INVESTIGATING THE EFFECT OF CAPPING LAYERS ON FINAL THIN FILM MORPHOLOGY AFTER A DEWETTING PROCESS

by

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Investigating the Effect of Capping Layers on Final Thin Film Morphology After a Dewetting Process

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Utah State University, 2016

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Nanoparticles on a substrate have numerous applications in nanotechnology, from enhancements to solar cell efficiency to improvements in carbon nanotube growth. Producing nanoparticles in a cheap fashion with some control over size and spacing is difficult to do, but desired. This work presents a novel method for altering the radius and pitch distributions of nickel and gold nanoparticles in a scalable fashion. The introduction of alumina capping layers to thin nickel films during a pulsed laser-induced dewetting process has yielded reductions in the mean and standard deviation of radii and pitch for dewet nanoparticles. Carbon nanotube mats grown on these samples show a much thicker mat for the capped case. The same capping layers have produced an opposite effect of increased nanoparticle size and spacing during a solid state dewetting process of a gold film. These results also show a decrease in the magnitude of the effect as the capping layer thickness increases. Since the subject of research interest for using these nanoparticles has shifted towards producing ordered arrays with size and spacing control, the uncertainty in the values of these distributions needs to be quantified for any form of meaningful comparison to be made between fabrication methods. Presented here is a first step in the uncertainty analysis of such samples via synthetic images producing error distributions.
PUBLIC ABSTRACT

Investigating the Effect of Capping Layers on Final Thin Film Morphology After a Dewetting Process

Benjamin C. White

Nanoparticles on a substrate have numerous applications in nanotechnology, from enhancements to solar cell efficiency to improvements in carbon nanotube growth. Producing nanoparticles in a cheap fashion with some control over size and spacing is difficult to do, but desired. This work presents a novel method for altering the size and spacing of nickel and gold nanoparticles. Dewetting is a methodology to reduce thin films to an ensemble of discrete droplets. The introduction of alumina capping layers to thin nickel films during a pulsed laser-induced dewetting process has yielded reductions in the mean and standard deviation of radii and pitch for dewet nanoparticles with no noticeable difference in final morphology with increased capping layer thickness. The differences in carbon nanotubes grown on these samples is also presented here, with a much thicker matrix being present for the capped case. The same capping layers have produced an opposite effect of increased nanoparticle size and spacing during a solid state dewetting process of a gold film. These results also show a decrease in the magnitude of the effect as the capping layer thickness increases. Since the subject of research interest for using these nanoparticles has shifted towards producing ordered arrays with size and spacing control, the uncertainty in the values of these distributions needs to be quantified for any form of meaningful comparison to be made between traditional nanoparticle fabrication methods and alternate fabrication methods that are being used to alter the final characteristics of the nanoparticles. Here, we also present a first step in the uncertainty analysis of such samples via synthetic images producing error distributions.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Nanostructured materials present a promising route to both enable a broad range of new technology applications as well as make improvements upon existing technologies. Some examples include flexible sensors or electronic skin based on NPs [1] or improvements to solar cell efficiency via plasmonic NPs [2, 3]. Another application may come from a correlation evidenced between the diameter of NPs catalyzing the growth of CNTs and the final diameter of CNTs synthesized via CVD [4–6]. From this correlation, many studies have been completed to produce narrower distributions of catalytic particle radii in the hope of narrowing the diameter distribution of any CNTs synthesized later. Much of this research has been on reducing the mean size of the particles and, consequently, by applying simple statistics, a narrower size distribution [7]. Regardless of application, some measure of control over nanoparticle size and spacing is desired, however, none of the methods yet presented are a cheap and scalable process producing ideal or near-ideal distributions for particle size and spatial order.

CNTs can be thought of as one or more layers of graphene rolled up into a seamless cylinder. The combination of this lattice geometry and strong carbon-carbon bonding makes CNTs a high performance material with exceptional material properties such as a thermal conductivity larger than diamond, ability to carry large current densities, and a large elastic modulus. These extraordinary properties have placed CNTs at the forefront of materials research. Current and future applications span a wide range such as inclusion in composite materials for heat conduction, mechanical strength, or increased electrical conductivity, dispersion in coatings such as paints that can reduce the biofouling on the hulls of ships, and multiple applications in microelectronics, energy storage and biotechnology [8].

