. The emission of blackbody radiation by the hot Ga blob allowed the measurement of its temperature. The miniature spectrometer used in previous chapters was employed for infrared thermometry. The spectrometer was calibrated for relative irradiance using a blackbody furnace (M335, LumaSense Technologies). The fiber was terminated with a plano-convex lens which was aligned in such a way that through a window it viewed a 4 mm diameter spot on the hot Ga blob (Figure 7.3). The spot was smaller than the blob itself. Temperature of the blob was estimated by fitting a Wien distribution to the spectra acquired (Figure 7.4a). Increasing applied power led to a sublinear increase in blob temperature (Figure 7.4b). The mass output of the source (see below for measurements) increased with the temperature of the blob as expected (Figure 7.4c), and it correlated closely with the calculated vapor pressure of Ga\textsuperscript{119}. Throughout this study, Ga mass flow rates of mainly 0.3 and 0.5 mg/min, as measured on filters \textit{(vide infra)}, were employed, which corresponded to a temperature range of 1350 to 1450 K for the blob. The mass output of the evaporator was steady with no appreciable drift (Figure 7.4d). This was due to a small increase in the temperature as the blob shrank, which compensated for the decrease in the gas-liquid contact area. Produced Ga aerosols were highly polydisperse (Figure 7.4e). The tail of the distributions grew into larger particles as the mass output was increased. Aerosol mass and primary particle number concentrations downstream of the evaporator were on the order of 1 mg m\textsuperscript{-3} and 10\textsuperscript{14} m\textsuperscript{-3}, respectively.
Figure 7.4. Characterization of the hot-filament evaporator. (a) Blackbody radiation emitted by the Ga blob. Curves were acquired at different powers applied to the filament. (b) Filament temperature as a function of applied power. Measurements were done for two different filaments at 4.2 Torr with 500 sccm Ar flow. (c) Evaporator output and filament temperature as function of applied power. (d) Evaporator output as a function of time. “Exp.” stands for experiment, and $m_{Ga,0}$ is the mass flow rate set at the beginning of the experiment. (e) Frequency distributions of the Ga aerosols produced with the hot-filament evaporator. Dotted curves are the distributions corrected for collection efficiency [GaN]. Mass flow rates given in panels (c-e) are the values measured on filters, and due to filter collection efficiency being approximately 50% (vide infra), actual flow rates were 2 times higher.
Downstream of the aerosol source, N₂ (UHP 5.0, Praxair. Further purified through the same type of scrubber used for Ar) was added to the aerosol stream and the mixture was sent into the tubular flow-through reactor through a 6 mm diameter orifice (Figures 7.1 and 7.5). Plasma power set at the power supply was 80 W unless otherwise noted. Reported power values are the values measured at the power supply. The power transmission efficiency of the matching network was measured as 65% in Chapter 5. A tube with 16 mm ID was used for experiments with a residence time greater than 20 ms. Tubes with smaller inner diameters having 10 and 7 mm were used to decrease residence times below 20 ms. The stainless-steel flange downstream of the tube was grounded. At this point, pressure was measured with a capacitive diaphragm gauge. In all experiments, plasma extended primarily downstream and coupled with the grounded flange. Two viewports placed downstream of the tube were used to estimate the total length of the plasma for residence time calculations. Gas flow rates through the reactor were adjusted by mass flow controllers. Mass flow rates were in the range from 100 to 600 sccm for Ar and 4 to 24 sccm for N₂. The Ar:N₂ ratio was 25:1, and total mass flow rates were adjusted to obtain the desired residence time. The reactor was cooled with two fans.

![Flow-through reactor with Ar/N₂ plasma.](image)

**Figure 7.5.** Flow-through reactor with Ar/N₂ plasma. The pressure was 4.2 Torr. The Ar/N₂ plasma was sustained with 80 W RF power. The ring denoted by PWR is the powered electrode. The ground electrode used in the previous chapters was removed, and the flange downstream of the fused silica tube was grounded. Particles were absent.
By diverting the flow from a bypass line into a collection section, synthesized NCs were deposited on removable 400 mesh stainless steel filters and on vertically suspended lacey carbon TEM grids. The filters were weighed, and the aerosol mass flow rates were calculated. Such measurements were used to tune the output of the evaporator. In the results presented in this chapter, the measured mass flow rates are reported. The total mass-based collection efficiency of the mesh filters was estimated by placing two filters back-to-back, separated by 8 cm. The efficiency measured was roughly 50%. Thus, the actual mass flow rates were approximately 2 times greater than the values reported in this chapter. The effluent from the collection section passed through a diaphragm valve, before going through a vacuum pump (Trivac D65B, Leybold).

As a proof of concept for making GaN NC films, a portable impaction stage was inserted into the collection section (Figure 7.6). The aerosol stream coming from the plasma was sent into a 10

![Figure 7.6. Schematic of the impaction apparatus.](image)

The apparatus was only used for deposition of thin films comprised of GaN NCs.
mm long rectangular nozzle with dimensions of 1.2 x 20 mm. The pressure ratio across the nozzle, measured by a second pressure gauge, was approximately 4.2. NCs reach sonic velocities within the nozzle\textsuperscript{233} and just downstream of the nozzle the aerosol beam impacts on the substrate with velocities on the order of hundreds of m/s\textsuperscript{234}. The NCs were deposited on Si substrates that were moved back and forth through the beam in reciprocating motion.

7.4. Material Characterization

7.4.1 Electron Microscopy

Most of the imaging of the collected particles was done by using a thermal emission microscope with a LaB\textsubscript{6} filament operating at 200 kV accelerating voltage (JEM-2000 FX, JEOL). TEM images were used to extract the aerosol frequency distributions. By using ImageJ software, particle sizes were measured by drawing ovals that encapsulate the particles, and the diameter of the area-equivalent circle was taken as the particle size. A minimum of 200 particles were counted for samples that had a mean size larger than 10 nm. For smaller sizes, up to 1000 particles were counted. High resolution TEM (HRTEM) was conducted with a field emission scanning microscope (JEM-2100F, JEOL). The same microscope was used for energy-dispersive x-ray spectrometry (EDXS, XFlash 6T, Bruker).

7.4.2 Powder Characterization

Part of the powder collected on the filters was scraped off and characterized in its dry form. The production rate of GaN NC was in the range from 5 to 50 mg/hr. Powders were subjected to X-ray diffraction (XRD, d8 Advance, Bruker) on a miscut silicon wafer with a low background signal. Fourier transform infrared (FTIR) spectroscopy was conducted to characterize the surface of the particles (Nicolet 470, Thermo Scientific). An attenuated total reflectance (ATR) tool with
a germanium crystal was employed. Absorption spectra were qualitatively corrected for the wavenumber-dependent depth of penetration, $\Delta z$, of evanescent waves into the sample. Corrected absorbance, $A_{corr}$, is inversely proportional to $\Delta z$, which is in turn inversely proportional to the wavenumber of light, $w$:

$$A_{corr} \propto \frac{A}{\Delta z} \propto Aw.$$  

This approach assumes that the sample’s refractive index, $n_s$, is constant across the spectral window, which is a fair assumption as long as the condition for total reflection is satisfied. $n_c$ is the refractive index of the crystal (For Ge, $n_c = 4$).

Three methods were used to determine the stoichiometry of the powders. First, EDXS was conducted with a scanning electron microscope (SEM, JSM-7001 LVF, JEOL, equipped with Aztec Live X-Max EDXS detector, Oxford). Secondly, thermogravimetric analysis (TGA) was utilized to estimate the Ga:N ratio by measuring the weight gain during oxidation (Q5000, TA Instruments). Ceramic pans were used, and air was selected as the oxidizer during TGA. And finally, X-ray photoelectron spectroscopy (XPS) was employed. The spectrometer (5000 VersaProbe II, Physical Electronics) had an Al Kα source.

After the dry portion of the powder had been scraped off, the remaining portion of the powder was recovered by placing the filter in either methanol (99.9%, Sigma Aldrich) or dimethyl sulfoxide (DMSO, 99.5%, Sigma Aldrich), and subsequently sonicating it to generate a dispersion. Absorbance spectroscopy in the UV and visible range (UV-VIS) was conducted (UV-1800, Shimadzu) and the photoluminescence (PL) of the sample was measured using a fluorimeter (RF-6000, Shimadzu). Concentrations of NC suspensions were typically 0.1 mg/mL. Dynamic light scattering (DLS) was utilized to estimate the aggregate sizes (Zetasizer Nano ZS, Malvern Panalytical).

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$^a \sin(\theta_c) = n_s/n_c$, where $\theta_c$ is the angle of incidence. In the instrument used, $\theta_c$ was fixed: $\theta_c = 45^\circ$. 

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7.4.3 Film Characterization

Films deposited on silicon wafers were characterized by SEM to obtain the film thickness. An X-ray fluorescence spectrometer (XRF, MID01, Spectro Midex) was calibrated by using solid GaN templates (~500 nm thickness measured with SEM, on Si substrate, MTI Corporation) with measured thickness to estimate the porosity of the films.

7.5. GaN NCs – Size and Crystallinity

Upon sending the polydisperse spherical droplets of Ga (Figure 7.7a) along with N\textsubscript{2} into the NEP, NCs of different shapes and sizes were produced. Selective area electron diffraction (SAED,
Figure 7.7a-d insets) immediately revealed that these NCs were crystalline GaN.

The NPA method is capable of providing good size control in the synthesis of GaN NCs (Figure 7.7e). Extensive TEM investigations on collected NCs showed that one of the most straightforward process parameters for size control is the residence time in the plasma. As the residence time in the plasma increased, the mean particle diameter, $<d_p>$, also increased; and the size distributions became narrower. For residence times longer than 45 ms, size distributions approached to the definition of a monodisperse size distribution: $\sigma_g \leq 1.1$. The fitted curves given in Figure 7.7e are lognormal distributions. Interestingly, the Ga precursor aerosol was found to be highly polydisperse at all of the aerosol mass flow rates employed (Figure 7.4e), and yet, it was possible to synthesize GaN NCs with much narrower size distributions. Furthermore, in some cases the GaN NCs were smaller than the Ga precursor aerosol, and in other cases they were larger than the Ga precursor aerosol. Figure 7.7f summarizes the trends in particle size and geometric standard distribution obtained during experiments conducted at a pressure of 4.2 Torr with 0.3 mg/min mass input. A limited number of experiments conducted at a slightly lower pressure of 2.8 Torr indicated that the effect of pressure on $<d_p>$ and $\sigma_g$ was modest over that range. NCs smaller than 10 nm appeared to be approximately spherical in shape (Figure 7.7b), however, larger particles were found to be faceted (Figures 7.7c and 7.7d).

NC size distributions could also be tuned by changing the Ga aerosol mass flow into the reactor. Increasing the mass input led to larger NCs. For example, at a residence time of 22 ms, ramping the Ga feed rate from 0.3 mg/min to 0.5 mg/min approximately doubled the average diameter (Figure 7.7e). After scanning residence times between 10-150 ms and mass inputs between 0.15 to 1.5 mg/min, the maximum $<d_p>$ that could be obtained was found to be approximately 45 nm. Increasing the Ga mass flow beyond 1.5 mg/min resulted in a higher GaN
throughput, but $\langle d_p \rangle$ and $\sigma_g$ remained approximately constant. In all experiments, the mass concentration and primary particle number concentration of the GaN aerosol were on the order of 0.1 mg m$^{-3}$ and $10^{13}$ m$^{-3}$, respectively.

An interesting feature of the NPA method is that it is capable of making monodisperse and hollow particles (Figures 7.8a). HRTEM imaging revealed that hollow particles had a polycrystalline shell (Figure 7.8b). The hollowness of the core was demonstrated by EDXS. Line scans across hollow particles were conducted and the Ga Kα counts were found to dip in the middle of the particle, indicating a hollow core (Figure 7.8c). These particles were found to form under higher pressures, and at lower powers. The emergence of hollow morphology, and the conditions

![Hollow GaN particles](image)

Figure 7.8. Hollow GaN particles. (a) Hollow particles synthesized at 6 Torr (see Figure 8.7 for an overview) (b) HRTEM image of two superposed hollow particles. (c) EDXS line scan across a hollow particle.
at which these particles form, provide insights into the formation mechanism of GaN NCs in the NPA process (Chapter 8).

XRD analysis showed that all particles synthesized with plasma powers larger than 40 W were crystalline, confirming SAED results. Both XRD and SAED indicate that the product was a mixture of cubic and hexagonal GaN (Figures 7.9). No presence of metallic or oxidized Ga was detected. Rietveld refinement and quantitative phase analysis suggested that the phase composition was from 50 to 66% hexagonal, balance cubic [GaN]. Using the Scherrer equation on the diffraction peaks of the black curve in Figure 7.9, which corresponds to the sample with black markers in Figure 7.7e, yields a crystallite size of 8 nm. For that sample comprised of small particles, the crystallite size from XRD was very close to the average NC diameter measured by TEM, indicating the particles were single crystals. However, the green curve in Figure 7.9 that corresponds to the sample with green markers in Figure 7.7e, yields a crystallite size of 5 to 9 nm.

Figure 7.9. XRD spectra of GaN NCs. The color coding is the same as in Figure 7.7. “h” stands for the hexagonal phase and “c” stands for the cubic phase.
depending on the peak used for analysis, which is significantly smaller than the diameter measured by TEM. Therefore, for these larger sizes, the NCs were polycrystalline. In general, NCs larger than 15 nm were found to be polycrystalline, and smaller NCs were found to have a single crystallographic orientation.

7.6. GaN NCs – Stoichiometry

ATR-FTIR spectroscopy (Figure 7.10) showed that the surface of the GaN NCs were populated by physisorbed water and N-H bonds. A sharp peak for the phonons of GaN at 580 cm\(^{-1}\) is consistent with the high level of crystallinity revealed by SAED and XRD. The feint shoulder at 715 cm\(^{-1}\) next to the phonon peak is associated with the Ga-O-Ga center\(^{236}\), likely coming from a native surface oxide. No presence of the features belonging to nitrogen deficiencies or antisite defects were found\(^{237}\). It was reported that over the course of a year under ambient atmosphere,

![Figure 7.10. Evolution of FTIR spectra of GaN NCs with time. The spectrum corresponding to as synthesized GaN powder and the spectrum corresponding to the same sample stored under ambient conditions for 2 months are given.](image)

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GaN NCs transform into gallium oxy hydroxide (GaOOH)\textsuperscript{238}. For our samples, after two months, the transformation to GaOOH became visible in FTIR spectra due to the appearance of a doublet at 947 and 1014 cm\textsuperscript{-1} that corresponds to Ga-OH\textsuperscript{239}.

The Ga:N ratio of the NCs was found to be close to 1:1. SEM-EDXS and TGA gave similar results, and XPS qualitatively verified the measurements. None of the listed characterization techniques are ideal for analyzing GaN nanopowders, thus all three were employed to reach a reliable conclusion. EDXS was conducted and multiple measurements on multiple samples indicated a Ga:N ratio of 1.0±0.2 (Figure 7.11). Although the measured stoichiometry had the desired value, the spread in measurements was relatively large. The relatively large spread can be due to the common errors in the quantification of light elements such as nitrogen in EDXS, or from the rough texture of the powder. TGA was used as a second method to confirm EDXS results. It was assumed that all particles were essentially comprised of Ga and N with arbitrary Ga:N ratio, and the amount of the initially present oxide on the surface was omitted. It was further assumed

![Figure 7.11](image.jpg)

**Figure 7.11. EDXS on GaN powder in the SEM.** A sample EDXS spectrum is given. The inset shows the flattened surface of fine and uniform GaN powder used for acquiring the spectrum.
that all Ga atoms end up forming Ga$_2$O$_3$. Thus, the percent change in sample weight allowed the calculation of the Ga:N ratio. Results indicated that the stoichiometry of powders was very close to 1:1 [GaN].

XPS analysis qualitatively confirmed that the product was GaN and no free Ga was present. In principle, XPS can be quantitative by either using the empirical elemental sensitivity factors or by using a reference material. However, quantitative analysis was hindered by the overlap of the Ga Auger transitions ($\text{L}_2\text{M}_{45}\text{M}_{45}$ and $\text{L}_3\text{M}_{45}\text{M}_{45}$) with the N 1s transition, which is inevitable when an Al Kα x-ray source is used. Furthermore, using a reference material, in this case single crystal (SC) GaN, was found to have its own difficulties. Sputtering was required to expose the bulk of the reference material and to detect the N 1s transition, and thus the well-known preferential sputtering of N in nitrides$^{240,241}$ made quantification unreliable. Instead of having a quantitative analysis, the XPS spectra of GaN NCs were compared qualitatively with the spectrum of the SC. The SC was sputtered for 1 minute under 2 keV Ar$^+$ beam. The survey spectra of the NCs and of the SC looked very similar (Figure 7.12a) and both had peaks corresponding to Ga and N. The only difference was the O and C detected in the NCs. Oxygen 1s signal was expected to be due to the surface oxide, and C 1s signal was due to adventitious carbon. These features were always present on the NCs even when sputtering was employed because the surface of some of the NCs was always exposed during analysis. Higher resolution spectra gathered from the NCs and SC of the Ga 3d and N 1s transitions were also found to be similar. The Ga 3d peak for NCs was initially positioned at 18.8 eV due possibly to some sub-oxide or oxynitride on the surface (Figure 7.12b). Upon sputtering, the peak appeared corresponding to GaN at 17.3 eV, which was also seen in the GaN SC (Figure 7.12c). Similar correspondence between the NCs and SC were found for the N 1s and Ga Auger peaks between 388-400 eV. Sputtering of NCs lead to an increase in the intensity
Figure 7.12. XPS results on GaN NCs and GaN reference single crystal (SC). (a) Survey spectra. (b,c) Ga 3d peaks of the NCs and the SC, respectively. Sputtering durations were incrementally increased by 1 minute. (d,e) N 1s and Ga Auger peaks of the NCs and the SC. Sputtering durations were similar to as in (b,c).
of Ga Auger peaks, especially at 392 eV (Figure 7.12d), indicating preferential sputtering of N. The same shoulder was also observed for the SC (Figure 7.12e).

Complimentary to the aforementioned evaluations of stoichiometry, the color of the synthesized powder can be used to assess the quality of the NCs in terms of Ga:N ratio, defects, and oxygen impurities. Dark brown color in GaN has been associated with defects, oxygen impurities and N deficiency. Since GaN single crystals are completely transparent in the visible region of the spectrum owing to their large band gap, perfectly stoichiometric powder is expected to be white due to scattering. Most of the samples characterized in this study either had a pale-yellow color or they were white (Figure 7.13), indicating that the stoichiometry of the NCs was close to 1:1 and defect densities were low.

7.7. GaN NCs – Optical Properties

Explicit control on the particle size distributions of high quality GaN NCs allows the NPA method to provide control over optical properties. Absorption and PL spectroscopy performed on
colloidal suspensions of GaN NCs was used to investigate the effect of particle size on optical properties. Since no organic ligands were used in this work to aid dispersion, the GaN NCs tended to form large agglomerates in solution. To prevent scattering from the agglomerates as much as possible, NCs were suspended in DMSO during absorption spectroscopy. DMSO was selected due to its unique nanoparticle solvation capability, as evidenced by much smaller agglomerate size (~200 nm z-average size as measured by DLS) in comparison to very large agglomerates formed in methanol (500-1000 nm). However, methanol was employed during PL measurements due to its low absorption coefficient at UV excitation wavelengths. UV-VIS absorption spectroscopy indicated that the smallest GaN particles exhibited quantum confined states (Figure 7.14a). As particle size was made to be smaller, the extent of scattering was decreased, and an excitonic absorption peak emerged at 4.45 eV. It is interesting that this excitonic state is approximately 1 eV more energetic than the band gap.

PL measurements indicated band-gap emission from particles that were larger than 8 nm (Figure 7.14b). When excited with 5.9 eV light, the emission profile includes a peak at 3.13 eV.

**Figure 7.14. Optical properties of GaN NCs I – Absorption and photoluminescence.** (a) UV-VIS absorption spectra of NCs obtained at different residence times \( \tau \). (b) PL spectra of NCs with different mean sizes obtained at different residence times. An excitation wavelength of 5.9 eV was used.
and another peak at 3.26 eV. With some Stokes shift, these peaks likely correspond to band gap emission from cubic and hexagonal phases, respectively. As particle size decreased below 7 nm, the PL peak abruptly shifted to 4.06 eV. The PL peak further blue-shifted as the particles were made even smaller, demonstrating behavior consistent with quantum confinement. Apart from the long tail of the near-band gap emission and the weak emission at 2.65 eV for larger particles, which was likely present due to a shallow donor-acceptor pair caused by defects on the surface of the particles, additional defect emissions, such as the common yellow PL seen in GaN thin films, were absent. Over the course of two months, particles that exhibited near-band gap PL were found to be relatively stable. The emission intensity decreased approximately 20% each month and the 3.26 eV emission corresponding to hexagonal GaN became relatively stronger in comparison to the 3.13 eV emission from cubic GaN as time proceeded. This result might indicate that the cubic phase, which is metastable, might be deteriorating faster than the thermodynamically stable hexagonal phase in methanol.

The optical properties of GaN NCs appear to depend significantly on the solvent that they are dispersed in. The particles given in Figure 7.15a were dispersed in methanol (MeOH) and DMSO. Half of these particles have sizes that were larger than the exciton Bohr diameter, thus their steady-state extinction spectra displayed excitonic absorption peaks in both solvents. In DMSO, the lowest energy excitonic state that was visible had the energy of 4.45 eV (Figure 7.15b, also present in Figure 7.14a). The visibility of the peak associated with this state was independent of the concentration of the dispersion. A methanol dispersion exhibited strong scattering, due to large agglomerates as verified by DLS, but when the dispersion is diluted enough, two excitonic absorption peaks, one at 4.45 eV and one at 3.77 eV, were found to appear. The lower energy state
Figure 7.15. Optical properties of GaN NCs II – Effects of the solvent. (a) Size distribution of the GaN NCs studied in panels (b) and (c). The dotted curve is the distribution corrected for sampling bias [GaN]. The scale bar is 20 nm in width. (b) Extinction spectrum of the GaN NCs given in panel (a) in different solvents and with different concentrations. Dilute: ~0.1 mg/mL, concentrated: ~1 mg/mL. Solid vertical bars label the positions of excitonic peaks. (c) Extinction and PL spectra of a diluted sample in MeOH. PL peak are given as a function of excitation wavelength.

was not visible in the DMSO dispersion, likely due to the extensive passivation of this state. The passivation of the lower energy state caused the higher energy state to be densely populated in DMSO. A zoomed-in version of the extinction spectrum for the dilute methanol dispersion is shown in Figure 7.15 c, along with the PL emission as a function of excitation energy. As the excitation energy was decreased from 5.1 eV, emission shifted from the second excitonic state to
the first excitonic state at lower energy. At an excitation energy of 4.1 eV, the emission was quantum confined, however the rate of change in the bandgap with respect to particle size across the sizes investigated was very slow (Figure 7.14b). This result is in agreement with \textit{ab initio} studies of the electronic structure of GaN quantum dots\textsuperscript{246}. Therefore, the abrupt shift in Figure 7.14b is likely due to a small amount of quantum confinement combined with a significantly higher quantum yield for emission from the second excitonic energy state.

Like the absorption spectra, PL spectra also depended on the concentration of the dispersion. Concentrated dispersions (~1 mg/mL, turbid solution) of the same GaN NC sample given in Figure 7.15a were found to display the PL behavior of NCs with large sizes based on the excitation energy of choice (Figure 7.14b), whereas dilute dispersions (~0.1 mg/mL, clear solution) showed quantum-confined PL emission. An example of this observation is shown in Figure 7.16 in the form of excitation-emission contour maps. These maps indicate that the PL of the solvated NCs

![Excitation-emission contour maps](image)

\textbf{Figure 7.16. Optical properties of GaN NCs III – Effects of dispersion concentration.} (a) Dilute sample. (b) Concentrated sample.
depend strongly on the agglomeration state. Different extents of agglomeration may explain the differences in the PL spectra of different ~8 nm NC samples given in Figures 7.14b and 7.15c.

7.8. Demonstration of GaN NC Films

Although the production of bare NCs in NPA presents some difficulties in doing optical measurements in simple NC dispersions due to agglomeration and solvent-dependent surface passivation, these bare NCs are in fact the desired form for films comprised of NCs. The absence of ligands is expected to lead to films with higher electrical conductivity\textsuperscript{39,40}, and these films can be subjected to common post-processing methods for thin films, such as annealing, etching and further packaging. For porous films, supersonic impaction is a capable method of making films out of NCs, right after they have been synthesized\textsuperscript{233}. Porous GaN NC films were prepared, and a cross sectional SEM image of a 900 nm film is presented in Figure 7.17. The film was composed of particles that were relatively large, 35 nm mean diameter, when compared to particles that have previously been used to make NC films by supersonic impact deposition\textsuperscript{233,247}. In films comprised of particles with several tens of nm size, it was found that the film fill fractions were high, despite the low pressure ratios employed. The fill fraction of the film shown in 7.17 was 34\% as measured

![SEM image of a film comprised of GaN NCs.](image)

**Figure 7.17. SEM image of a film comprised of GaN NCs.** The film was porous, with 34\% fill fraction ($\phi$) and 900 nm thickness. Mean particle size was approximately 35 nm.
by XRF, and the pressure ratio during deposition was approximately 4.2. Such NC films are expected to find applications in optoelectronics and photonics.

7.9. Conclusions and Comments

In this chapter, a new gas phase synthesis method for making NCs of compound semiconductors was presented. By sending an elemental aerosol into a reactive plasma, it was shown that the aerosol can be converted into a compound material. The advantages of this new method, termed nonequilibrium plasma aerotaxy (NPA), were displayed by demonstrating the synthesis of pure and bare GaN NCs from Ga aerosols in an Ar/N₂ plasma. The NCs can be collected either as a nanopowder, or as porous films. Produced GaN NCs can be made to be any desired size between 5-45 nm, and size distributions can be made to be narrow. NCs were found to be crystalline, with a mixture of hexagonal and cubic phases, and stoichiometric. Particles larger than 15 nm were observed to be polycrystalline. GaN NCs were photoluminescent with emission ranging from 3.1 to 4.2 eV but characterizing the quantum confinement in solutions of bare GaN NCs appeared to be difficult due to combined effects of agglomeration and preferential passivation of excitonic energy states based on the solvent of choice. Characterization of the PL of porous film samples is expected to be more informative.
Observations on GaN Growth During NPA

In the previous chapter, the characterization of GaN NCs produced by NPA was presented in detail, but no discussion on the growth mechanism was given. This chapter contains all the observations made on the growth of GaN NCs, primarily by using optical emission spectroscopy and electron microscopy. The evidence is consistent with a synthesis mechanism that involves vaporization of the Ga precursor aerosol in the vicinity of the powered RF electrode, followed by reaction of that Ga vapor and remaining Ga particles with reactive N$_2$ species further downstream to nucleate and grow GaN NCs by an aerotaxy process.

8.1. Plasma Characterization

A schematic of the proposed overall mechanism is presented in Figure 8.1. The intense zone was present during GaN synthesis, as in the experiments with Bi aerosols described in Chapter 3, and it acted as the vaporization zone for Ga as well. In this vaporization zone nearby the powered electrode, excited atomic gallium, excited argon, and high-energy excited states of N$_2$ were
observed in the emission spectrum from the plasma, while further downstream, emission from low-energy excited states of N$_2$ molecules was dominant (Figure 8.1).

To infer the growth mechanism from the results of NC size control experiments, one should first know whether the particles sampled on TEM grids actually represent the produced GaN aerosol. Calculations done by using computational fluid mechanics and Lagrangian particle tracking indicated that the size distributions obtained from particles deposited on the TEM grids during synthesis closely represent the actual particle size distributions of the as-produced aerosols.

**Figure 8.1. GaN formation mechanism in the NPA process.** The plots on the top represent the plasma emission collected from the spots shown by red dashed circles. The photograph shows the reactor during GaN synthesis.
[GaN]. The result partially stems from the fact that the size distributions of GaN NCs are usually narrow. However, the Ga precursor aerosol was found to have a significantly larger mean size and a broader size distribution that spanned across more than a decade in size, after correcting for sampling bias (Figure 7.4e). Interestingly, the highly polydispersed precursor aerosol vanished in the plasma, and a GaN aerosol with a much narrower size distribution was obtained in all cases, which is very reminiscent of the experiments with Bi aerosols (Chapter 3). The similarity of the disappearance of the Ga precursor aerosols, and the formation of GaN NCs with narrower size distributions and with smaller mean sizes in the experiments reported in the previous chapter suggest that Ga droplets should shrink down to very small sizes in the plasma, possibly vaporizing completely, before reacting with nitrogen and growing as GaN.

Results from OES suggest that the Ga aerosol vaporizes in the NEP, in a way that is very much similar to the Bi aerosol example (Figure 8.2). With no Ga aerosol present, the Ar/N₂ plasma produced feint Ar I emission and emission from the second positive system of molecular N₂ (C³Π_u - B³Π_g)₂₄⁸ in the vicinity of the powered electrode (Figures 8.2b and Figure 7.5), due to resonant energy transfer between Ar metastables and N₂. Downstream of the powered electrode, emission was primarily dominated by the first positive system of molecular N₂ emission (B³Π_g - A³Π_u⁺)₂₄⁸, which could be seen as a bright orange glow by naked eye (Figure 7.5). When Ga aerosol was sent into the plasma, bright blue Ga I emission was observed just downstream of the powered electrode, along with a more intense Ar I emission (Figures 8.1, 8.2a and 8.2c). Adding Ga quenched the Ar metastables, and the emission from the second positive system of N₂ was of significantly lesser intensity downstream of the powered electrode. However, emission from the first positive system was still quite distinct, likely caused by lower excitation energies of this system and consequent direct electron excitation. Ga I emission was present throughout the
Figure 8.2. Optical emission spectroscopy on the Ar/N₂ plasma with and without the presence of the Ga aerosol. (a) Plasma with Ga aerosol at 80 W and at 4.2 Torr pressure. Ar:N₂ = 25, and total flow rate was 520 sccm. Ga feed rate was 1 mg/min. (b) Emission spectra as a function of axial position when there was no Ga aerosol flow into the plasma. The axial position at 0 cm corresponds to the plane that splits the powered electrode in half. (c) Emission spectra as a function of axial position for the case pictured in (a). Plasma downstream of the powered electrode, which is in contrast to what was observed with Bi aerosols in Ar plasma (Figure 3.10).

It should be mentioned that the background temperatures measured with an FDP inserted at a position 1.5 cm downstream of the powered electrode (<400 K) were much lower than the temperatures necessary to vaporize the Ga aerosol [GaN]. When compared to the results presented in Chapter 5 (Figure 5.7), the decrease in gas temperature despite using high plasma power was due to the fans that cooled the reactor. Therefore, the vaporization mechanism is non-thermal in nature, and it is expected to occur primarily due to ion and electron bombardment. An unexpected aspect of the Ga I and N₂ emission was that these features were found to fluctuate with a period on the order of minutes (Figure 8.3). Although the reason for this effect is unidentified, it could have been caused by particle trapping in the plasma (vide infra), which was previously shown to

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α In the rest of this dissertation, given mass flow rates take the overall filter mass collection efficiency, ~50%, into account.
Figure 8.3. Fluctuations in emission lines. The data was collected during powder collection downstream of the powered electrode (4 cm position in Figure 8.2). The decrease in the intensity of Ga I emission is due to the formation of a yellowish film on the tube walls. The film, likely a form of nonstoichiometric GaN, absorbs the Ga I emission but it is mostly transparent to the N I emission. The fluctuations were observed in all experiments, although their periods differed slightly. Parameters used during recording of this data were: $p = 4.2$ Torr, $\tau = 22$ ms, Ar:N$_2$ = 25, $\dot{m}_{Ga} = 1$ mg/min.

follow periodic trends on similar time scales\textsuperscript{249}.

In Chapter 5, double Langmuir probe measurements in Ar plasma indicated a higher ion density inside and nearby the powered electrode, which is expected to cause higher particle temperatures and vaporization rates according to calculations (Chapter 6). In the case of the Ar/N$_2$ plasma employed in this study, ion densities were measured 2 cm downstream of the powered electrode. At this location, the ion density of the pristine plasma with no Ga precursor aerosol was found to be $7.21 \times 10^{17}$ m$^{-3}$ at 4.2 Torr. The ion density inside the powered electrode is expected to be 2 to 3 times larger than this measured ion density. In the presence of an aerosol and metal vapor, common expectation is a decrease in electron temperature and an increase in ion density\textsuperscript{163,250}. With the precursor aerosol being sent into the plasma, double Langmuir probe measurements were done nearby the zone with intense bright blue Ga I emission. In accord with
the expectations, electron temperature dropped from 2.74 eV to 2.30 eV, and ion density increased to 8.3 x10^{17} m^{-3}. A major problem encountered while doing Langmuir probe measurements was contamination of the probe tips. During NC synthesis, probes were coated with particles (Figure 8.4a and 8.4b), which partially formed a dielectric layer. A dielectric layer is known for creating an additional resistance on the probe circuit and erroneously increasing the measured electron temperature due to changes in electron absorption capability of the probe surface. On the contrary, when the coated tips were used to measure the parameters of the pristine plasma in our experiments, an even lower electron temperature, 2.01 eV, was obtained, but ion density of the pristine plasma was recovered. Cleaning the probe tips with a fine sandpaper (1000 grit) allowed us to re-measure similar values for the electron temperature as the pristine plasma without Ga.

Figure 8.4. SEM images of platinum Langmuir probe tips before and after use in Ar/N\textsubscript{2} plasma during GaN synthesis\textsuperscript{251}. (a) A clean tip before use. (b) A tip used during synthesis. (c) A tip cleaned with fine sandpaper after being used during synthesis. The scale bars are 200 μm in width.
However, a higher value for the ion density was measured after cleaning the tips, likely due to an increase in surface area (Figure 8.4c). A summary of Langmuir probe measurements is given in Table 8.1. Although measurements provided some insight, it is clear that the use of a double Langmuir probe is hindered by contamination of the tips during NPA. Therefore, either active cleaning of the probe tips by sputtering or other diagnostic methods are necessary to assess the effect of the precursor aerosol and metal vapor on the plasma parameters. Since plasma parameters determine particle charge and rates of ion bombardment, the extent of vaporization of the precursor aerosol depends on the parameters of the dusty plasma. Hence, the precursor aerosol and the plasma are expected to be coupled.