The electronic structure and the extraordinary transport properties of CNTs mentioned above are strongly dependent on the corresponding physical structure, primarily dictated by the diameter, wall number and the orientation of the graphene lattice with respect to the
tube axis (chiral angle) [9]. From this, it is evident that controlling the structure of CNTs during growth would provide some measure of control over the end electronic and transport properties of as-grown CNTs. Despite several decades of research, an in situ process for total control of CNT structure during growth has yet to be determined [10]. Advancements in the field have allowed for some control by evidencing relationships between catalytic film thickness and diameter, and between diameter and wall number [11, 12]. Complete chiral control has recently been achieved through the use of templated molecules to engender specific orientations of carbon atoms [13]. Yet these methods are not processes that exhibit good manufacturing qualities, indicating that there is a need for a scalable process with an element of control over the physical structure of CNTs.

One strategy to create and organize structures at the nanoscale is to harness the inherent self-assembly mechanisms of a material. The physical properties of liquid metals, such as low viscosity and high surface energy, make them prime materials to produce self-assembled metallic nanostructures [14]. Dewetting is a process that uses the self-assembly mechanisms of a material to transform a homogeneous, metastable thin film into a series of NPs through rapid thermal annealing, such as solid state dewetting [15] or PLiD [16, 17]. From this, we propose that dewetting phenomena in thin, catalytic metal films may hold an answer to altering the diameter distributions of as grown CNTs in a self-assembled, scalable process.

By using the method of dewetting to produce NP arrays, an analysis of the array size and spacing statistics needs to be done. A method of doing so is through thresholding, where a greyscale value is chosen such that the vectors are converted to binary. This process is such that any value above this threshold is set to the maximum and below this value, color is set to the minimum. It is evident that during this process some loss of information is unavoidable, however, no uncertainty analyses have been performed to determine how well this process works. Since the goal of this study will be to determine the difference in NP morphology between experimental samples, the uncertainty in the values for particle array statistics needs to be determined for any form of meaningful comparison to be made.
1.2 Literature Review

Dewetting is a physical process where a thin film contacting a solid surface spontaneously rearranges itself into an ensemble of discrete droplets. For example, the rupture of water on a hydrophobic surface for fast drying or an undesired transition from a protective film coating to particles. This process begins with film break up and the formation of holes, then hole growth, and finally film edge retraction and particle formation [15]. The fundamental driving force of this process is a decrease in the system energy that proceeds from one of three different mechanisms: 1) homogeneous nucleation (thermal nucleation of holes), 2) heterogeneous nucleation initiated by some form of “seed” in the form of dust particles, surface defects, etc, and 3) spinodal instabilities initiated by the amplification of small thermal or surface perturbations [18]. The spinodal instability possesses characteristic intermediate nanostructures and consequently can produce NPs with well-defined length scales related to the original film thickness, the properties of the materials, and the ambient gas [18].

Recent years have evidenced an emerging application of dewetting as a tool for creating useful structures at the nanoscale. The use of dewetting for spatial control of NPs already includes probe-assisted dewetting, solvent assisted dewetting [19], laser-assisted dewetting or PLiD, pre-patterning of substrates [20], e-beam assisted dewetting, and a few more [21]. None of these methods exhibit ideal manufacturing qualities (i.e. cheap, self-assembled, scalable, etc.). Thermally activated dewetting techniques are the most scalable of the dewetting process listed here. Solid state and PLiD are the two primary options for thermally activated dewetting, with both having their own distinct benefits. The nanosecond time scales evidenced in PLiD minimize the time that the different materials can interact, indicating that inter-diffusion and chemical interaction are also kept to a minimum. This has the advantages of minimizing film evaporation and ablation as well as stopping the dewetting process at the nanosecond time scale. The combination of these factors leads to a dewetting process that can be carried out with minimal mass loss and interface property changes [18]. Solid state dewetting requires self-diffusion of chemical species, and since this chemical
species is in the solid state, the process is much slower. This can engender oxidation and significant chemical interaction if care is not taken with the choice of elemental systems. However, when care is taken, inter-diffusion can be minimized and larger samples can be used. This indicates that solid state dewetting is a more scalable dewetting technique that lacks the short time scales evidenced with PLiD [15].

Typical films are dewet with a free vertical surface and have their final morphology dictated by the thin film spinodal instability [22]. In addition, islands that form but are connected by thin lines or rivulets of dewet material will become disconnected via the well known Rayleigh-Plateau like instability [23] commonly seen with a jet of falling liquid. The instability mechanisms leading to completion of dewetting are dependent on minimizing the surface free energy of the sample [15, 24] and are commonly dependent on the surface tensions at material boundaries.

Methods for spatial control that exploit alterations to surface tensions have been evidenced using confinement, extra films, or capping layers. For example, non-contact confinement techniques have been seen to produce highly ordered arrays of NPs in certain regions of a polymer film but not for an entire sample [25]. Another group made the addition of a sacrificial antimony layer under a dewetting gold film of varying thickness and saw a tunable increase in particle size [26]. This was a method that exhibited good manufacturing techniques and a large amount of control but was only used to increase size and spacing with the method never being demonstrated as capable of altering size and spacing in both directions. This same group also used a contact foil during a dewetting process to remove some gold from the NPs produced [27]. This has the desired effect of reducing the size but is not an additive process, consequently, the spacing between particles was increased as the gold was removed. Another investigation shows a suppression of dewetting in metallic films by use of a SiO$_2$ capping layer [28]. While this result indicates that capping layers will have an undesired effect in this case of suppressing dewetting behavior, the samples used in this study had metal film thicknesses of 200 nm, with capping thicknesses larger than this. The limited thickness range for dewetting metallic films with capping layers in combination with
the use of films less than 10 nm thick for growing CNTs indicates that samples at smaller length scales need to be tried.

We have two regimes that can occur when dewetting metallic films with capping layers. These options are depicted below in panels (b) and (c) of Fig. 1.1, with panel (a) being the case with no capping layer.

Fig. 1.1: Different dewetting regimes for no capping layer in panel (a) and capping layers in panels (b) and (c). Panel (b) shows the capping film deforming to fill void space with panel (c) not allowing the capping layer to deform and filling the void with a gas through porosity in the capping film.

From here we can determine the difference in energy barriers associated with a dewetting process via an analysis adapted from Reference [29] for samples dewet via PLiD. For the case with no capping layer, the energy change associated with a dewetting perturbation (change in area) can be described by

\[ \Delta E_{\text{uncapped}} = \gamma_{LG} A_1 - \gamma_{LG} A_0, \]  

(1.1)

with \( \gamma_{LG} \) being the interface energy density between the liquid film and ambient and \( A_0 \) and \( A_1 \) being the initial and final surface area of the metallic film. For the case of a capped sample following the regime of panel (c) in Figure 1.1, we have that the change in energy from a dewetting perturbation can be described by

\[ \Delta E_{\text{capped}} = \gamma_{LG} A_1 + \gamma_{SG} A_0 - \gamma_{LS} A_0, \]  

(1.2)
where $\gamma_{S_2G}$ and $\gamma_{LS_1}$ are the interface energy densities at the solid-gas and liquid-solid interfaces, respectively. The difference in these energy barriers is

$$\Delta E_{\text{capped}} - \Delta E_{\text{uncapped}} = A_0 \left( \gamma_{S_2G} - \gamma_{LS_1} + \gamma_{LG} \right).$$  \hfill (1.3)

From here if we include Young’s equation for the capping layer interaction with the melted film, $\gamma_{S_2G} - \gamma_{LS_2} = \gamma_{LG} \cos \theta$, we have the following relation:

$$\Delta E_{\text{capped}} - \Delta E_{\text{uncapped}} = A_0 \left[ (\gamma_{S_2G} - \gamma_{S_1G}) + \gamma_{LG} (1 + \cos \theta) \right].$$  \hfill (1.4)

For dewet films, $0 \leq \theta < \pi$, meaning that the second term in brackets of the equation above is always greater than zero, and the difference of surface tensions (dictated by material choice) is the tunable parameter for adjusting the energy barrier to dewetting. This result indicates that the addition of a capping layer can increase or decrease the energy barrier to dewetting if the substrate and capping layers are chosen appropriately. A change in the energy barrier means that the addition of capping layers will alter the kinetics involved and produce different final morphology. It is important to bear in mind that this analysis assumes short time scales during the dewetting process and that the metallic film is in the liquid phase, making it more applicable to PLiD than to solid state dewetting.

1.3 Hypothesis

Previous studies have shown that alterations in film surface tensions can significantly alter the final distributions of NPs. The goal of this work is to investigate a novel method for spatial control of metallic nanoparticles by altering the surface tension of dewetting thin nickel and gold films through the addition of alumina ($\text{Al}_2\text{O}_3$) and Si capping layers. Even though a previous study shows a suppression of dewetting with the addition of capping layers, use of thinner films ($\sim 5 \text{ nm}$) should reduce the energy barrier enough to allow dewetting to occur. The alterations to the surface tension will change the kinetics of the dewetting process and produce particles of altered size and spacing. The major benefits to
this method, as opposed to others, is that it provides a scalable process for the self-assembly of nanoparticles that has not been evidenced in the literature.