A qualitative observation was made on the extent of vaporization of the precursor aerosol. It was observed that the zone emitting bright blue Ga I emission became longer when applied power was increased (Figure 8.5). As power was increased, yield decreased due to more Ga vapor being lost to the walls just nearby the powered electrode. At low powers, however, Ga did not vaporize as much. Moreover, at low powers the N2 glow was weaker, and the reaction happening downstream was incomplete (vide infra). Therefore, an optimum intermediate power, e.g. 80 W, was required to obtain both acceptable yield and good-quality GaN NCs.

The majority of the reaction between Ga clusters, Ga vapor and excited N2 molecules is hypothesized to occur downstream of the powered electrode. That hypothesis is supported by the

<table>
<thead>
<tr>
<th>Fresh tips, no aerosol</th>
<th>$k_B T_e$ (eV)</th>
<th>$n_i \times 10^{18}$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ Ga aerosol</td>
<td>2.74 ± 0.07</td>
<td>1.78 ± 0.02</td>
</tr>
<tr>
<td>Coated tips, no aerosol</td>
<td>2.30 ± 0.02</td>
<td>2.05 ± 0.12</td>
</tr>
<tr>
<td>Tips cleaned with fine sandpaper</td>
<td>2.01 ± 0.03</td>
<td>1.79 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2.69 ± 0.06</td>
<td>2.28 ± 0.01</td>
</tr>
</tbody>
</table>
Figure 8.5. Expansion of the blue vaporization zone with increasing power. Photos were taken when the following parameters were used: \( p = 4.2 \) Torr, \( \tau = 22 \) ms, Ar:N\(_2\) = 25, \( \dot{m}_{\text{Ga}} = 1 \) mg/min. A similar expansion of the vaporization zone was observed when pressure was decreased from 4.2 Torr to 2 Torr.

The presence of both Ga I emission and molecular N\(_2\) emission in that region (Figure 8.2). Therefore, the Ga-vapor rich plasma downstream of the powered electrode, in which excited nitrogen species were also present, is considered as the reaction zone and the length of that plasma was used to estimate the residence times reported in the second half of this dissertation. The Ga I emission was likely coming from either a minute quantity of Ga aerosol that was still vaporizing, or from newly formed GaN. The increase in size with longer residence time suggests that some GaN particles disappeared throughout the reactor and growth of larger particles was more favorable than smaller particles. While the mechanism of this selection is unclear, it could be due a portion of particles having a higher temperature due to charge fluctuations or some of them being smaller in size as discussed in Chapter 6, or due to the radial profile of ion density, which has a maximum at the center of the tube.
8.2. Effects of Operating Parameters on Particle Size and Morphology

Reactor pressure was found to significantly affect the particle size when it was set to values higher or lower than the ones given on Figure 7.7f. At 2 Torr, the mean particle size was found to be approximately 36 nm (Table 8.2). Doubling the residence time did not change the mean particle size, but as can be inferred from the decreasing values of $\sigma_g$, size focusing was observed. Mass yields were noticeably lower at lower pressure. At a higher pressure of 6 Torr, growth was slower and the final particle sizes were smaller (cf Figure 7.7f), but size focusing occurred faster. These results suggest that there might be an equilibrium particle size, and it is reached rapidly at lower pressure, hence at higher ion density (Figure 5.4b). Furthermore, it is possible that size focusing depends on solid-state kinetics rather than aerosol dynamics, and it occurs on a time scale and parameters that are different than the ones that control growth. A similar observation is given in Chapter 10.

Table 8.2. Effect of pressure on the parameters of particle size distribution. $\dot{P}_{\text{set}} = 80$ W, Ar:N$_2$ = 25, $m_{\text{Ga}} = 0.6$ mg/min.

<table>
<thead>
<tr>
<th>$p$ / Torr</th>
<th>$\tau$ / ms</th>
<th>$&lt;d_p&gt;$ / nm</th>
<th>$\sigma_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Torr</td>
<td>21</td>
<td>35.7</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>36.4</td>
<td>1.15</td>
</tr>
<tr>
<td>6 Torr</td>
<td>32</td>
<td>9.4 ± 0.2</td>
<td>1.405 ± 0.065</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>22.9</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Limited data obtained at different Ar/N$_2$ feed ratios show that particle size depends on the mole fraction of N$_2$, albeit slightly. Two examples given in Figure 8.6a and 8.6b show that at a higher Ar:N$_2$ ratio (less N$_2$) the particle size decreases, likely due to the production of a lesser amount of reactive nitrogen species. At a low Ar:N$_2$ ratio, a similar trend is observed, and the growth rate appears to be slower as well (Figure 8.6c). Again, this is likely because of the reduced
Figure 8.6. Effect of Ar:N\textsubscript{2} ratio on particle size. Size distributions with lower N\textsubscript{2} mole fraction at (a) 2 Torr (τ = 71 ms) and at (b) 4.2 Torr (τ = 112 ms). (c) Effect of increasing the residence time at a lower Ar:N\textsubscript{2} ratio. Ar:N\textsubscript{2} = 5 and p = 4.2 Torr. The inset shows the hollow particles formed at long residence times. The scale bar corresponds to 50 nm. For all cases shown: \( P_{\text{set}} = 80 \) W, \( \dot{m}_{\text{Ga}} = 0.6 \) mg/min.

amounts of reactive species, even though the N\textsubscript{2} mole fraction was high. In support of this hypothesis, it was shown that in a radiofrequency Ar/N\textsubscript{2} plasma the concentration of excited nitrogen species reach a maximum as the N\textsubscript{2} mole fraction is increased\textsuperscript{255}. Above a critical mole fraction of nitrogen in the feed, concentration of excited nitrogen was found to decrease\textsuperscript{255}. At a ratio of Ar:N\textsubscript{2} = 5 (Figure 8.6c), particles were solid at low residence times (not shown), but when the residence time was increased to approximately 100 ms, particles transformed into hollow spheres (Figure 8.6c inset).
Figure 8.7. Effect of background gas temperature on particle size and morphology. TEM images obtained for samples synthesized (a) with fans on and (b) with fans off. Wall temperature, $T_w$, was measured nearby the powered electrode with an infrared camera, as described in Chapter 5. Following conditions were employed: $P_{set} = 80$ W, $p = 4.2$ Torr, $\tau = 22$ ms, Ar:N$_2 = 25$, $m_{Ga} = 1.2$ mg/min.

Background gas temperature was found to change the particle shape. Turning the fans off lead to an increase in gas temperature by approximately 300 K. At a higher gas temperature, particles were irregularly shaped, mostly in the shape of a triangle, and were highly faceted when
compared to particles synthesized at a lower gas temperature (Figures 8.7a and 8.7b). Furthermore, they were found to have a wider size distribution (Figure 8.7c).

### 8.3. Formation of Hollow Particles

Formation of hollow particles suggests that the growth mechanism of the GaN NCs has to involve the condensation of Ga and surface reaction of excited N\textsubscript{2} species on Ga droplets and GaN clusters. At lower ion densities, i.e. low power and/or higher pressure (Figure 5.4b), the Ga aerosol is expected to vaporize less. TEM images of particles collected at 20 W applied power support this expectation. Some large Ga droplets were seen to pass through the plasma relatively unchanged (Figure 8.8a). Since the N\textsubscript{2} glow was weak at 20 W power, the reaction was incomplete. SAED indicated that the GaN phase nucleated as small crystallites only (Figure 8.8b). Some of these crystallites were found to form on the shell of hollow particles (Figure 8.8.c).

![Figure 8.8. Hollow particles obtained at low power (20W).](image)

(a) Low magnification TEM image of small and hollow particles, together with large and solid particles. Large spherical particles are unreacted Ga. (b) SAED pattern corresponding to the sample shown in (a). The hazy rings indicate the presence of very small GaN crystallites (e.g. on the shell of hollow particles) and amorphous Ga. (c) HRTEM image showing a string of hollow particles. Following conditions were used: \( \dot{P}_{set} = 20 \text{ W} \), \( p = 4.2 \text{ Torr} \), \( \tau = 22 \text{ ms} \), Ar:N\textsubscript{2} = 25, \( \dot{m}_{Ga} = 0.6 \text{ mg/min} \).
There are two major mechanisms that can describe the formation of hollow materials. First is the Kirkendall effect, during which different diffusivities of the components that neighbor an interface lead to the translation of the interface or to the formation of voids in a geometry that has radial symmetry. In the case of GaN NC synthesis, the core of the particle is composed of Ga, and GaN forms on the surface due to reaction with reactive nitrogen species. If the diffusivity of Ga in the GaN layer is greater than that of nitrogen, then the high outward diffusion rate of Ga through the GaN shell eventually causes the formation of a hollow particle when Ga at the core gets depleted. The second mechanism is the opposite of the Kirkendall effect where nitrogen diffuses faster than Ga through the GaN shell. In this case, GaN that forms in the Ga core leads to a radial expansion since the molar specific volume of GaN is 20% larger than that of Ga. Deciding on which mechanism is responsible for the growth of hollow particles requires comparing the diffusivities of Ga and nitrogen in GaN. Since such data is not readily available, determination of the formation mechanism was not possible. However, assuming that the Kirkendall effect was responsible, a schematic that shows the possible steps for hollow particle growth at low applied power is given in Figure 8.9. When power was increased, more hollow particles were formed, and

![Figure 8.9. Formation of hollow particles by the Kirkendall effect.](image)

The figure depicts the growth of a hollow particle from cross-sectional view. Transport of species is shown with colored arrows and italic text.
under some cases hollow particles were found to be highly monodisperse (Figure 8.10). At powers above 20 W, higher ion densities lead to the disappearance of large Ga particles. When growth starts from Ga particles of similar sizes, hollow particles are expected to grow uniformly. As power, or ion density, was increased even further, vaporization became more intense, and growth was likely initiated on very small Ga clusters, which lead to the formation of solid particles due to short diffusion lengths. In summary, solidity is expected to depend on Ar ion density, and the thickness of the shell of a hollow particle is expected to depend on the amount of reactive nitrogen species compared to Ar ion density, due to the competition between GaN growth and vaporization.

Figure 8.10. Monodisperse hollow GaN particles. Particles were synthesized at the following conditions: $\dot{P}_{set} = 80$ W, $p = 6$ Torr, $\tau = 64$ ms, Ar:N$_2$ = 25, $\dot{m}_{Ga} = 0.6$ mg/min. $<d_p> = 23$ nm and $\sigma_p = 1.12$. 

150
8.4. Effect of Tube Diameter on Growth

When the residence time was decreased, GaN NCs with smaller sizes were synthesized, as discussed in the previous chapter (Figures 7.7e and 7.7f). In order to reduce the residence time without increasing gas flow rates, which would require higher pumping rates to keep the pressure constant, tubes with smaller diameters were employed. At the right-most end of Figure 7.7f, longer residence times were experimented on by decreasing the gas flow rate, but the mass flow rate of the aerosols were kept constant. Based on the limited data in Figure 7.7f, the trend in growth indicates that after 100 ms of residence time mean particle size started to saturate. To validate whether there is an equilibrium size with respect to residence time, tubes with inner diameters larger than 16 mm were installed (Figure 8.11a), and residence times were consequently increased.

![Figure 8.11. Tube with 32 mm ID.](image)

(a) The reactor during GaN synthesis at 6 Torr and at 500 W. Line intensities (b) 0.8 cm and (b) 4.5 cm downstream of PWR as a function of power. REF stands for the intensities recorded in the 16 mm ID reactor. The intensities were scaled with respect to path length.
up to a second. In a tube with a larger ID than 16 mm, the power density and field strength in the reactor decreases when compared to a 16 mm ID tube. Therefore, plasma power was set as very high (>300 W) for tubes larger than 16 mm ID. Despite applying high power, it was observed that in a 32 mm ID tube, the line intensities of nitrogen was lower than that of the reactor with 16 mm ID. This observation is represented in Figures 8.11b and 8.11c. While it was possible to match argon line intensities nearby the intense zone at a power of 400 W, matching the line intensities of nitrogen was not possible. Under these circumstances, it is expected that the reactor with 32 mm ID would produce particles that are either nonstoichiometric or hollow.

TEM confirmed that the particles that came out from the 32 mm ID tube were mostly hollow (Figure 8.12a), which supports the arguments presented in the previous section. Since the concentration of reactive N\textsubscript{2} species was low, the shell of the hollow particles were found to be thin. This observation is most likely a manifestation of why N\textsubscript{2} is not preferred as a precursor for nitrogen in large plasma-enhanced vapor deposition chambers. Unless the field is very high, as it likely is in a small diameter tubular reactor, the concentration of reactive nitrogen species is low in a NEP due to the inertness of N\textsubscript{2}. Therefore, NH\textsubscript{3} is usually the precursor of choice in the synthesis of nitrides in the industry\textsuperscript{258}. Alternatively, NH\textsubscript{3} can be simulated by sending both N\textsubscript{2} and H\textsubscript{2} into a plasma. When 1 sccm of H\textsubscript{2} was sent into the reactor, along with 60 sccm Ar and 0.5 sccm N\textsubscript{2}, solid GaN particles were produced (Figure 8.12b). An interesting feature of the GaN particles synthesized with H\textsubscript{2} was that the cubic phase was more pronounced (Figures 8.12c and 8.12d). However, these particles were not as uniform as the NCs produced with smaller tubes. As initially expected from Figure 7.7f, particle size was found to saturate at high residence times. After increasing the residence time by a factor of 10, particle sizes remained usually between 50-70 nm, which supports the likely existence of an equilibrium size in the reactor.
Hydrogen is a known etchant of GaN. During metalorganic vapor phase epitaxy of GaN films at high temperatures (>1200 K), H$_2$ was found to etch the entire film, sometimes even when trimethylgallium was present in the reaction mixture$^{259}$. However, the microscopic rate of etching was found to be dependent on the crystal plane$^{260}$, and H$_2$ was shown to favor the removal of defects, namely dislocations and stacking faults, the most$^{261}$. In contrast to these observations, H$_2$ appears to promote growth in the case of NPA of GaN NCs. This result suggests that GaN NC growth is likely limited by defects that form on the GaN layer at the gas and particle temperatures and reactive species concentrations that arise during the operation of the 32 mm ID reactor. H$_2$
removes the rate-limiting defect sites, and thereby accelerates adsorption and further reaction on the GaN surface at the expense of the hexagonal phase.

Although the experiments with a large reactors did not yield a material with desirable properties, a fascinating phenomenon was observed when aerosol feed rates were increased (~3 mg/min) and gas flow rates were decreased (0.1-0.2 m/s), which leads to a highly concentrated aerosol (130-180 mg/m³ mass concentration.). When the plasma was turned off during synthesis, a ring of composed of particulates was observed to get ejected from a region close to the powered electrode. The ring, which was very similar to a smoke ring, was visible by naked eye (Figure 8.13). The ring flowed with the gas velocity and dispersed slightly in the axial direction as it traveled along the reactor, which indicates that it was composed of particles with moderate diffusivity, likely with a mean size around 100 nm or below. The ring appeared to be highly

![Figure 8.13. Ejection of a GaN dust ring in the 32 mm ID reactor. (a-d) Frames obtained from a 120 fps video, which was recorded during and after the plasma was turned off during GaN synthesis.](image-url)
concentrated, and the color of it was pale yellow, indicating that these particles were most likely GaN. The phenomenon depicted in Figure 8.13 is very similar to the particle trapping phenomena shown in Figure 1.3. A possible reason for the formation of the ring could be electrostatic trapping when the plasma is on, during which the particles align at a position where the plasma potential is maximum. At this position, the force that the particles experience due to the field is balanced by drag, which is expected to be low nearby the tube wall due to low gas velocity.

8.5. Conclusions and Comments

The structure of the Ar/N\textsubscript{2} plasma during NPA of GaN NCs was found to be quite different than that of an Ar plasma with a metallic aerosol in it. Different zones with different speciation were detected, and a wide range of operating parameters, such as plasma power, pressure, residence time, background gas temperature and tube diameter, was found to affect the size and morphology of GaN NCs. In order to elucidate the range of operating parameters that would provide NCs with the desired size distribution and morphology with good yield, the growth mechanism in the NPA process has to be clarified.

On the way to achieving this goal is the characterization of dusty NEP, such as the one used for NPA of GaN NCs. Measuring plasma parameters in a dusty plasma is a challenging but crucial step that needs to be accomplished. With the plasma parameters in hand, the effect of aerosol and metal vapor on plasma properties can be identified, and it might be possible to resolve the structure of the plasma shown in Figure 8.1 in greater depth. The ideal tube diameter, which was shown to change the speciation in the plasma, can be determined based on the measured plasma parameters and species concentrations if plasma characterization is available. Furthermore, predictive models of aerosol dynamics and growth in NEP can be developed. Growth models may need to be
modified to accommodate surface reactions and solid-state transport, which govern the formation of hollow or solid particles depending on the plasma parameters, tube diameter and gas composition.