1.4 Objectives

The objectives of this thesis are:

1. Investigate the effect of capping layers as a vertical constraint during the dewetting of metallic films on the final film morphology (i.e. NP diameter and pitch distributions). This investigation will be confined to:

   (a) Dewetting metallic films of Ni or Au.

   (b) Capping layers of either Al\textsubscript{2}O\textsubscript{3} or Si.

   (c) Surface microscopy techniques (SEM, EDS, etc.) to determine the final film morphology.

   The focus of this investigation will not include an optimization of film thickness or material for diameter and pitch distributions.

2. Investigate the differences in individual and group CNT structure grown from any NPs fabricated above. This investigation will be confined to:

   (a) CNTs grown at Utah State University via a CVD process.

   (b) SEM and Raman spectroscopy to determine individual and group structure.

   The focus of this investigation will not include any investigation into the CNT growth process. Raman spectroscopy is a powerful tool for characterizing CNTs, but is not a focus of this thesis. Consequently, the use of this tool is not reviewed in this document but can be found elsewhere in extensive reviews [30,31].

3. Quantify the uncertainty in size and spacing statistics stemming from the use of thresholding programs neglecting any uncertainty from the SEM.
CHAPTER 2
EXPERIMENTAL METHODS

2.1 Sample Fabrication

Samples were fabricated in a class 1000 cleanroom environment at the Center for Nanophase Materials Science at ORNL using RCA clean Si wafers with a 100 nm thick thermally grown oxide. Samples had a 5 nm thick Ni or Au film deposited via DC magnetron sputtering using an AJA International-ATC 2400 Sputtering System. The wafers were not checked for film uniformity, but samples of $\sim$1 cm$^2$ were taken from the same region of the Si wafer, so uniformity is expected. The samples then had one of four different thickness, [0,5,10,20] nm, Al$_2$O$_3$ or Si films deposited by Atomic Layer Deposition (ALD) using an Oxford Instruments FlexAl ALD system.

CNT growth is typically done using thinner catalytic films than the 5 nm thick Ni films used here. The choice of thickness was predicated upon producing a continuous film via sputtering that, once dewet, would have particles of a size that would be easy to image as well as be large enough to show evidence of changes to particle array statistics within the uncertainty calculated later in this document. This choice may not provide conclusive results as to the ability of this method to alter the diameter distribution of as-grown CNTs since the particles are big enough for more than one CNT to grow from them, but will ensure that conclusive results are arrived at as to the ability of this method to alter the size and spacing of dewet NPs.

The solid state dewetting process for the Ni-Al$_2$O$_3$ system was performed in a First nano Easy Tube 3000 Rapid Thermal Processor. The samples were introduced to an Ar:H$_2$=65:35 sccm atmosphere and ramped to 700°C in 10 seconds, baked at this temperature for another 30 seconds, and then ramped down to room temperature in 10 seconds. The PLiD process for the Ni-Al$_2$O$_3$ and Ni-Si systems were carried out using a pulsed, KrF excimer laser, with a wavelength of 248 nm, pulse-width of $18 \pm 2$ ns at full-width-at-half-max, with only one pulse delivered per sample. The area of the laser spot is $\sim$1 cm$^2$ with a fluence of $250 \pm 10$ mJ/cm$^2$, which is sufficient to melt the Ni film [32]. Ni Samples were
then etched in a 3:1:1=$H_2O:NH_4OH:H_2O_2$ solution at 80°C. Each of the experimental samples were etched twice and imaged before and after each etch. Each of the etch processes for the Ni-$Al_2O_3$ system was carried out for three hours. CNT growth was performed in a quartz tube, with feedstock flow of $H_2:Ar:C_2H_4=100:80:20$ sccm at 750°C for 15 minutes.

The solid state dewetting process for the Au-$Al_2O_3$ and Au-Si systems were carried out on a hot plate. Samples were raised to a temperature of $\sim$ 300°C and held at this temperature for 1 hr. Au samples with a $Al_2O_3$ capping layer were etched in the same solution as the Ni samples but for only 1 hr. The difference in time is due to the difference in the dewetting process. The speed of the dewetting process using PLiD produces alumina nanoparticles which have a diameter larger than the original capping layer thickness. The samples dewet in the solid state maintained their capping layer thicknesses and consequently need less time to etch. Au samples with a Si capping layer were etched for 15 minutes in a $KOH:H_2O=10.2g:30ml$ solution @ 50°C. A summary of the samples fabricated is presented in Table 2.1.

Since the energy barrier to dewetting for a gold film is significantly less than that of nickel, the phenomena of Ostwald Ripening, such as that demonstrated later for the etch process of the 5 nm cap layer for the Ni samples, is even more of a problem. To ensure that Ostwald Ripening is not the driving mechanism for any increases in particle statistics, the control sample was imaged both before and after an anneal process. This anneal process simulates the etch that the samples with capping layers undergo by raising the sample to a temperature of 80°C and holding it there in an aqueous solution of water for 1 hour.

Table 2.1: A summary of the samples fabricated, the processes for each, and where to find the results for each type of sample.

<table>
<thead>
<tr>
<th>Film</th>
<th>Capping Layer</th>
<th>Dewet Method</th>
<th>Capping Layer Etch</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>$Al_2O_3$</td>
<td>PLiD</td>
<td>3:1:1=$H_2O:NH_4OH:H_2O_2$ @ 80°C</td>
<td>Sec. 3.2</td>
</tr>
<tr>
<td>Ni</td>
<td>$Al_2O_3$</td>
<td>Solid State</td>
<td>3:1:1=$H_2O:NH_4OH:H_2O_2$ @ 80°C</td>
<td>App. B.1</td>
</tr>
<tr>
<td>Ni</td>
<td>Si</td>
<td>PLiD</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Au</td>
<td>$Al_2O_3$</td>
<td>Solid State</td>
<td>3:1:1=$H_2O:NH_4OH:H_2O_2$ @ 80°C</td>
<td>Sec. 3.3</td>
</tr>
<tr>
<td>Au</td>
<td>Si</td>
<td>Solid State</td>
<td>$KOH:H_2O=10.2g:30ml$ @ 50°C</td>
<td>App. B.2</td>
</tr>
</tbody>
</table>
2.2 Morphology Investigation

The surface morphology of the films and any as-grown CNTs was investigated with the use of a FEI Quanta FEG SEM. The particle sizes extracted from any SEM images were analyzed using a Monte Carlo Search Method in a nanoparticle analyzer written at ORNL. An example of what the analyzer does to the SEM images is presented in Figure 2.1 for the case of no capping layer.

![Fig. 2.1: The left panel illustrates an SEM image taken of Ni NPs. The right panel illustrates the image after the thresholding, edge removal, particle filling and noise reduction processes from the nanoparticle analyzer.](image)

In this figure several processes have been completed going from the standard SEM image to the black and white image. The image has already been cropped to remove the scale bar. Any particles on the edge of the image that are not complete have already been removed. The image was then set to a threshold to convert the greyscale image to black and white. Noise reduction and particle filling routines were run multiple times to achieve the best match with the initial SEM image. For the cases where there is an dewet alumina capping layer on top of the Ni NPs, the cropping function was used to manually reduce the areas that are being analyzed to not include the large $\text{Al}_2\text{O}_3$ particles and then iterated through the image to include all possible Ni NPs. Aspects of as-grown CNTs were investigated using Raman spectroscopy, performed using a Renishaw in-via Raman Microscope with a 633 nm wavelength HeNe laser.
2.3 Uncertainty

Any uncertainty for size and spacing values arrived at via thresholding will stem from two sources: the microscope and the thresholding process. Due to time constraints and the difficulty involved in quantifying the effect of microscope focus, beam alignment, stigmation, and other parameters that affect images taken with a SEM, the uncertainty stemming from use of the microscope is neglected in this analysis. Because microscope uncertainty is neglected, the only source of uncertainty will come from a calibration of the thresholding programs. For all calibration cases, the image pixel density and particle coverage (how many pixels a particle covers) will couple into the resolution (i.e. how well the curvature of a particle can be approximated). Additionally, since the particles in actual images have a range of sizes, varying levels of resolution should be used in calibration. Therefore, different ratios of coverage to image pixel density will be used for each type of calibration sample. Computer code to fabricate an image has been included in Appendix A.3.

Typical images that are being processed using this program have many particles covering the substrate. Therefore, calibration samples will be an array of NPs generated in the computer with known radius and pitch statistics. A truncated Gaussian shaped curve will be used as a greyscale intensity of each nanoparticle with a pseudorandom background set below the intensity of the particles used as the substrate. Additionally, random noise will be added to the greyscale vectors in an attempt to more closely simulate the noise coming from the microscope and the fluctuations seen in real samples.