The dust ring phenomenon observed in the 32 mm ID reactor is probably the first ever report on particle trapping in flow reactors. The mass concentration and the particle size in the dust ring should be measured by means of light scattering and absorption, and the conditions which lead to the formation of the ring should be studied. Particle trapping might also be occurring to some extent in reactors with smaller diameters, and the fluctuations in plasma emission intensity (Figure 8.3) could be related to particle trapping. If the mass concentration of the ring is significantly higher than anywhere else in the reactor, then it means that zone nearby the ring is essentially a backmixing zone. In chemical reaction engineering, such a reactor is a compartmental reactor, and the residence time in such a reactor might not be accurately represented by using the mean residence time of the gas. Controlling the mass in the ring might make way for new approaches in NEP synthesis, during which the particles suspended at a fixed location in NEP can be processed for a time that is significantly longer than the residence time of the gas.
Chapter 9

Extending NPA to Other Nitrides: Synthesis of InN Nanocrystals

NPA was shown to be a flexible method for the synthesis of GaN NCs. With NPA, it was possible to make size-controlled and stoichiometric GaN NCs with adjustable PL in the UV. Size distributions were narrow for particle sizes larger than 10 nm. In this chapter, by extending NPA synthesis to indium nitride (InN), it is further demonstrated that NPA is capable of producing III-V nitride semiconductors with tunable optical properties. InN NCs synthesized by NPA were found to be stoichiometric and crystalline with hexagonal structure. NCs had a blue-shifted absorption edge due to the Burstein-Moss effect, and they were plasmonic in the mid infrared. Plasmon peak position is shown to be tunable across 0.22-0.34 eV (~3650-5600 nm). Carrier densities were estimated to be between $1.6-6.0 \times 10^{20} \text{cm}^{-3}$. 
9.1. Indium Nitride (InN)

InN is a direct band gap semiconductor that belongs to the III-V family. It is one of the least developed semiconducting nitrides, because the methods of synthesizing high-quality InN thin films have only been developed in the last two decades. Thus, some basic information about the semiconductor remains under debate, for example the band gap. In early films synthesized by reactive sputtering, a band gap around 1.9 eV was measured\textsuperscript{262,263}. Later, films synthesized by molecular beam epitaxy demonstrated a much smaller band gap of approximately 0.7 eV\textsuperscript{264–266}. The early value of the band gap was associated with oxygen impurities\textsuperscript{267}, which donate electrons and lead to a partially populated conduction band. Consequently, an increase in the energy of the absorption edge was observed, and that increase was caused by the Burstein-Moss effect. However, the debate on the fundamental band gap of InN is still ongoing, for example arguments have been made that the narrow band gap might be caused by deep traps\textsuperscript{268–270}. The results of this chapter contribute additional evidence to the debate.

From a practical viewpoint, the tunability of the optical band gap and the level of degeneracy makes InN a versatile semiconductor. InN with low amount of defects and impurities has high mobility (~4000-5000 cm\textsuperscript{2}/Vs)\textsuperscript{271,272} and low electron effective mass (~0.1 m\textsubscript{e0}. m\textsubscript{e0} is the electron rest mass)\textsuperscript{267}. Therefore, such a material with a narrow band gap is suitable for detectors in the short-wave infrared\textsuperscript{273}, broad spectrum solar cells, high frequency devices\textsuperscript{274}, terahertz emitters\textsuperscript{275,276} and possibly for high field applications due to the absence of low-valleys in its band structure\textsuperscript{277}. On the other hand, the degenerate material, especially in nanomaterial form, is suitable for plasmonic applications due to its localized surface plasmon resonance across a window covering the mid and far infrared. Adjusting carrier density in InN between 10\textsuperscript{19}-10\textsuperscript{21} cm\textsuperscript{-3} can
yield an alternative to graphene\textsuperscript{278}, phosphorous- and boron-doped silicon NCs\textsuperscript{279}, indium-cadmium oxide\textsuperscript{280} and aluminum-zinc oxide\textsuperscript{281} in mid infrared plasmonic applications, all while providing high mobility and a small band gap.

Early reports on the synthesis of free-standing InN nanomaterials mostly relied on liquid-phase methods, and in those reports, obtaining InN that is photoluminescent in the near infrared (NIR) was the primary goal\textsuperscript{282-286}. Although PL in the NIR was demonstrated to some extent, tuning of optical properties were mostly left unexplored, largely due to then developing synthesis methods of colloidal nitrides. More recently, researchers advanced colloidal methods of InN synthesis and focused more on the degenerate material\textsuperscript{287,288}. Plasmon resonances from colloidal InN nanocrystals were reported in the range between 0.35-0.4 eV (~3000-3600 nm) and the tuning the position of the plasmon peak was accomplished by oxidizing the surface of the NCs via reversible redox reactions\textsuperscript{287,289}. On the other hand, a recent study on the gas-phase synthesis of InN nanocrystals (NC) reported adjustable plasmon resonances across a wider range, between 0.27-0.49 eV (~2500-4600 nm)\textsuperscript{290}. Authors of that study have utilized a high power pulsed low temperature plasma in a hollow cathode configuration. Compared to this setup, the NPA system is completely built from off-the-shelf vacuum parts, its plasma reactor is much simpler to modify and characterize, and it employs only rough vacuum, thereby reducing pumping requirements.

\section*{9.2. Synthesis of InN NCs}

The same NPA setup used for the synthesis of GaN particles (Chapter 7) was employed to make InN NCs. Approximately 1 gram of indium (99.999\%, Sigma Aldrich) was placed in the hot-filament evaporator to generate in the indium precursor aerosol. The indium vapor generated above the hot filament was swept with Ar with a flowrate of 500 sccm. The temperature of the
indium melt was usually set between 1225 and 1275 K, lower than the temperatures employed with gallium since indium is more volatile\textsuperscript{119}. At these temperatures, the evaporator produces approximately 0.6 mg/min flow of indium aerosol. This mass flow rate corresponds to aerosol mass and primary particle number concentrations on the order of $1 \text{ mg m}^{-3}$ and $10^{14} \text{ m}^{-3}$, respectively. N\textsubscript{2} flow was varied between 5-50 sccm. The inner diameter of the tube was 16 mm. Pressure was kept at 4.2 Torr. The reactor was cooled by two fans, and the wall temperature of the reactor did not exceed 400 K. The same methods and instruments used for the characterization of GaN NCs were employed for InN NCs.

9.3. InN NCs – Size, Crystallinity and Stoichiometry

Sending the indium precursor aerosol into the Ar/N\textsubscript{2} plasma led to the formation of free-standing and crystalline InN NCs (Figure 9.1). The precursor aerosol was found to be composed of highly polydisperse spherical particles as can be seen in Figure 9.1a and Figure 9.1c, with a mean size of 7.2 nm. SAED indicated that these particles were mostly amorphous (not shown). In the Ar/N\textsubscript{2} plasma, this precursor aerosol was transformed into crystalline particles with plate and rod-like morphology (Figure 9.1b). SAED patterns corresponded to those of hexagonal InN \textit{(vide infra)}. Although the particles were of irregular shape, the size distribution acquired from TEM images was narrower than that of the precursor aerosol, and the particles had a larger mean size of 12.5 nm when the residence time was set at approximately 22 ms.

In the NPA of GaN NCs, it was shown that residence time can be adjusted to control particle size. Increasing residence time leads to larger particles, and this trend applies to InN as well. When the residence time was doubled, particle size was found to increase approximately by 2
Figure 9.1. TEM images and size distributions of InN NCs. (a) Indium aerosol. (b,c) InN aerosols produced at 50 W power and at different residence times. Ar:N$_2$ ratio was 25 (20 sccm and 10 sccm N$_2$ flow respectively). (c) Size distributions. Dots represent the distributions measured from the TEM images and solid lines are lognormal fits to the measured distribution. Dotted curves are the fits corrected for sampling bias [GaN].

In the previous chapter, it was shown that the Ga aerosol vaporizes during the NPA process, and this vaporization step is the crucial step for the subsequent formation of the nitride particles. In the case of InN, a similar mechanism was observed to be occurring in the plasma. Inside the region covered by the powered ring electrode and downstream of it, the precursor aerosol
Figure 9.2. Vaporization of the In precursor aerosol and optical emission spectroscopy. (a) A digital image providing a partial view of the tubular flow-through plasma reactor during the synthesis of InN NCs. The emission from the region indicated by a white dotted circle was acquired with a miniature spectrometer calibrated for relative irradiance. In order to prevent the interference of the wall film with plasma emission (Figure 9.3), a clean tube was used, and the digital image was acquired right after the plasma was ignited. (b) Acquired optical emission spectrum. In I emission results from the vaporization of the precursor aerosol. At wavelengths longer than 500 nm, the emission from the plasma is dominated by N$_2^*$ emission.

vaporized, as observed via OES. Emission from neutral indium (In I), visible as a blue glow, emerged when the plasma was on (Figure 9.2a).

The growth mechanism of InN during NPA appeared to be very much similar to that of GaN. In I emission blends with the emission from atomic and molecular nitrogen species downstream of the powered electrode (Figure 9.2b). This zone, where both excited species are present, is the reaction zone of the NPA process (Chapter 8), which is mediated by the nonequilibrium vaporization of the indium precursor aerosol inside the powered electrode. In the reaction zone, growth and vaporization happens simultaneously. The indium vapor can lead to nucleation of indium clusters and these clusters can react with excited nitrogen species. Alternatively, indium vapor condenses either on clusters that are already available, or on the walls of the reactor, as evidenced by the formation of a partially metallic and partially reddish black film in all cases reported in this study (Figure 9.3).
Figure 9.3. The reactor during InN NC synthesis at 60 W power. The wall film downstream of the powered electrode (PWR), which is likely a form of InN since it is reddish black, glows red during synthesis. The red glow is not completely due to a filtering effect. When excited with a LED that emits at 3.1 eV (400 nm), the film exhibited red PL at 1.75 eV.

Plasma power is also an important parameter for the NPA synthesis of InN NCs. Ion density increases proportionally with increasing power (Chapter 5). Higher ion density leads to higher particle temperatures in the plasma (Chapter 6), and accordingly, higher vaporization rates are achieved at higher particle temperatures. Increasing the plasma power from 50 to 80 W, the power used for synthesizing GaN NCs, resulted in very high vaporization rates, and a very low yield. On the other hand, reducing power to 35 W resulted in a highly conductive film that slowly deposited on the wall and eventually caused a short circuit that significantly dimmed the plasma, thereby limiting experimentation at low power. In the short-circuited plasma at 35 W applied power, ion density decreased significantly since coupled power was lower than its value at the beginning of the experiment. Interestingly, the aerosol that came out from the short-circuited reactor contained hollow particles (not shown). This observation indicates that the formation of hollow InN NCs follow similar trends when compared to hollow GaN NCs, and the growth mechanism in NPA might be general for III-V nitrides. In most of the cases reported in this chapter, power was maintained in the range 50-60 W, which resulted in solid particles. The production rate of InN
NCs was approximately 10 mg/hr. In all cases explored, InN NCs were in the form of a black ultrafine powder.

InN NCs had hexagonal crystal structure as determined by XRD (Figure 9.4). The peak positions were in accord with hexagonal InN and no presence of metallic indium was detected. The only visible impurity in the spectra was the shoulder at $2\theta = 35.48^\circ$, which corresponded to In$_2$O$_3$. This oxide peak is possibly due to a native oxide layer formed when the particles were exposed to air after their extraction from the NPA setup. An interesting detail on the XRD data is the mismatch of the peak intensities obtained by XRD with that of hexagonal InN. A likely reason for this mismatch is preferred orientation effects within the powder during XRD measurements. This hypothesis can be supported by using the SAED patterns and converting the intensities of the Debye-Scherrer rings to conventional Cu Kα XRD spectra. The collection of InN particles on the TEM grid happens primarily via diffusion due to the small size of the particles and due to low

![XRD spectrum of InN NCs](image)

**Figure 9.4. XRD spectrum of InN NCs.** NCs were synthesized at 50 W power. Ar:N$_2$ ratio was 25 (20 sccm N$_2$ flow).
pressure [GaN]. Therefore, particles are expected to land randomly on the grid and the line intensities in the SAED patterns should be free of preferential orientation effects. Indeed, conversion of the SAED data (Figure 9.5) produced an XRD spectrum very close to that of hexagonal InN. Minor discrepancies can be attributed to the nonuniform angular distribution of line intensities due to speckles in the SAED image. Hence, preferred orientation during XRD measurements can be associated with the non-uniform, plate and rod-like particle shape observed during TEM. The crystallite sizes calculated by using the Scherrer equation on different XRD peaks of InN NCs were 7-10 nm. Given the nonuniformity of the particle shape, these crystallite sizes indicate that particles were predominantly single crystals of InN.

**Figure 9.5. Selective area electron diffraction and conversion on InN NCs.** (a) Overview TEM image used for obtaining the SAED pattern. (b) Obtained SAED pattern. Intensity data was extracted along the red line. (c) Raw intensity data across the red line in (b). The baseline due to scattering is shown by the red curve. (d) Baseline subtracted SAED data converted into a conventional Cu Kα XRD spectrum.
Figure 9.6. EDXS of InN NCs. In:N ratio in the NCs as a function of N$_2$ flow rate is given at 50 W power.

EDXS measurements showed that at 50 W plasma power, the stoichiometry of the NCs was close to 1:1 across the range of N$_2$ flow rates investigated. Figure 9.6 shows the In:N ratio obtained at different Ar:N$_2$ ratios by doing EDXS in SEM on zoomed out images of softly flattened InN powder, imaging a large ensemble of particles. Along with XRD patterns, which showed no evidence of metallic indium, EDXS results indicate that the synthesized InN NCs had near 1:1 stoichiometry when N$_2$ flow rate was set at 10 sccm or higher.

9.4. InN NCs – Optical Properties

Measurements of IR absorption of InN NCS revealed three main features: A doublet in the 58-70 meV range, another doublet within 160-200 meV, and a broad peak spanning across a window from 130 to 500 meV, which was the highest energy detectable by the spectrometer (Figure 9.7). The first doublet corresponds to the longitudinal (phonon-plasmon coupled) and transverse optical phonons of InN$^{291-293}$. The location and width of the peaks comprising the doublet were found to
Figure 9.7. Full range ATR-FTIR absorbance spectrum of InN NCs. InN NCs were synthesized at 50 W power with 20 sccm N₂ flow. The kink is shown by (*) was unidentified. It was verified that the kink was not an artifact stemming from the ATR crystal, since the feature was still observed at the same position (257 meV) when diamond was used instead of germanium.

be shifted by few meV. In previous reports, it was argued that such shifts could be due to changes in free carrier density (vide infra), defect density and stress. In addition to these factors, low signal-to-noise ratio of the FTIR spectrometer in that energy range might be responsible for such shifts in our case. The second doublet is due to nitrous groups on the surface. It was shown that the native oxide of InN is an oxynitride, and during its formation, the In:N ratio was found to be undisturbed. These groups can be associated with an oxynitride layer on the bare InN NCs formed due air exposure. The final feature, which is the broad peak with a full-width at half maximum (FWHM) of 150-300 meV, is assigned to collective oscillations of the free carriers, i.e. localized surface plasmons. This is an indication that as with most forms of InN, the NCs synthesized by NPA were also degenerate.
Figure 9.8. Plasmons in InN NCs. Normalized IR absorption spectra of InN NCs synthesized at 50 W with different N$_2$ flow rates. N$_2$ flow was changed from 20 to 50 sccm in steps of 10 sccm.

The position of the plasmon peak can be tuned by changing N$_2$ flow rate. Increasing N$_2$ flow rate from 20 sccm to 50 sccm in steps of 10 sccm shifted the plasmon peak position from 0.325 eV to 0.225 eV (~3800-5500 nm, Figure 9.8). This shift and its connection with carrier density can be analyzed by using the classical Drude-Lorentz model$^{297}$. At plasmon resonance, the simple Drude-Lorentz model can be rearranged to express the plasmon frequency explicitly as

$$\omega_{sp} = \sqrt{\frac{\omega_p^2}{\varepsilon_\infty + 2\varepsilon_m} - \gamma^2},$$

(9.1)

where $\omega_{sp}$ is the plasmon peak frequency, $\omega_p$ is the plasma frequency, $\varepsilon_\infty$ is the high frequency dielectric constant of the NCs, $\varepsilon_m$ is the dielectric constant of the surrounding medium and $\gamma$ is the scattering frequency. The plasma frequency is defined as

$$\omega_p = \sqrt{\frac{N_e e^2}{\varepsilon_0 m_e}}.$$

(9.2)
where \( N_e \) is the majority carrier density, \( e \) is unit charge, \( \varepsilon_0 \) is permittivity of free space and \( m_e^* \) is the effective mass of majority charge carriers, which are electrons in unintentionally doped InN. By approximating the scattering frequency as the FWHM of the plasmon peak, equations 9.1 and 9.2 can be used to estimate \( N_e \). However, one needs to know the electron effective mass.