The real samples analyzed will be NPs composed of either gold or nickel. These two systems exhibit different characteristics in how they interact with the SEM. An example of a difference can be seen in a histogram of intensity values, Figure 2.2, from a typical Au and Ni NP array. Consequently, images have been fabricated to resemble the trends seen here. An example of a typical fabricated image of both the Ni and Au type can be seen in Figure 2.3 along with a histogram of intensity values for comparison to Figure 2.2.

The fabricated images of Figure 2.3 are an example of the first calibration sample.
Identical NPs have been placed equidistant from each other to simulate a single particle many times within one image. The particle radius was varied as \( r = [10, 15, 20, 30] \) pixels. This type of image will yield information as to the ability of the programs to correctly identify the size of a single particle. Additional calibration samples will differ only in that the radius and pitch will be distributed as \( r = N(\bar{r}, s_r) \) and \( p = N(\bar{p}, s_p) \) instead of as \( r = N(\bar{r}, 0) \) and \( p = N(\bar{p}, 0) \), which is the first calibration sample. The first calibration sample will only be simulated once at each value of \( r \) and for each of the two elemental systems. Subsequent samples will be simulated 250 times at each of the factor levels mentioned previously. After analysis, error distributions will be extracted from the error in the mean of radius and pitch for each of the 250 images for each case. These error distributions will be used to estimate an uncertainty in the values determined from the real images analyzed. Since this analysis is only being done using a single computer, by a single person, there will be no calculation of a bias distribution. This indicates that the bias uncertainties calculated here persist in only one direction. As a result, they will not be included in the 95% confidence intervals reported later.

Fig. 2.2: An example of both the Au and Ni systems imaged via SEM and a histogram of intensity values from the images.
Fig. 2.3: An example of both the Au- and Ni-like systems fabricated and a histogram of intensity values from the images, attempting to resemble those seen in Fig 2.2.
CHAPTER 3
RESULTS AND DISCUSSION

A brief summary of the experimental systems, some of their issues, and where to find the results is briefly presented here, followed by the results themselves. From the objectives and Table 2.1, there will be 5 different dewetting systems of interest. The solid state dewet Ni-Al$_2$O$_3$ system, the liquid phase dewet Ni-Al$_2$O$_3$ system, the liquid phase dewet Ni-Si system, the solid state dewet Au-Al$_2$O$_3$ system, and the solid state dewet Au-Si system. The results for the liquid phase dewet Ni-Al$_2$O$_3$ system and the solid state dewet Au-Al$_2$O$_3$ system are presented in sections 3.2 and 3.3 of this chapter. The solid state dewet Ni-Al$_2$O$_3$ system shows results that will not produce homogeneous NP arrays, indicating that this system is not a good one for the method of altering NP size and spacing presented in this document. The initial results of this study are depicted in Appendix B.1. The Ni-Si system was dewet in the liquid phase. The initial goal of this system was to see if we could alter the size and spacing of nickel silicide particles. This presents a very complicated material process where the nickel and silicon can bond together in the liquid phase. These samples were to be compared to PLiD NiSi$_2$ films to see if having the two constituent materials be separate at the beginning would affect the final morphology. Due to the complexity of this system and the difficulty in imaging due to a much smaller size, results are not presented in this document. The Au-Si system suffers from a small flaw in the material system choice. The etch to remove the Si capping layer also etches SiO$_2$, which is the substrate the Au film is deposited on. Upon attempting to remove the Si capping layer, part of the substrate is etched as well and information about the size and spacing of the nanoparticles is not capable of being extracted. Some images prior to these attempted etches are presented in Appendix B.2. In the future this system would be better attempted using an alumina substrate with a Si capping layer so that the substrate will be unaffected by the etch process. Additionally, the results of the uncertainty analysis are presented first in section 3.1 so that uncertainty may be included in the following sections.
3.1 Uncertainty

The first calibration sample shows results for the ability of the program to identify
the size of a single particle. Particle size distributions are pictured in Figures 3.1 and 3.2
for the gold and nickel systems, respectively. The data result in bias and random single
particle errors as enumerated in the Tables 3.1 and 3.2. From the tables it is clear that the
program will always underestimate the size and spacing of the nanoparticles due to loss of
information at the particle edge during the thresholding process. The relative magnitude
of this error will depend on the image parameters. From the data, the nickel system has a
significantly worse error, as expected, due to the histogram of intensities seen in Figure 2.3.
This figure indicates that for the nickel system it is more difficult to identify the distribution
of the background separate from that of the NPs, leading to more loss of information when
the thresholding is executed, as compared to the Au system.