Effective mass of the electrons can be extracted from the curvature of the conduction band minimum. Experimental measurements\(^{298}\) and \textit{ab-initio} computational studies\(^{299}\) demonstrated that the effective mass in InN depends on free electron density, therefore the conduction band dispersion in InN is argued to be non-parabolic\(^{289,298}\). It was shown that the simplified \( k \cdot p \) perturbation model of Kane\(^{300}\),

\[
E_C = E_{bg} + \frac{\hbar^2 k^2}{2m_{e0}} + \frac{1}{2} \left( \sqrt{E_{bg}^2 + 4E_P \frac{\hbar^2 k^2}{2m_{e0}^2} - E_{bg}} \right), \tag{9.3}
\]

can represent the changes in electron effective mass with respect to the changes in free electron density. Equation 3 is the conduction band dispersion relation where \( E_{bg} \) is the band gap energy (taken as 0.64 eV\(^{301}\)), \( k \) is the wavevector, \( m_{e0} \) is the electron rest mass, and \( E_P \) is a parameter associated with the momentum matrix element in Kane’s model. 10 eV is the accepted value of \( E_P \) for InN\(^{298}\). The exciton Bohr diameter\(^{200}\) of InN was estimated to be approximately 12 nm. Since more than half of the InN NCs had a size larger than 12 nm (Figure 9.1d), quantum confinement effects are expected to be small, and the use of the bulk band gap energy in equation 3 is justified. From

\[
m_e^* = \frac{\hbar^2 k}{d \frac{d E_C}{d k}}, \tag{9.4}
\]
$m_e^*$ can be evaluated at the Fermi level, where $k = k_F = (3\pi^2 N_e)^{1/3}$. Evaluating the derivative in equation 9.4 by using equation 9.3 results in:

$$m_e^* = m_e 0 \left( 1 + \frac{E_p}{\sqrt{E_{bg}^2 + 4 E_p \frac{\hbar^2 k_F^2}{2 m_e 0}}} \right)^{-1}. \quad (9.5)$$

Equations 9.1, 9.2 and 9.5 can be used to estimate $N_e$. The experimentally measured value of $\varepsilon_{\infty} = 6.7$ for hexagonal InN\textsuperscript{292} is used. The dielectric constant of the surrounding medium, $\varepsilon_m$, is approximated as an averaged dielectric constant for close-packed spheres of InN NCs, which roughly represents the compressed powder during ATR-FTIR spectroscopy. By simple volume averaging, $\varepsilon_m = 0.74 \varepsilon_{\infty} + 0.26 \varepsilon_{\text{air}}$, where 0.74 is the volumetric density of close packed spheres. Accordingly, $\varepsilon_m$ is estimated as 5.22. The calculated values of $N_e$ are found to be between $2.2-3.6 \times 10^{20}$ cm$^{-3}$ (Figure 9.8). This range of $N_e$ corresponds to 1 electron per 140 to 90 molecules of InN, and to 200 to 400 electrons per NC of mean size. The quality factor of the plasmon peak\textsuperscript{297}, $Q_F = \omega_{sp} / \gamma$, was found to have a maximum value of 2. Intensity of the plasmon peaks decreased as the peaks red-shifted, as expected from decreased free electron density [InN]. Increasing the $N_2$ flow rate higher than 50 sccm caused the plasmon peak position to shift back to higher energies. The scattering frequencies indicated a mean free path of a maximum of 7 nm for the free electrons. Since only a minor portion of NCs are smaller than this size, surface scattering effects\textsuperscript{302} are expected to be insignificant.

The tendency of InN to be n-type conductive has been argued to have three major reasons. First is the intrinsic electron accumulation on InN surfaces, second is the presence of oxygen and hydrogen impurities, and the third is the presence of positively charged nitrogen vacancies\textsuperscript{303}. 

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Although the effect of N$_2$ flow rate on the extent of electron accumulation and the density of impurities is not evident, the abundance of nitrogen vacancies is expected to be related with N$_2$ flow rate. The red-shift in plasmon peak position with increasing N$_2$ flow rate can be associated with increasing amount of excited nitrogen species in the plasma. A higher concentration of excited species may have led to more nitrogen incorporation in the InN NCs, thereby reducing the density of nitrogen vacancies and the number of electrons donated by these vacancies. As mentioned in the previous chapter on GaN synthesis, the concentration of excited nitrogen species reach a maximum as the nitrogen mole fraction is increased in an Ar/N$_2$ plasma$^{255}$, which supports this hypothesis. Above a critical mole fraction of nitrogen in the feed, concentration of excited nitrogen was found to decrease$^{255}$, which is in accord with the blue-shift of plasmon peaks when N$_2$ flow rates were above 50 sccm (not shown). If all electrons are assumed to stem from positively charged (+1) nitrogen vacancies, a limiting value of nitrogen deficiency can be calculated, which is realistic only when the density of acceptor defects are relatively low. According to the formula InN$_{1-x}$, the nitrogen deficiency turns out to be small, a maximum value of 0.018 for $x$ was found. This means that if other mechanisms listed above are also playing a role in increasing the free electron density, then InN NCs should be highly stoichiometric. The significant difference in this predicted stoichiometry with EDXS measurements can be explained by the low accuracy and precision of EDXS for lighter elements, and by errors due to rough powder surfaces, as evidenced by large error bars during measurement. A curious aspect of the plasmon series given in Figure 9.8 is that the FWHM of the peaks slightly increase as peaks red-shift. This effect might be caused by the creation of neutral scattering centers in the NCs.

In addition to N$_2$ flow rate, plasma power was also found to be effective at shifting the plasmon peak. Within range of plasma power values explored, a higher plasma power was found to red-
Figure 9.9. **Plasmon peak shift as a function of plasma power.** Error bars correspond to InN powders synthesized in different experiments.

Shift the plasmon peak, indicating the formation of NCs with lower free electron density (Figure 9.9). At 60 W power and 20 sccm N₂ flow, lowest electron density of $1.6 \times 10^{20}$ cm$^{-3}$ was obtained. Using a lower power of 35 W resulted in the highest value of $N_e$: $6 \times 10^{20}$ cm$^{-3}$. The mobility of electrons, given as $\mu_e = 1/(\gamma m_e^*$), was found to have a maximum value of 44 cm²/Vs when 60 W power was employed. Accounting for phonon-limited mobility was found to have no significant effect on this value$^{304}$ [InN].

Since all InN NCs were found to be highly degenerate, an absorption edge energy that is significantly higher than the band gap of InN is expected due to the Burstein-Moss effect. VIS-NIR absorption spectroscopy on NC dispersions is the primary method for measuring the absorption edge. By contrast, the method was not suitable for our NCs. Since the NCs were bare, they aggregated when dispersed in a solvent as observed by DLS measurements, as in the case of the measurements with GaN NCs reported in Chapter 7. Dispersing the particles in dimethyl sulfoxide (DMSO) resulted in the most stable solutions. The minimum aggregate size was found
Figure 9.10. VIS-NIR absorption spectrum of InN NCs in DMSO. NCs had an estimated carrier density of $1.6\times10^{20} \text{ cm}^{-3}$. The inset shows the corresponding Tauc plot. Due to scattering, the Tauc plot is curved, and the linear portion of the plot is not evident.

to be approximately 45 nm. These aggregates, although they were smaller than GaN aggregates in solution, still resulted in significant amount of scattering, thus the optical features in VIS-NIR absorption spectroscopy was smeared (Figure 9.10). Therefore, the absorption edge was calculated by using the dispersion relation given in equation 9.3 instead. Calculations were done in a way similar to an approach previously reported$^{305,306}$. The energy required for a direct vertical transition from valence band to conduction band was estimated, whereby accounting for the band gap renormalization effects due to electron-electron and electron-ionized impurity scattering [InN]. The absorption edge $E_{abs}$ was found to span across a large range between 1.34 and 2.04 eV, increasing monotonically as free electron density was increased (Figure 9.11). Transient absorption spectroscopy validated the calculated band edge values and the degeneracy of InN NCs [InN]. During steady-state measurements on InN dispersions in DMSO, no PL was detected for any of the samples at energies above 1.38 eV, which was the lower energy limit of the fluorimeter.
Figure 9.11. Calculated absorption edge. NCs synthesized at 50 W are the samples presented in Figure 9.8. The dashed line represents the full model results as a function of free electron density.

9.5. Conclusions and Comments

It is shown that free-standing and stoichiometric InN NCs with tunable plasmon resonance can be synthesized by using NPA. Unlike GaN NCs, InN NCs were found to have a single crystalline phase, which was hexagonal, and the NCs were found to be rod- and plate-like.

Based on the GaN and InN NCs produced, NPA appears to be a promising platform for the synthesis of III-V nitride semiconductors. Next chapter deals with the synthesis of a stibnide, during which two precursor aerosols are sent into a noble gas plasma, in absence of a gaseous precursor like N₂.
Chapter 10

Dual Aerosol Sources During NPA: Synthesis of GaSb Nanocrystals

During the synthesis of GaN and InN NCs by NPA, the aerosol precursor was combined with a gas phase precursor, N$_2$. Having a gas-phase precursor is convenient in the sense that the excess precursor can leave without disrupting the stoichiometry of the product. In other words, the reaction is terminated when all of the aerosol precursor is used. This chapter investigates the problem that involves the vaporization and reaction of two aerosol precursors in the absence of a gaseous precursor. At the same time, NPA is extended to stibnides.

By using NPA, the synthesis of free-standing gallium antimonide (GaSb) NCs is demonstrated for the first time. It is shown that when elemental aerosols are used as precursors for Ga and Sb, the elements mix at the nanometer length scale as the aerosols pass through a NEP. At sufficiently high plasma power, the mixing produces free-standing GaSb NCs, with a small amount of excess Ga segregated at the periphery of the particles. As in the case of GaN and InN synthesis, the reaction is initiated by vaporization of elemental aerosols in the plasma. Ion bombardment
determines the extent of vaporization of Ga and Sb and provides control of the ensemble stoichiometry and solid-state reaction rates.

10.1. Gallium Antimonide

GaSb is a member of the III-V semiconductor family with a direct band gap of 0.73 eV and high hole mobility\textsuperscript{307}. The material is promising in many applications, for example: detectors in the short wave infrared\textsuperscript{308}, broadband absorbers in solar and thermophotovoltaic cells\textsuperscript{309-311}, and p-type field-effect\textsuperscript{312} and single-hole transistors\textsuperscript{313}. The large exciton Bohr diameter of GaSb (~44 nm) is intriguing since it allows manufacturing of quantum-confined materials with relative ease. Nanomaterials comprised of GaSb have been investigated, with emphasis placed on the synthesis and characterization of nanowires\textsuperscript{314,315}. Beyond nanowires, spheroidal nanocrystals (NCs) of GaSb are interesting since they can provide beneficial features, especially when used in a free-standing form in charge-based memory devices\textsuperscript{316}, or alternatively, when deposited into porous films as materials with new photonic properties\textsuperscript{317}. Studies on the growth of unsupported GaSb NCs, however, have been scarce when compared to the nanowire literature.

Previous studies on the synthesis of unsupported GaSb NCs employed liquid phase methods\textsuperscript{318–321}. There are currently no reports on the gas phase synthesis of free-standing GaSb NCs. Reported liquid phase GaSb synthesis methods involve procedures that often require more than a day of time to complete, and the GaSb nanocrystals produced by these methods were found to be either heavily aggregated or impure due to residual precursor. A gas phase approach for synthesizing GaSb NCs could provide a chemically pure product, and continuous operation with high yield and decreased cost when compared to liquid phase methods. However, there is a gap in knowledge of how to synthesize free-standing spheroidal GaSb NCs by a gas-phase route. By using dual aerosol
sources, it is shown below that NPA can mix Ga and Sb aerosols of high concentration at the atomic scale, yielding nanocrystalline GaSb.

10.2. Dual Aerosol Sources

For generating the Ga aerosol, the hot-filament evaporator described in detail in Chapter 7 is used. The evaporator was swept with 500 sccm Ar, and it was tuned to produce 0.6 mg/min Ga aerosol. Sb aerosol was generated in a tube furnace. The same furnace used to generate the Bi aerosol in Chapter 3 was employed, but this time the furnace was kept under vacuum. Sb pieces (99.999%, Bayville Chemicals) of approximately 27 grams were placed in an alumina boat, and the boat was inserted into a tube furnace. To collect the Sb vapor produced, the furnace was swept with 500 sccm argon. Cooling of the argon-vapor mixture led to rapid formation of the Sb aerosol. Among all elemental precursors generated in this dissertation, Sb has the highest vapor pressure. The mass output of the furnace was proportional to the vapor pressure of Sb (Figure 10.1a). When operated at 853 K, the furnace had an Sb aerosol output of $2.30 \pm 0.16$ mg/min. After a 10 minute

---

**Figure 10.1. Furnace aerosol generator.** (a) Mass output of the furnace and calculated Sb vapor pressure $^{322}$ as a function of temperature. Mass output takes the overall filter mass collection efficiency into account. (b) Time trend of mass output during three different experiments as measured on filters. $T_f$ is furnace temperature. The measurement duration, which was usually 1 min, was shown with horizontal error bars.
period of equilibration at the temperature set point, which produced a smooth Sb surface in the boat, it was found that the mass output was reproducible (Figure 10.1b). Although it was previously reported that the furnace aerosol generator is a stable generator, at the high aerosol throughputs employed in the experiments (vide infra), it was observed that the Sb aerosol mass flow rate drifted in time (Figure 10.1b). Therefore, all synthesis experiments were conducted within a time window of 12 minutes, which was the period during which the furnace generator was approximately stable. The furnace generator had a very low mass yield, approximately 1 percent, which is about an order of magnitude lower than the yield of the hot-filament evaporator. Most of the Sb aerosol was lost to the walls at the exit of the furnace due to thermophoresis.

Downstream of the evaporation-condensation generators, the precursor aerosol streams were combined at a T-junction (Figure 10.2a). At the exit of the T-junction, Ga and Sb aerosols had mass concentrations of approximately 4.4 and 21 mg/m$^3$ respectively, and total number

![Figure 10.2. Experimental setup for NPA of GaSb.](image)

(a) Schematic of the nonequilibrium plasma aerotaxy setup for GaSb synthesis. (b) Photograph of the flow-through Ar plasma at 6 Torr and with 80 W power.
concentration exceeded $10^{15} \text{ m}^{-3}$. Aerosols leaving the T-junction passed through an orifice with 6 mm diameter and entered the tubular flow-through reactor. The plasma reactor is essentially the same as the reactors used in the NPA of GaN and InN. RF power was coupled to a stainless steel ring placed outside of fused silica tube, which acted as the plasma reactor (Figure 10.2b). The tube had 19 mm OD and 16 mm ID. The steel flange downstream the fused silica tube was grounded. The pressure in the reactor and the aerosol generators was maintained at 6 Torr. Total flow rate through the plasma was 1000 sccm, and residence time was approximately 20 ms. The reactor was cooled by two fans. The product and the plasma were characterized with the methods and instruments described in detail in the previous chapters. The only difference was the use of the JEM-2000 FX microscope with an EDXS detector (Thermo Noran) to measure stoichiometry during TEM.

10.3. Aerosol Delivery

When the plasma was off, it was obvious from the deposition patterns on filters that the aerosols did not mix radially throughout the reactor volume (Figures 10.3a-c). This result is expected because the diffusion path length of the precursor particles is on the order of a millimeter, whereas the diameter of the tubular path between the T-junction and the filter was 16 mm. Therefore, in order to mix aerosols before they entered the reactor, a laminar static mixer (FMX8481s, Omega Engineering) was installed between the T-junction and the plasma reactor (Figure 10.3f and 10.3g). The mixer provided radial mixing, albeit rather limited, as observed from the swirls of gray (Ga) and black (Sb) on the filter (Figure 10.3d). Interestingly, a visibly uniform and black deposit was obtained when the mixer was installed and when the plasma was turned on at a power of 80 W (Figure 10.3e). Scans of X-ray fluorescence across the width of the
Figure 10.3. Delivery of mixed aerosols. (a-e) Filters with particle deposits: (a) Ga, (b) Sb, (c) Ga and Sb without the mixer installed, (d) Ga and Sb particle deposits with the mixer installed, and (e) Ga and Sb deposits with the mixer installed and with the plasma on at 80 W. Helical laminar static mixer, (f) before use, and (g) after use. Shiny gray deposit is Ga and black deposit is Sb. XRF scans on filters with particle deposits: (h) radial scan on the filter given in (c) along the white dashed line of 16 mm width, plasma was off, and (i) radial scan on the filter given in (e), plasma was on.

Filters revealed that elements had mixed along the radial dimension when the plasma was on, but not when the plasma was off (Figures 10.3h and 10.3i).
After the aerosols leave the mixer, they pass through a 6 mm orifice before they enter the plasma reactor (Figure 10.2a). Downstream of this orifice, aerosols get focused, and they primarily populate a region around the centerline with an expected radius of 4-5 mm. Removal of the orifice lead to the loss of almost the entire Sb aerosol. However, during experiments conducted without using the orifice it was observed that the remaining Ga aerosol went through in-flight size tuning (Figure 10.4), indicating that the effect is not specific to the Bi aerosols employed in Chapter 3. In order to reduce losses in Sb aerosol mass, the orifice was kept in place during the experiments described in the next section.

In spite of their large number concentrations, both precursor aerosols were found to be mostly unaggregated (Figure 10.5). The major reason for the absence of aggregation is the short residence
time spent by the precursor aerosols between their production and collection (~160 ms), which is an order of magnitude smaller than the characteristic time of aggregation:\footnote{Characteristics here refer to features of the plasma environment, such as gas temperature, concentration, and electric field.}

\[
\tau_{agg} = \frac{2}{\beta N_\infty},
\]

where \(\beta\) is the collision frequency for monodisperse particles in the free-molecular regime:\footnote{Values of \(\beta\) were calculated using the equation \[\beta = 0.707 \left( \frac{192k_B T_g d_p}{\rho_p} \right)^{1/2} \] where \(k_B\) is Boltzmann's constant, \(T_g\) is the gas temperature, \(d_p\) is the particle diameter, and \(\rho_p\) is the particle density.}

\[
\beta = 0.707 \left( \frac{192k_B T_g d_p}{\rho_p} \right)^{1/2}.
\]

**Figure 10.5.** TEM images of precursor nanoparticles. (a) Ga. (b) Sb. (c) Ga and Sb. These particles were collected when the plasma was off. During the collection of particles given in panel (a), only the hot filament evaporator was on. Similarly, for panel (b), only the furnace generator was on. Particles in panel (c) was obtained with both aerosol sources on. Panel (c) appears to be a direct superposition of panels (a) and (b), indicating that aggregation between particles is insignificant. Scale bars are 100 nm in width.
was found to be on the order of a second. Increasing the number concentrations of the precursor aerosols by more than an order of magnitude is expected to lead to aggregation, unless total residence times in the setup is decreased.

10.4. GaSb NCs – Size and Crystallinity

TEM showed that the black uniform powder in Figure 10.3e was GaSb. The Ga aerosol used for making GaSb was found to be highly polydisperse (Figure 10.6a), whereas the Sb aerosol was comprised of particles of similar sizes.

With the plasma on during the NPA process, the precursor aerosols appeared to vanish. From those precursor aerosols, GaSb nanocrystals were synthesized (Figure 10.6c). At 80 W plasma power, GaSb nanocrystals had a mean diameter of approximately 21 nm, which is between the mean diameters of the precursor aerosols. In addition, the size distribution of GaSb was found to be significantly narrower than those of the precursor aerosols (Figure 10.6d). The number concentration of the GaSb aerosol was on the order of $10^{14}$ m$^{-3}$. Similar to the precursor aerosols, the GaSb aerosol was found to be mostly unaggregated, however, some bridging between the particles was visible. Unlike the precursor aerosols, selective area electron diffraction (SAED) indicated that GaSb particles were crystalline. X-ray diffraction (XRD) further proved the crystallinity of the GaSb particles (Figure 10.6e). No peak corresponding to metallic Sb was visible, however, a broad feature that could be related to metallic Ga was present. A crystallite size of 19 nm was estimated using the Scherrer equation, which is similar to the mean of the size distribution measured from TEM, indicating that GaSb particles were mostly comprised of single crystals.
Figure 10.6. Characterization of precursor nanoparticles and GaSb NCs. (a-c) TEM images. (a) Ga nanoparticles, (b) Sb nanoparticles, (c) GaSb NCs. GaSb NCs were produced at 80 W. Insets are SAED patterns. Scale bars are 50 nm in width. (d) Size distributions of collected Ga, Sb and GaSb particles. $<d_p>$ is mean diameter, and $\sigma_g$ is the geometric standard deviation. Size distributions were corrected for sampling bias [GaN]. (e) XRD pattern of GaSb NCs produced at 80 W.

10.5. Vaporization of Ga and Sb Aerosols – Effects on Size and Stoichiometry

The formation of GaSb NCs was promoted by the vaporization of precursor aerosols in the plasma. Optical emission spectroscopy indicated the presence of excited metal vapors in the plasma at all powers employed between 5-110 W$^{109}$. Plasma photoemission was collected in an
Figure 10.7. Optical emission spectroscopy in the presence of Ga and Sb. (a) Experimental schematic. (b-d) Emission spectra with (b) only Ga aerosol present, (c) only Sb aerosol present, (d) both Ga and Sb aerosols present in the plasma. Insets depict the change in intensity ratios of the indicated lines as a function of plasma power.

axially integrated manner, as shown in Figure 10.7a. Figures 10.7b and 10.7c show the emission spectrum at 80 W when either one of the precursor aerosols was sent into the plasma. The emission spectrum when both Ga and Sb were sent into the plasma is presented in Figure 10.7d. Emission
lines in the ultraviolet, corresponding to Ga I at 403.3 nm \((4s^2 5s \rightarrow 3d^{10} 4s^2 4p)\) and Sb I at 326.8 nm \((5p^2 (^3P) 6s \rightarrow 5p^3)\), were clearly visible, despite the low gas temperature, which was less than 400 K as measured with a FDP (measured 1.5 cm downstream of the powered electrode [GaSb]).

Experiments were done to assess the vaporization of either Ga or Sb without the other precursor present. Actinometry was performed as a function of plasma power to estimate the relative vapor amount from the emission spectra (Figure 10.7b-d insets)\(^{110}\). The intensity ratio \(I_{M}/I_{Ar} \), where \(I_{M} \) is the emission from excited metal vapor atoms and \(I_{Ar} \) is emission from neutral Ar at 750.4 nm \((3s^2 3p^5 (^3P^0_1/2) 4p \rightarrow 3s^2 3p^5 (^3P^0_1/2) 4s)\) provides an estimate of the relative vapor content in the plasma\(^{110}\). As plasma power was increased, the \(I_{Ga}/I_{Ar} \) ratio increased (Figure 10.7b inset). Qualitatively, the corresponding increase in Ga vapor content can be explained by more intense ion bombardment experienced by the particles at higher applied powers. As discussed in chapters 2 and 5, the ion bombardment rate at the particle surface is typically proportional to ion density, which increases with applied power. Increasing ion bombardment rate can lead to higher particle temperatures, and/or higher vaporization rates. In contrast to the \(I_{Ga}/I_{Ar} \) ratio, the \(I_{Sb}/I_{Ar} \) ratio decreased when power was increased (Figure 10.7c inset). While Ga vapor is monoatomic, Sb primarily forms tetramers in the vapor phase\(^{324}\). The expectation is that the dissociation of Sb\(_4\) molecules upon increasing power would result in more atomic Sb vapor, thus a more intense Sb I emission. On the contrary, the decreasing trend in \(I_{Sb}/I_{Ar} \) was likely a manifestation of Sb vapor loss to the reactor walls. Loss of the vapor was visually observed through the rapid formation of a shiny metallic film on the walls of the fused silica tube. The film on the wall was mostly comprised of Sb, and it formed primarily a few cm downstream of the powered electrode. The deposition pattern of vapor on the walls is due to the spatial profile of ion density in tubular flow-through plasma reactors, which was shown to have a maximum in the vicinity of the powered
electrode in Chapter 5. A film deposited on the reactor wall under all conditions investigated. Furthermore, mass yields of both aerosols, but especially the yield of antimony, decreased with increasing power.

When both precursor aerosols were sent into the plasma during GaSb synthesis, emission lines from both Ga and Sb were observed (Figure 10.7d). Presence of these emission lines indicates that both aerosols were vaporized in the plasma. However, under these conditions, Sb vapor is expected to condense on the less volatile Ga particles. At the same time, the presence of both vapors enhances the species exchange between the remaining clusters, which is likely the major cause of mixing of the elements in the radial direction within the reactor volume, as demonstrated in Figures 10.3e and 10.3i. When power was increased, the relative abundance of the Ga vapor increased with respect to the Sb vapor (Figure 10.7d inset). Although the relative increase in Ga I emission with increasing power could be caused by resonant energy transfer from excited Sb species to Ga vapor, the apparent loss in Sb species at high powers suggest that Ga vapor was increasingly present in the plasma at high powers. A larger amount of Ga vapor in the plasma is expected to cause the Ga content of the product to increase.

Over the range of plasma power shown in the inset of Figure 10.7d, the size distribution of the product aerosol evolved in a distinct manner (Figure 10.8a). At very low powers, the product aerosol had a broad size distribution, similar to the Ga precursor aerosol, but the mean size was slightly larger. Increasing power first resulted in growth, however, powers higher than 20 W led to a gradual decrease in size. At 80 W, particle size was approximately 20 nm and further increase in power did not change the size. Interestingly, the widths of the size distributions decreased as power increased and $\sigma_g$ approached 1.1 (Figure 10.8b). A possible mechanism for the trends in size and width of the distributions can be given as follows. At low powers Sb aerosol preferentially
vaporizes, as can be inferred from emission measurements given in Figure 10.7. This vapor partially condenses on the Ga aerosol, which leads to an aerosol similar to that of Ga precursor aerosol in terms of the width of size distribution, but particles are not as spherical as in the Ga precursor aerosol (Figure 10.8b inset, Figure 10.6a). Increasing power initially leads to growth,

![Figure 10.8](image.png)

**Figure 10.8. Particle size distributions as a function of plasma power.** (a) Lognormal fits to size distributions obtained from TEM. Size distributions were corrected for sampling bias [GaN]. (b) Geometric standard deviation of lognormal fits to size distributions given in (a). The dashed line is a guide to the eye. Insets show TEM images of 10 W and 110 W samples. Scale bars are 50 nm in width.
which might have been caused by a larger amount of Sb vapor scavenged. The slight decrease in size at higher powers and the associated narrowing of the size distribution is expected to occur when all aerosols within the plasma start to vaporize significantly. As power was further increased, an equilibrium size was reached due to the likely decrease in electron temperature in the presence of concentrated metallic vapors\(^{250}\), which lowered the particle charge and associated ion bombardment. At this stage, condensation-vaporization in the plasma was balanced, and such aerosol dynamics were shown to be capable of narrowing the size distribution (Chapter 4). Above the 80 W threshold, widths of the size distributions further decreased at constant mean size. The uniformity of particle size across the whole powder was verified by scraping the powder off the filter and imaging it in a SEM (Figure 10.9). It is important to note that at powers higher than 80 W, the mass yields were lower. The decrease in mass yield was visible on the filters, as the spot size of black GaSb powder became smaller. At 80 W and higher power, the particles were oblong (Figure 10.8b inset), which could be due to the formation of a new crystalline phase, i.e. GaSb.

![Figure 10.9. GaSb powder imaged in under a SEM.](image)

**Figure 10.9. GaSb powder imaged in under a SEM.** The powder was produced at 110 W. Particle size is roughly 20 nm throughout the entire image. The stoichiometry of the whole powder, as measured by doing EDXS in SEM, gave \( \%75 \pm 7 \) Ga, which is similar to the results obtained via TEM.
Measurements of stoichiometry by energy-dispersive X-ray spectroscopy (EDXS) during TEM demonstrated that Ga percentage in the material increased when power was increased, in a trend similar to the Ga vapor in the plasma (Figure 10.10a). Even when the inlet molar composition was Sb rich, near 1:1 ensemble stoichiometry was obtained in the product at a very low plasma power of 10 W. However, SAED patterns indicated the presence of metallic Sb at low powers (Figure 10.10a inset). In other words, the product contained particles with a segregated metallic Sb phase. The near 1:1 stoichiometry at such a low power, considering that the feed rate of Sb is significantly higher than the Ga feed, further indicates that the majority of Sb is lost to the walls. By sorting the plasma powers that caused very low yields for each of the elemental aerosols used up to this chapter, which are Bi, Ga, In and Sb, it can be said that Sb vaporizes at the lowest power (Figure 10.7c inset). Approximately, the tendency of the elemental aerosols to vaporize in the plasma can be sorted as: Sb > Bi > In > Ga. This order applies to the vapor pressure of the elements as well, and it supports thermal evaporation being the dominant vaporization mechanism.

Even though the change in ensemble stoichiometry with power was small above 20 W, increasing the power beyond 65 W produced mostly oblong particles, and SAED on these particles indicated the presence of GaSb only. At 80 W, we measured an ion density of $1.98 \pm 0.04 \times 10^{18}$ m$^{-3}$ and an electron temperature of $1.79 \pm 0.04$ eV in the absence of aerosols by using the double Langmuir probe at a position 15 cm downstream of the powered electrode. These values are in close agreement with previous measurements done at similar conditions (Chapter 5 and 8). Crystallization of GaSb thin films requires growth temperatures between 750-900 K$^{325-327}$. Particles can easily reach such temperatures for the plasma parameters measured at higher powers in our reactor (Chapter 6). Thus, as power was increased, ion density increased, and consequently, particle temperatures were elevated due to higher ion bombardment rates which lead to
crystallization. In other words, above a power threshold, in our case approximately 65 W, particles reach temperatures necessary for the growth of crystalline GaSb, thereby causing metallic Sb to react with Ga. However, at high powers, NCs had excess Ga, which was not easily visible in SAED due to its amorphous atomic structure.

By EDXS mapping during scanning TEM, it was found that excess Ga was segregated, and was usually located as an outer shell on the particles (Figure 10.10b). This preferential location of

Figure 10.10. GaSb Stoichiometry. (a) Stoichiometry of GaSb NCs measured by EDXS as a function of plasma power. Insets are SAED patterns. Green circles on the SAED images correspond to metallic Sb, and black circles correspond to GaSb. (b) Bright field image of GaSb NCs synthesized at 80 W and corresponding EDXS maps of constituting elements. Scale bar corresponds to 20 nm.
Ga at the surface could be a result of Ga being in liquid phase due to melting point depression as a consequence of small particle size\textsuperscript{328}. It is important to note that GaSb nanoparticles were previously found to be sensitive to phase segregation caused by electron beam damage\textsuperscript{329–331}, likely due to the low enthalpy of formation of GaSb (\(-45.9\) kJ/mol)\textsuperscript{332}, therefore some of the local deviations from 1:1 stoichiometry might have formed in-situ during TEM. Nevertheless, EDXS mapping indicated that there was good local mixing of Ga and Sb in the NCs. The GaSb nanocrystals had a thin native oxide, likely caused by air exposure during handling.

Adjustment of the GaSb stoichiometry in the NPA process can be accomplished by several means. The most convenient approach is to increase the initial molar ratio of Sb to Ga. However, preliminary experiments indicated that whenever the mass throughput was increased, plasma power must also be increased to obtain a well-mixed product. If the plasma power was held constant as the mass throughput was increased, then significant amounts of unreacted Sb and Ga were observed in the product [GaSb]. In other words, ensemble stoichiometry can be tuned by adjusting inlet mass concentrations of precursor aerosols, however, providing the optimal ion bombardment conditions for complete reaction is also dependent on the aerosol concentration in the plasma. The result suggests that ion and electron bombardment, and associated properties, such as particle charge and temperature, can be strongly dependent on the aerosol concentration in synthesis plasmas, perhaps due to a decrease in electron temperature in the presence of metallic vapors and aerosols of high concentration. Another method to adjust the GaSb stoichiometry could be acid-etching during post-processing. HCl treatment could remove some of the excess Ga at the periphery of the GaSb nanocrystals. An alternative and interesting approach would be conducting the GaSb synthesis in the presence of a gaseous pnictogen, which might allow the consumption of
excess Ga and at the same time yield ternary semiconductor nanocrystals with different morphologies.

Although the exact mechanism for NPA of III-V semiconductors is not entirely clear, the results discussed in the preceding paragraphs and in Chapter 8 present a qualitative overview of the mechanism. It can be summarized as follows. The precursor aerosols vaporize nearby the powered electrode, where the ion density is higher. Sb aerosol vaporizes much more than the Ga aerosol, and downstream of the vaporization zone, some of the Sb vapor condenses on the Ga aerosol that did not vaporize. This vapor transport mechanism is a unique feature of NPA. Therefore, it is this mechanism that differentiates the plasma from a thermal reactor, such as a furnace. Unlike a furnace, in NPA, the elements are mixed in a largely nonthermal background. Furthermore, the gradients in background temperature in the plasma are less severe than those of a furnace. As a result, thermophoretic losses in a plasma reactor are expected to be much less than in a furnace reactor. That issue is apparent in the present work as a very low yield of Sb aerosol from the furnace aerosol generator employed. Upon the completion of vapor transport, the mixed aerosol continues to travel within the plasma. In this part of the plasma with lower ion density, rapid solid-state reaction between Ga and Sb occurs to yield crystalline GaSb if the requisite ion bombardment rates are provided. In experiments, this threshold was demonstrated by increasing power, and consequently, by increasing ion density. However, some excess Ga was found to be segregated from the GaSb phase, especially at the periphery of the particles. The excess of Ga did not increase or decrease substantially with increasing power, but the overall mass yield decreased. In-situ diagnostics on synthesis plasmas would help to elucidate the dynamics of growth in NPA, especially when two precursor aerosols with different physicochemical properties, such as Ga and Sb, are employed.
10.6. Comments and Conclusions

By synthesizing free-standing GaSb NCs, NPA was extended to the synthesis of stibnides and the use of dual aerosol precursors. In the Ar NEP, Ga and Sb were both found to vaporize. The presence of the elemental vapors, especially that of Sb, led to a re-distribution of the elements across the whole aerosol with little to no aggregation. When the plasma power was sufficiently high, Ga and Sb elements reacted and mixed rapidly at the nanometer scale, thereby forming GaSb nanocrystals with narrow size distributions. It was found that the product was typically rich in the less volatile element, in this case Ga. In the presence of a gaseous precursor, the process may allow the synthesis of binary or ternary semiconductor nanocrystals that are free from organic contaminants.
Chapter 11

Conclusions and Outlook

Nonequilibrium plasmas (NEPs) are extraordinary environments. Due to their inherent nonequilibrium, they are highly complex and unpredictable, but at the same time, they have great potential in opening up novel pathways for processing materials. This dissertation shed light on some of the fundamental aspects of dusty nonequilibrium plasmas (NEP) which are relevant to materials synthesis and processing. Furthermore, a new and flexible NEP-based synthesis method, termed nonequilibrium plasma aerotaxy, was presented. This method can deliver compound semiconductor nanomaterials that are difficult to make by other methods. I expect the work presented in this dissertation to have a significant impact on various communities of research, especially the ones that involve plasma synthesis, semiconductor nanomaterials and aerosol physics. Below, a summary of the work is given. The summary is followed by an outlook on various aspects of the work.

11.1. Summary of results

1) A simple experimental framework that allows the study of plasma-aerosol interactions was established. The framework involves the generation of test aerosols and sending of these
aerosols into a plasma. As long as an aerosol of the test material can be generated, the framework would provide the opportunity to investigate the physical and chemical effects a NEP can induce on a particulate material, as well as the changes made to the plasma by sustaining a dust and vapor concentration within. Plasma diagnostics and ex situ material characterization were shown to constitute a sufficient set of analytical tools that can unveil the essential plasma-aerosol interactions.