Table 3.1: Tabular values of the radii and pitch error distribution statistics for fabricated
Au samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>$\beta_r$</th>
<th>$\varepsilon_r$</th>
<th>$\beta_p$</th>
<th>$\varepsilon_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.03</td>
<td>0.021</td>
<td>0.0</td>
<td>0.041</td>
</tr>
<tr>
<td>15</td>
<td>-0.03</td>
<td>0.019</td>
<td>0.0</td>
<td>0.028</td>
</tr>
<tr>
<td>20</td>
<td>-0.1</td>
<td>0.024</td>
<td>0.0</td>
<td>0.034</td>
</tr>
<tr>
<td>30</td>
<td>-0.4</td>
<td>3.1</td>
<td>1.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Table 3.2: Tabular values of the radii and pitch error distribution statistics for fabricated
Ni samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>$\beta_r$</th>
<th>$\varepsilon_r$</th>
<th>$\beta_p$</th>
<th>$\varepsilon_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-1.25</td>
<td>0.13</td>
<td>-1.0</td>
<td>0.25</td>
</tr>
<tr>
<td>15</td>
<td>-1.3</td>
<td>0.12</td>
<td>-1.0</td>
<td>0.18</td>
</tr>
<tr>
<td>20</td>
<td>-1.4</td>
<td>0.12</td>
<td>0.2</td>
<td>0.18</td>
</tr>
<tr>
<td>30</td>
<td>-4.0</td>
<td>5.8</td>
<td>-5.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>
Fig. 3.1: Radius and pitch histograms from the first calibrations samples for the Au systems. These show single particle uncertainties. All values are in pixels.

Fig. 3.2: Radius and pitch histograms from the first calibrations samples for the Ni systems. These show single particle uncertainties. All values are in pixels.
In the previous tables and figures the values shown for \( r = 30 \) pixels could be seen as an anomaly. The difference between this case and the cases with smaller radii are that the program finds particles that are not actually there. A more detailed discussion of this will appear later in this document.

The rest of the calibration samples were decomposed into error distributions for each case. A histogram of each of these error distributions can be seen in the first and second sections of the appendix for the Au and Ni systems, respectively. The median and the range containing 95\% of the data for the error in radius statistics, for each case, can be found in Tables 3.3 and 3.5 for the gold and nickel samples, respectively. The median and the range containing 95\% of the data for the error in pitch statistics, for each case, can be found in Tables 3.4 and 3.6, for the gold and nickel samples, respectively. Here, the median and 95\% coverage can be thought of as bias and random errors, respectively.

Table 3.3: Tabular values of the radii error distribution statistics for fabricated Au samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>( m_r )</th>
<th>( s_{r,95} )</th>
<th>( m_{s_r} )</th>
<th>( s_{s_r,95} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.128</td>
<td>[-0.0346,0.0384]</td>
<td>0.0306</td>
<td>[-0.0292,0.0327]</td>
</tr>
<tr>
<td>15</td>
<td>-0.121</td>
<td>[-0.0426,0.0311]</td>
<td>0.0177</td>
<td>[-0.0312,0.0561]</td>
</tr>
<tr>
<td>20</td>
<td>-0.118</td>
<td>[-0.0723,0.0377]</td>
<td>0.018</td>
<td>[-0.0377,0.143]</td>
</tr>
<tr>
<td>30</td>
<td>-0.92</td>
<td>[-0.758,0.516]</td>
<td>1.93</td>
<td>[-1.18,1.26]</td>
</tr>
</tbody>
</table>

Table 3.4: Tabular values of the pitch error distribution statistics for fabricated Au samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>( m_p )</th>
<th>( s_{p,95} )</th>
<th>( m_{s_p} )</th>
<th>( s_{s_p,95} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.021</td>
<td>[-0.0323,0.0176]</td>
<td>-0.0167</td>
<td>[-0.0479,0.0226]</td>
</tr>
<tr>
<td>15</td>
<td>-0.0185</td>
<td>[-0.028,0.0849]</td>
<td>-0.0167</td>
<td>[-0.115,0.0199]</td>
</tr>
<tr>
<td>20</td>
<td>-0.0268</td>
<td>[-0.0976,0.0846]</td>
<td>-0.0223</td>
<td>[-0.0655,0.0485]</td>
</tr>
<tr>
<td>30</td>
<td>-2.29</td>
<td>[-2.12,1.51]</td>
<td>5.57</td>
<td>[-3.26,3.07]</td>
</tr>
</tbody>
</table>
Table 3.5: Tabular values of the radii error distribution statistics for fabricated Ni samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>$m_r$</th>
<th>$s_{r,95}$</th>
<th>$m_{sr}$</th>
<th>$s_{sr,95}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.94</td>
<td>[-0.36,0.34]</td>
<td>0.0937</td>
<td>[-0.0863,0.0637]</td>
</tr>
<tr>
<td>15</td>
<td>-1.35</td>
<td>[-0.729,0.427]</td>
<td>0.173</td>
<td>[-0.185,0.1]</td>
</tr>
<tr>
<td>20</td>
<td>-1.82</td>
<td>[-1.26,0.717]</td>
<td>0.151</td>
<td>[-0.203,0.488]</td>
</tr>
<tr>
<td>30</td>
<td>-5.35</td>
<td>[-3.02,3.27]</td>
<td>4.25</td>
<td>[-3.01,1.80]</td>
</tr>
</tbody>
</table>