2) A new growth mechanism with important implications on nanomaterials processing has been elucidated. It was shown that small particles in a noble gas NEP vaporize amidst a cold background gas. Based on the experiments done with Sb, Bi, In and Ga, which are listed in descending order with respect to their vapor pressures, the extent of nonequilibrium vaporization was found to be correlated with the vapor pressure, indicating that nonequilibrium thermal evaporation due to particle heating might be the physics responsible. This vaporization process might be a key factor that determines the properties of the nanomaterials synthesized by NEP, such as the final size of the particles, width of the size distribution and mass yield.

3) A sectional aerosol dynamics model that can capture the growth of small particles in a plasma was developed. It was shown that a simple set of mechanisms that involve condensation, vaporization and nucleation can qualitatively replicate the experimentally observed results. The model can guide new experiments and it especially can assess the feasibility of the proposed mechanisms for a NEP-based process.

4) The capacitively coupled, tubular flow-through reactor was characterized spatially for the first time. The reactor was found to have a nonuniform distribution of ion density and gas temperature. Nearby the powered electrode both the ion density and gas temperature were
found to be significantly elevated, and this intense zone was found to dictate the extent of ion bombardment, hence of particle heating and vaporization. On the overall, ion densities were found to be about an order of magnitude higher than the previously reported values, and gas temperature was found to be significantly higher than room temperature at moderate applied powers. In the meantime, the practice of using fiber optic probes for the measurement of gas temperature in NEPs was established. The results on materials processing and synthesis clearly show that the tubular reactor should be characterized as a function of position because of the presence of the intense zone.

5) A new model on the temperature history of a particle in a tubular flow reactor have been proposed. The model indicated that particles in the reactor can acquire very high temperatures, and they can go through very fast heating and cooling cycles in the plasma. When placed in a tubular reactor, NEP is proposed to be capable of acting as a rapid thermal processing tool, which can induce nonequilibrium atomic transformations in a material.

6) A new method of synthesis that can deliver high-quality nanocrystals (NCs) of compound semiconductors have been developed. The method is termed as nonequilibrium plasma aerotaxy (NPA). NPA relies on using pre-made elemental aerosols as precursors. The elemental aerosols was found to vaporize in the intense zone, and this step was followed by the growth of a compound material downstream of the intense zone. Employing elemental aerosols in place of metalorganic vapor precursors lead to a chemically pure product, and at the same time, the use of toxic and/or pyrophoric chemicals was avoided. NPA was shown to be capable of producing size-controlled, monodisperse and freestanding NCs with tunable optical properties. NCs of GaN, InN and GaSb were
synthesized successfully with either superior or similar quality when compared to existing reports in literature.

11.2. Outlook

11.2.1. On Plasma-Aerosol Interactions

The materials that were either used as probe or precursor aerosols, which are Bi, Ga, In and Sb, usually had high to intermediate vapor pressure. Extending the experiments to materials that have lower vapor pressure, such as Ag, Cu and Sn, would be highly informative. For these materials, evaporation-condensation generators would still work. Investigating how the extent of vaporization scales with ion density and vapor pressure could be used to study the fundamentals of the vaporization mechanism. Experiments in reactors with controlled gas temperature would provide insight on the role played by nucleation, and on crystal growth. Using different plasma gases, such as helium, would help in elucidating the properties of a plasma gas, e.g. $\Delta H_{rec}$, that are responsible for vaporization.

For experiments that only involve monitoring the change in size distributions, an instrument that is capable of measuring size distribution online would certainly speed up experimentation. The difficulty in conducting online size measurements comes primarily from the plasma being at low pressure, which is not suitable for many of the well-established aerosol monitoring instruments. Particle extraction methods that can transfer aerosols from low to high pressure might work, but their transfer functions should be characterized accurately.

11.2.2. On Aerosol Modeling

Sectional models should be modified to account for charging, particle heating, vaporization, ionized vapor deposition, nucleation and vapor losses. Coagulation is expected to be important
for highly concentrated particles that are smaller than 10 nm. When spatially-resolved plasma parameters are fed into the sectional model, the model should be able predict the transformations that an aerosol undergoes in the plasma with better accuracy than the models presented in this work. Furthermore, the sectional model can be made to be self-consistent, so that the effect of the aerosol on the plasma can also be taken into account. In this dissertation, modelling and plasma characterization was done in the region nearby the centerline of the tubular reactor. However, radial gradients in plasma parameters and aerosol properties are expected to exist in the reactor, and these nonuniformities might play a role in the width of the size dispersion and overall stoichiometry of the final product. Modelling can shed light onto these nonuniform aspects of growth.

Approaches that are simpler than sectional formulation, such lognormal, moment and monodisperse models, would also be useful. Their major advantage would be the simplicity in incorporating them into existing codes that simulate plasmas, in order to achieve full coupling between aerosol and plasma physics.

The primary goal of the modelling should be determining the operating parameters necessary for obtaining a material with the desired size, size dispersion and stoichiometry. During the NPA of GaN, particle size distributions were found to be broader for the smallest NCs produced. In order to control quantum confinement effects, a quantitative understanding of the growth process is required. In NPA, reactor geometry is another parameter that should be investigated. Results obtained on the NPA of GaN and GaSb indicate that solid-state kinetics and surface reactions also play a major role in NC growth.

11.2.3. On Plasma Diagnostics

There is a need for measuring plasma parameters more accurately since the potential of models of aerosol dynamics depend on the accuracy and validity of the measured plasma parameters.
Probe methods are relatively straightforward for pristine plasmas, but the methods of analysis used for the data that they generate are usually too simplistic. Verifying the plasma parameters and gas temperatures obtained with probe-based methods with other diagnostic approaches, such as optical emission spectroscopy, would be valuable. Furthermore, being able to do measurements in the presence of aerosols would provide valuable information about how the plasma parameters change in presence of the aerosol and vapor.

11.2.4. On NPA of GaN

The range of particle sizes deliverable by NPA should be extended. The ability to make GaN NCs that are smaller than 5 nm would be attractive for devices in which quantum confinement is exploited (e.g. deep UV LEDs). It appears that studying the quantum confinement effects in the PL of GaN NCs would be easier if NCs are optically characterized in the form of porous films, instead of dispersions. On the other side of the size spectrum, the capability of synthesizing larger particles (>150 nm) would be promising for photonic devices (e.g. random lasing). Two stringent requirements for such applications are controllable particle size and narrow size distributions. The effects of the tube size, aerosol feed concentration, gas temperature and hydrogen on the characteristics of the particle size distribution are not entirely clear, and they should be studied.

11.2.5. On the Synthesis of NCs with NPA

NPA can be extended to many other materials. For example, making of ternary semiconductors should be experimented on with the NPA method. It seems like the presence of at least one gaseous precursor is required for producing stoichiometric materials. Therefore, an immediate group of materials that seem to be highly suitable for NPA synthesis are ternary nitrides. Doped semiconductors is another path that should be explored, since most of the devices that are going to be made out of NCs will eventually require n- and p-type, doped NCs to be synthesized.
The extension of NPA to other materials depends on two constraints. First, the constituent metals and/or semi-metals must be aerosolized. If an evaporation-condensation generator is to be employed, such as the hot-filament generator, then the constituent element must have sufficiently high vapor pressure. Fortunately, a large class of elements fulfill that criterion (Figure 11.1). The second constraint is that the plasma should be able to vaporize the aerosol, which is essential for size control. This constraint is expected to be satisfied with low pressure NEP.

Finally, NPA should be complimented with aerosol sources that have high-throughput. A 10-fold increase in throughput would allow the synthesis of powder quantities larger than 100 mg, and such quantities can be used in the manufacture of NC composites. Furthermore, the stability of the sources in terms of their mass output is crucial for maintaining the desired stoichiometry of materials that are synthesized with more than one aerosol source.

![Figure 11.1](image)

**Figure 11.1. Compatibility of elements for aerosol generation by evaporation-condensation.** Elements shown in red are either already in gas phase in STP or their aerosols can be generated by thermal evaporation methods. The red elements written in bold letters are the elements that were studied in this dissertation. Gray elements have very low vapor pressure, and their aerosols cannot be generated with thermal evaporation. Aerosols of green elements can be generated, but extreme measures should be taken due to their high toxicity. Phosphorus can be aerosolized, but care must be taken to avoid the formation of the pyrophoric white allotrope after cooling of the aerosol generator.
Appendix I – Lognormal Models

Lognormal models present approximate solutions to aerosol growth by assuming that the size distribution of the aerosol stays lognormal during whole process. These models are computationally light, yet capable. Many aerosol mechanisms can be represented by a lognormal model, including condensation, nucleation, coagulation, diffusion and thermophoresis.\textsuperscript{333,334}

Lognormal representations are derived by integrating the growth equation, the across the size spectrum. For example, the Liouville equation (Equation 4.6) is integrated in the case of condensation. The integrations result in the temporal evolution equations for the moments of the size distribution, and any moment can be described by the zeroth, first and the second moment by the Hatch-Choate equations.\textsuperscript{335} Without derivation, the equations used to generate Figure 1.7 are presented in this appendix.

Condensation in the free molecular regime in the presence of a constant vapor reservoir can be described by the following equations:

\[
\frac{dM_1}{dt} = \sqrt{2} \frac{M_0^{2/9} M_1^{8/9} M_2^{-1/9}}{M_1}, \quad \text{(AI.1)}
\]

\[
\frac{dM_2}{dt} = 2 \sqrt{2} \frac{M_0^{-1/9} M_1^{5/9} M_2^{5/9}}{M_2}. \quad \text{(AI.2)}
\]
$M_0$, $M_1$ and $M_2$ are the zeroth, the first and the second moment, respectively. $\theta$ is a lumped parameter:

$$\theta = \frac{(36\pi)^{1/3} \alpha_M (p - p_s) m_v}{\rho_p \sqrt{2\pi m_v k_B T_g}}.$$  \hspace{1cm} (AI.3)

When calculating $p_s$, the Kelvin effect is neglected. Expectedly, there is no equation representing the change in $M_0$ since the number concentration is conserved during condensation ($N_\infty$ is equivalent with $M_0$). $T_g$ is the temperature of the vapor and the particles.

Coagulation in the free molecular regime is represented as follows:

$$\frac{dM_0}{dt} = -b_0 K \left( M_0^{151/72} M_1^{-13/36} M_2^{19/72} + 2M_0^{131/72} M_1^{7/36} M_2^{-7/12} + M_0^{127/72} M_1^{11/36} M_2^{-5/72} \right)$$ \hspace{1cm} (AI.4)

$$\frac{dM_2}{dt} = 2b_2 K \left( M_0^{19/72} M_1^{47/36} M_2^{31/72} + 2M_0^{-1/72} M_1^{-67/36} M_2^{11/72} + M_0^{-5/72} M_1^{7/36} M_2^{7/72} \right)$$ \hspace{1cm} (AI.5)

$$b_0 = 0.633 + 0.092\sigma^2 - 0.022\sigma^3$$ \hspace{1cm} (AI.6)

$$b_2 = 0.39 + 0.5\sigma - 0.214\sigma^2 + 0.029\sigma^3$$ \hspace{1cm} (AI.7)

$$\sigma = \exp \left[ \frac{1}{3} \ln \left( \frac{M_0 M_2}{M_1^2} \right) \right]$$ \hspace{1cm} (AI.8)

$$K = \left( \frac{3}{4\pi} \right)^{1/6} \left( \frac{6k_B T_g}{\rho_p} \right)$$ \hspace{1cm} (AI.9)

During coagulation, the total volume is conserved. Therefore, $M_1$ is constant throughout the growth process. This lognormal representation of coagulation leads to a self-preserving
distribution, but this distribution is narrower than the exact distribution\textsuperscript{114}. Accordingly, the asymptotic geometric standard deviation is 1.355, instead of the exact value of 1.462\textsuperscript{50}.

To generate Figure 1.7, Equations AI-1 – AI-9 were used to solve for the moments first. Then, the Hatch-Choate equations were used to obtain the parameters of the lognormal distribution:

\begin{align*}
V_g &= \frac{M_1^2}{M_0^{3/2}M_2^{1/3}} \quad \text{(AI.10)}
\end{align*}

\begin{align*}
\sigma &= \exp \left[ \frac{1}{3} \ln \left( \frac{M_0M_2}{M_1^2} \right) \right] \quad \text{(AI.8)}
\end{align*}

The lognormal distribution with respect to particle volume, \( V_p \), is given as:

\begin{align*}
N_v &= \frac{N_\infty}{3\sqrt{2\pi}V_p \ln \sigma_g} \exp \left[ \frac{-\ln^2 \left( \frac{V_p/V_pg}{\sigma_g} \right)}{18\ln^2 \left( \sigma_g \right)} \right] \quad \text{(AI.11)}
\end{align*}

This distribution is then transformed into a distribution based on \( d_{pl} = \log(d_p) \), with \( d_p \) in nm:

\begin{align*}
N_{d_{pl}} = \frac{dN_\infty}{d \log (d_p)} = \frac{\pi \ln(10)}{2} \frac{3(d_{pl}^{-9})}{10} n_v \quad \text{(AI.12)}
\end{align*}

The parameters used in the calculations are given in Table AI.1. Subscript zero indicates initial values.
Table AI.1. Parameters used in the lognormal model. $\alpha_M$ was set to 1. $S$ is the supersaturation ratio: $p = Sp_s$. Calculations were done for Bi particles. Particle temperature was assumed to be equal to the gas temperature. Initial values of the parameters are given with the subscript 0.

<table>
<thead>
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<th></th>
<th>Condensation</th>
<th>Coagulation</th>
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<tbody>
<tr>
<td>$T_g / K$</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>$d_{p0} / \text{nm}$</td>
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<td></td>
</tr>
<tr>
<td>$\sigma_{c0}$</td>
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<td></td>
</tr>
<tr>
<td>$N_{\infty0} / \text{m}^{-3}$</td>
<td>$1 \times 10^{16}$</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$S_{0}$</td>
<td>$5 \times 10^{20}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix II – Characteristic Times of Condensation and Evaporation

This appendix presents derivations for the characteristic times of condensation and evaporation. The expressions for the characteristic time scales were derived following a qualitative approach based on scaling of partial pressure and particle volume. Such a qualitative approach allows corresponding time scales for condensation, evaporation and complete evaporation, which turns out to be different, to be derived simply. The expression obtained for the time scale of condensation agrees very well with a previously reported expression derived from the exact solution of the equation of growth under limited vapor reservoir \(^{337}\).

In the following discussion, free molecular regime is assumed to apply. Vapor is generated or depleted only due to evaporation or condensation. The differential mass balance is used to extract the time scales. For a monodisperse aerosol, the mass balance is written as:

\[
\frac{m_v}{k_B T_g} \frac{d}{dt} p = -N_{\infty} \rho_p \frac{dV_p}{dt},
\]

where \(V_p\) is the particle volume, \(p\) is the partial pressure of the vapor. Its derivative with respect to time is described by the kinetic theory expression of growth:
\[
\frac{dV_p}{dt} = 6^{2/3} \alpha \frac{2}{3} \frac{\alpha M m_v V_p^{2/3}(p - p_s)}{\rho_p \sqrt{2\pi m_\gamma k_B T_g}} .
\] 

(AII.2)

The partial pressure and the particle volume can be scaled accordingly:

\[
\hat{p} = \frac{p - p_s}{p_0 - p_s}, \quad \hat{V}_p = \frac{V_p - V_{p0}}{V_{pf} - V_{p0}}.
\]

(AII.3)

\(p_0\) is the initial partial pressure, \(p_s\) is the vapor pressure of the particles, \(V_{p0}\) is the initial particle volume and \(V_{pf}\) is the final particle volume at the end of the condensation or evaporation process. Substitution of equation AII.2 in AII.1, and subsequent scaling of Equation AII.1 with respect to pressure yields:

\[
\frac{d\hat{p}}{dt} = -1.929 \alpha_M N_\infty \sqrt{\frac{k_B T_g}{m_v}} V_p^{2/3} \hat{p} .
\]

(AII.4)

The numerical constants of equation AII.2 were evaluated in the equation given above. The terms that are in front of the dimensionless pressure term in equation AII.4 constitute the inverse of the normalization scale for time, i.e. the characteristic time. Upon normalizing \(V_p\), expressions for the time constant can be derived, but first, some simplifications have to made. The \(V_p^{2/3}\) term in the equation above can be expressed as:

\[
V_p^{2/3} = \left[\hat{V}_p (V_{pf} - V_{p0}) + V_{p0}\right]^{2/3} .
\]

(AII.5)

For condensation, if the final particle volume is much larger than the initial volume, \(V_{pf} \gg V_{p0}\):

\[
V_p^{2/3} \approx \hat{V}_p^{2/3} V_{pf}^{2/3} .
\]

(AII.6)

Hence:

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\[ \tau_{\text{cond}} = \frac{1}{\alpha_M N_\infty V_{pf}^{2/3} \sqrt{\frac{m_v}{k_B T}}}, \quad (\text{AII.7}) \]

where the numerical constant was neglected due to being on the order of unity. This characteristic time for condensation is similar to the one given by Wu and Biswas. Converting volume to particle diameter, re-arranging the square root, and ignoring the constants on the order of 1 yield

\[ \tau_{\text{cond}} = \frac{1}{\alpha_M N_\infty d_{pf}^2 \beta_v}, \quad (\text{AII.8}) \]

where \( \beta_v = (8k_B T_g/\pi m_v)^{1/2} \) is the mean thermal speed of vapor molecules. The characteristic time of condensation is inversely proportional to the total surface area available for condensation.

If \( V_{pf} \) and \( V_{p0} \) are comparable, then:

\[ V_p^{2/3} \approx V_{p0}^{2/3}, \quad (\text{AII.9}) \]

and a slightly different formula obtained for the case of condensation and evaporation where the volume of the particle does not change much:

\[ \tau_{ce} = \frac{1}{\alpha_M N_\infty V_{p0}^{2/3} \sqrt{\frac{m_v}{k_B T_g}}}, \quad (\text{AII.10}) \]

which is equivalent to:

\[ \tau_{ce} = \frac{1}{\alpha_M N_\infty d_{p0}^2 \beta_v}. \quad (\text{AII.11}) \]

For evaporation, if \( V_{pf} \ll V_{p0} \):

\[ V_p^{2/3} \approx V_{p0}^{2/3} \left(1 - \dot{V}_p\right)^{2/3}. \quad (\text{AII.12}) \]
This simplification leads to the same characteristic time given in equation AII.11. Finally, there is the final case, which involves complete evaporation of the particles. For hot particles, the parentheses in equation AII.2 will be large and negative, leading to a fast decrease in particle volume. From mass balance,

\[ V_{pf} = V_{p0} + \frac{m_v (p_0 - p_s)}{\rho_p N \infty k_B T_g}, \]  

(AII.13)

and the final particle size is negative. However, the shrinkage in size is cut short whenever the particle volume reaches the molecular volume, \( V_{pm} \). To account for the fast evaporation of particles and for the molecular limit, a scaling factor that describes the ratio of initial size and the hypothetical change in particle size predicted by AII.13 is introduced into equation AII.11:

\[ \tau_{evap} = \frac{1}{\alpha_M N \infty V_{p0}^{2/3}} \sqrt{\frac{m_v}{k_B T_g}} \left( \frac{V_{p0}}{V_{p0} - V_{pf}} \right). \]

(AII.14)

Substitution of equation AII.13 in AII.14 and ignoring numerical constants of order 1 give:

\[ \tau_{evap} = \frac{d_{p0} \beta_v \rho_p}{\alpha_M (p_s - p_0)}. \]

(AII.15)

The summary of derived formulae and their applicability are given in Table AII.1. Expressions AII.8 and AII.16 were tested in cases that are relevant to the Bi experiments (Figure AII.1). Equation AII.2 was solved numerically along with the mass balance criterion for limited vapor reservoir (Equation AII.13). Equation AII.8 overpredicts that the speed of the process by an order of magnitude. A similar result for an expression equivalent to Equation AII.11 was presented by Wu and Biswas\textsuperscript{337}. Equation AII.16, however, predicts the dynamics accurately.
Table AII.1 Equations for the characteristic times of monodisperse condensation and evaporation. \(d_{pm}\) is the molecular diameter calculated from: \((6MW/\pi N_A \alpha p)^{1/3}\). \(N_A\) is Avogadro’s constant.

<table>
<thead>
<tr>
<th>Characteristic time</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau_{\text{cond}} = \frac{1}{\alpha M N_{\infty} \beta_d \beta_v} d_{pf}^2)</td>
<td>for condensation, if (d_{pf} \gg d_{p0})</td>
</tr>
<tr>
<td>(\tau_{\text{ce}} = \frac{1}{\alpha M N_{\infty} d_{p0}^2 \beta_v})</td>
<td>for condensation, if (d_{pf} \equiv d_{p0}) for evaporation, if (d_{p0} &gt; d_{pf} &gt; d_{pm})</td>
</tr>
<tr>
<td>(\tau_{\text{evap}} = \frac{d_{p0} \beta_v \rho_p}{\alpha M (p_0 - p_s)})</td>
<td>for complete evaporation, if (d_{pf} \ll d_{pm})</td>
</tr>
</tbody>
</table>

Mass balance: \(d_{pf}^3 = d_{p0}^3 + \frac{6m_v (p_0 - p_s)}{\pi \rho_p N_{\infty} k_B T_g}\) (AII.16)

Figure AII.1. Characteristic times of condensation and evaporation. (a) Condensation on a monodisperse aerosol. The parameters used resemble the Bi aerosol at the exit of the intense zone, where the particle size is the size of Bi dimer, and the particle concentration is the concentration of the dimer. The initial partial pressure is the maximum pressure that is experimentally possible. The characteristic time expression, Equation AII-8 shown with a dashed line, underpredicts the timescale of the process by an order of magnitude. (b) Evaporation of a monodisperse aerosol. Conditions resemble the high concentration Bi aerosol in the intense zone (Table 3.1 and Figure 6.3).
Appendix III – Ionized Vapor Deposition

This appendix presents a simple calculation on the enhancement in growth rate when the condensing vapor is ionized. Since particles are negatively charged in the plasma, any positively ionized vapor molecule will deposit with a much faster rate than a neutral molecule. Given the fact that metal vapors have lower ionization energies than noble gases, a significant amount of the metal vapor that arises during nonequilibrium vaporization is expected to ionize. The ionization energies\(^{165}\) for the metals employed in this dissertation are 8.61, 7.29, 5.79 and 6.00 eV for Sb, Bi, In and Ga respectively, whereas for Ar it is 15.76 eV.

We define the rate of enhancement in growth due to ionized vapor deposition, \(r_{ivd}\), as:

\[
  r_{ivd} = \frac{J_{i,m}}{J_{n,th}}, \tag{AIII.1}
\]

where \(J_{i,m}\) is the collision-enhanced ionized vapor flux to a particle (equation 6.3) and \(J_{n,th}\) is the net thermal flux of neutral vapor molecules to a particle with zero vapor pressure under perfect accommodation (equations 2.6 and 4.9). By defining the ionized fraction of the metal vapor,

\[
  \gamma = \frac{n_{i,m}}{n_n}, \tag{AIII.2}
\]

with \(n_{i,m}\) being the ionized vapor concentration and \(n_n\) being the total vapor concentration, the rate enhancement due to ionized vapor deposition (equation AIII.1) can be written as follows:
$$r_{ivd} = \gamma \left[ 1 - \frac{e\Phi_p}{k_B T_i} + 0.1 \left( \frac{e\Phi_p}{k_B T_i} \right)^2 \left( \frac{\lambda_D}{\lambda_{i,m}} \right) \right].$$  \hspace{1cm} (AIII.3)$$

$\lambda_{i,m}$ is the mean free path of the metal vapor ion. $\gamma$ has to be calculated from a global plasma model that solves for the ionization of Bi in the presence of metal vapor and particles. In such an environment, electron temperature of the pristine plasma is expected to change, and one has to solve for the concentration of the excited species of both the argon and metal vapor along with a power balance and quasineutrality to calculate the change in electron and ion density. Solution of such a model is not attempted here. Instead, the particle potential in equation AIII.3 was obtained by numerically solving the flux balance as a function of $T_e$ and $\gamma$:

$$J_i + J_{i,m} = J_e.$$  \hspace{1cm} (AIII.4)$$

by employing the collision-enhanced flux expressions for argon and Bi ion fluxes, and by using the OML expression for the electron flux. Then, $r_{ivd}$ was evaluated as a function of $\gamma$ at different electron temperatures. The values that were used in the calculation are as follows: $n_n = 5.8 \times 10^{18}$ m$^{-3}$, $T_g = 400$ K, $p = 1.5$ Torr and $n_i = 10^{18}$ m$^{-3}$. It was assumed that $n_i + n_{i,m} = n_e >> N_\alpha$. Bismuth was used as the vapor, and the vapor was assumed to be monoatomic. The value of $n_n$ corresponds to the maximum partial pressure of Bi that was experimentally possible, which was $2.4 \times 10^{-4}$ Torr (0.032 Pa). Due to the lack of data on the ion mobility and ion-neutral cross section of Bi, an ion-neutral cross section of $10^{-18}$ m$^{-2}$ was assumed. This value is slightly higher than the value that a mercury ion in Ar has.
Results of the calculations are given as a function of $\gamma$ and $T_e$. The results are given in Figure AIII.1. Calculations indicate that the growth enhancement can be higher than 100, but the exact value strictly depends on $\gamma$ and the resultant electron temperature upon the ionization of the metal vapor. A value for $\gamma$ that is close to 1 is quite feasible due to the low ionization energies of the metal vapors. The major support for this claim comes from the high ionization percentages of metal vapors observed in gas discharge lamps, such as the mercury-argon lamp.\textsuperscript{338,339}

As long as $d_p \ll \lambda_D \ll \lambda_i$, the particle potential and the ion flux is independent of size. Therefore, the mathematical description of the rate of growth due to ionized vapor deposition is similar to that of condensation, and no size-dependency is observed during growth.

\textsuperscript{a} This hierarchy means that the particle potential can be described by equation 2.10 instead of the more complete equation 6.4, and hydrodynamic ion collection (Equation 6.5) is negligible.
Appendix IV – Characteristic Time of Charging

An order of magnitude estimation for the time of a particle to acquire its mean charge is described in this appendix. In literature, it was argued that the time to acquire the mean charge is a good approximation to the time required for the charge distribution to settle\textsuperscript{89,340}. Considering the mean charge only, charging dynamics can be described with flux-balancing:

\[
\frac{dZ}{dt} = \pi d_p^2 (J_i - J_e).
\]

(AIV.1)

Various forms of approximate formulae were presented for the characteristic charging time in literature. For the OML regime, a simple approximation was given as\textsuperscript{341}:

\[
\tau = \frac{1}{\pi d_p^2 n_e \beta_e}.
\]

(AIV.2)

In the equation given above, \(\tau\) is independent of gas temperature. Note that it is very similar to the characteristic time for condensation given by equation AII.8, since the physical mechanisms of the capture of electrons and vapor molecules are similar for an uncharged particle. A more complete expression that depends on gas temperature is\textsuperscript{145}:

\[
\tau = \frac{1}{8} \frac{d_p \beta_g}{\lambda_D^2} \left( 1 + \frac{e |\Phi_p|}{k_B T_e} \right).
\]

(AIV.3)
Equation AIV.3 includes the particle potential, which needs to be calculated or estimated beforehand.

The derivation for the characteristic time that is presented here is semi-qualitative. Charging of a particle is the result of two competing processes, which are ion and electron bombardment. Ion fluxes to particles in most nonequilibrium synthesis plasmas are either initially much smaller than electron fluxes, or of similar order of magnitude. Therefore, the time constant can be derived only by considering the slower mechanism, i.e. charge deposition by ion bombardment. We work with a representative form of equation AIV.1, in which we omit $J_e$. When the collision-enhanced model is used to describe $J_i$, Equation AIV.1 can be written in the following form:

$$\frac{dZ}{dt} = \alpha_1 - \alpha_2 Z + \alpha_3 Z^2,$$  \hspace{1cm} (AIV.4)

where $\alpha_1$, $\alpha_2$ and $\alpha_3$ are lumped constants. The expression for the potential used in the equation above is the one given by Equation 2.10. In the case where $\alpha_2 \gg \alpha_3$, equation AIV.4 represents OML theory and it reduces to a linear equation. Thus, the time constant is the inverse of $\alpha_2$:

$$\tau_{OML} \equiv \frac{1}{\alpha_2} = \frac{e^2 n_i d_p}{\varepsilon_0 \sqrt{8\pi m_i k_B T_i}} = \frac{8\lambda_D^2}{\beta_i d_p},$$  \hspace{1cm} (AIV.5)

which is similar to a previously given expression$^{342,a}$. When $\alpha_3$ is comparable to $\alpha_2$, equation AIV.4 needs to be solved to obtain the charging time. Equation AIV.4 is a Riccati equation, and it can be solved by the substitution $Z = Z_{avg} + 1/z$, where $Z_{avg}$ is the mean steady-state charge. The solution is:

---

$^{a}$ A charging time that is based on electron parameters can be obtained if charging by electrons is assumed to be the mechanism that defines the time scale. By linearizing equation 2.9, one can obtain: $\tau_{OML} = 8\lambda_D/\beta_i d_p$, which is equivalent to expression given in Maravilla et al$^{342}$. For synthesis plasmas, this expression usually predicts a time scale that is an order of magnitude smaller than what is predicted by equation AIV.5.
The time constant can be expressed as:

$$\tau_C = \frac{1}{\alpha_2 - 2\alpha_3 Z_{avg}}. \quad \text{(AIV.7)}$$

which is equivalent to:

$$\tau_C = \left[ \frac{1}{\tau_{OML}} + \frac{1}{\tau_{CEM}} \right]^{-1}. \quad \text{(AIV.8)}$$

where

$$\tau_{CEM} \equiv \frac{1}{2\alpha_3(-Z_{avg})} = \frac{20(k_B T_i)^2}{e^3 \sigma_i p(-Z_{avg})} \sqrt{\frac{\pi^3 e_0^3 m_i}{n_i}} \approx 40 \frac{\lambda_i \lambda_D}{\beta_i d_p} \left( \frac{e |\Phi_p|}{k_B T_i} \right)^{-1}. \quad \text{(AIV.9)}$$

is the contribution of the collision-enhanced ion flux mechanism to overall charging time. Equation AIV.8 is the expression used in Chapter 6. Although the contribution of the hydrodynamic mechanism to charging time was not considered in Chapter 6, it should be mentioned that a time constant can be derived for this mechanism in similar fashion:

$$\tau_{HYD} \equiv \frac{\varepsilon_0 \sigma_i p}{n_i e^2} \sqrt{\frac{2 m_i}{k_B T_i}} = \sqrt{\frac{8 \lambda_D}{\pi \lambda_i \beta_i}}. \quad \text{(AIV.10)}$$

The constant prefactor equals to 1.6, and it can be ignored (See the footnote in Section 6.2.). Since charging time is inversely proportional to ion flux, the interpolation formula given by equation 6.2 asserts the final form of the charging time constant that is valid over all regimes:

$$\tau = \tau_C + \tau_{HYD}. \quad \text{(AIV.11)}$$
The equations for the charging time were tested over a wide range of parameters. The results are given in Figure AIV.1. The expressions developed in this appendix predict the charging time quite accurately.
Figure AIV.1. **Characteristic time of charging.** Charging of particles of various sizes at different pressures and with different plasma parameters are given. The pressures are indicated on the left-hand side along with the charging model used in the calculation. Vertical lines indicate the charging times predicted by the equations given in the text. Black dotted line: Eq. AIII.2, orange dash-dot line: Eq. AIV.3, blue dashed line: Eq. AIV.5, red straight line: Eq. AIV.8, green dotted line: Eq. AIV.9, gray straight line: Eq. AIV.11.
Appendix V – Relative Rates of the Mechanisms of Aerosol Growth

Throughout this entire dissertation, it was mentioned that multiple physical mechanisms of aerosol growth were present in NEP. Since the dynamics is rich, evaluating the relative rates of processes might simplify an analysis of material growth in NEP. The most obvious approach is to compare the characteristic times of the physical mechanisms in consideration, which is done in multiple sections of this dissertation (e.g. Chapters 4 and 6). The goal of this appendix is to gather the expressions for characteristic times of the processes that play a role in the growth of small particles in NEP. Table AV.1 is a collection of characteristic times of all the important processes mentioned in this dissertation, except for those that are relevant to solid-state kinetics and surface reactions. No comparative analysis using the expressions is given here, however, any future modelling study should consider such an analysis as the first step.
Table AV.1 Characteristic times of aerosol dynamics.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Characteristic time / s</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Convective transport</td>
<td>$\frac{L}{v_p}$</td>
<td>$L$ is the relevant length of the reactor. Neglects particle trapping. $v_p \equiv v_s$ if drag is significant.</td>
</tr>
<tr>
<td>Viscous drag</td>
<td>$\frac{\rho_p d_p^2 C_c}{18 \mu}$</td>
<td>Valid for Stokesian particles. Given in Chapter 6 (In equation 6.12)</td>
</tr>
<tr>
<td>Charging</td>
<td>$40 \frac{\lambda_i \lambda_D}{\beta_i d_p} \left(e^{\frac{</td>
<td>\Phi_p</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>$\frac{d_p \beta_v \rho_p}{\alpha_M \left(p_0 - p_s\right)}$</td>
<td>Valid if $d_pf &lt;&lt; d_pm$ (Complete evaporation). Given in Appendix II (Equation AII.15). See Table AII.1 for an alternative expression.</td>
</tr>
<tr>
<td>Condensation</td>
<td>$\frac{1}{\alpha_M N_x d_{pf}^2 \beta_v}$</td>
<td>Usually underestimates by an order of magnitude.</td>
</tr>
<tr>
<td>Ionized vapor deposition</td>
<td>$\frac{1}{N_x d_{pf}^2 \beta_v \Theta}$</td>
<td>Assumes all ions are captured. Based on CEM. Derived in similar fashion with the expression for condensation above. Similar accuracy is expected. $\Theta = \left[1 + \eta + 0.1 \eta^2 \left(\frac{\lambda_D}{\lambda_{i,m}}\right)\right]$, $\eta = \frac{</td>
</tr>
<tr>
<td>Particle heating</td>
<td>$\frac{d_p \rho_p C_p}{6U}$</td>
<td>Based on cooling by conduction and radiation. Given in Chapter 6 (Equation 6.19).</td>
</tr>
<tr>
<td>Nucleation</td>
<td>$0.05 \left(\frac{\rho_p^4}{m_s} \right)^{1/6} \left(\frac{k_B T_i}{p_0}\right)^{1/2}$</td>
<td>Assumes that the critical nucleus size is a dimer. Derived from the collision rate of monomers in the free molecular regime.</td>
</tr>
</tbody>
</table>
References


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