Table 3.6: Tabular values of the pitch error distribution statistics for fabricated Ni samples. All values are in pixels.

<table>
<thead>
<tr>
<th>Radius</th>
<th>$m_p$</th>
<th>$s_{p,95}$</th>
<th>$m_{sp}$</th>
<th>$s_{sp,95}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.023</td>
<td>[-0.032,0.0242]</td>
<td>-0.0149</td>
<td>[-0.0451,0.0349]</td>
</tr>
<tr>
<td>15</td>
<td>-0.023</td>
<td>[-0.158,0.0263]</td>
<td>-0.0124</td>
<td>[-0.0486,0.4385]</td>
</tr>
<tr>
<td>20</td>
<td>-0.27</td>
<td>[-1.28,0.269]</td>
<td>0.694</td>
<td>[-0.773,3.99]</td>
</tr>
<tr>
<td>30</td>
<td>-9.92</td>
<td>[-8.85,8.07]</td>
<td>16.9</td>
<td>[-12.4,7.14]</td>
</tr>
</tbody>
</table>

The tables above, again, indicate that the data for $r = 30$ have something different from the rest of the samples. To further investigate this, histograms showing the error in how many particles were found by the program were created. These are evidenced in Figures 3.3 and 3.4 for the Au and Ni systems, respectively. The histograms indicate that as the radius of the particles gets large there are more particles found by the program than actually exist. Upon further investigation it was determined that this is due to the creation of false particles at the receded edges of the actual particles when the thresholding program was executed. This will have the effect of artificially deflecting the mean of the radius and pitch and also artificially inflating the standard deviation of the radius and pitch. From this, it is clear that there is an optimum pixel coverage for particles that can be achieved via adjustments to microscope magnification to reduce the uncertainty engendered from the thresholding process.
Fig. 3.3: Histograms of the error in number of particles found for each size of particle for the Au system.

Fig. 3.4: Histograms of the error in number of particles found for each size of particle for the Ni system.
3.2 Ni-Al$_2$O$_3$ System

The control sample for this study was the case of no capping layer. An SEM image along with representative radii and pitch distributions for the control sample can be seen in Figure 3.5. For the cases with a capping layer, SEM images and their corresponding radii and pitch distributions, before and after each of the two etches, can be found in Figures 3.6-3.8, respectively.

For the case where the capping layer is 5 nm thick, the initial etch appears to have removed the majority of the Al$_2$O$_3$ with the second etch removing any small non-nickel particles from the surface. The second etch also appears to have allowed for the migration of NPs at the elevated temperature, a phenomena known as Ostwald Ripening, indicating that only one etch is necessary for this thickness. The final values presented, for samples with a 5 nm cap, will be acquired from images taken prior to the second etch.

These distributions were then used to calculate a mean and standard deviation of all the nickel particles that were affected by the addition of capping layers. Values illustrating trends in the mean and standard deviation with respect to capping layer thickness are presented in Table 3.7. From this table and figures of results, the reduction in particle size and distribution spread is evident. Final values from the table indicate that optimal results will be achieved for capping layer thicknesses of 10 and 20 nm. However, upon examination of the SEM images for the case with the 10 nm cap, the etch does not appear to have removed all of the alumina particles from the surface. This indicates that the optimum system would be to have a 20 nm capping layer.

The uncertainty of these values will be a combination of the conversion uncertainty from pixels to micron and the calibration uncertainty. The images analyzed have a scale bar of 2 $\mu$m spanning 370±1 pixels. With these parameters, this image will have particles that are $\leq$10 pixels in radius. The conversion uncertainty is 1 pixel or 5.41 nm and will only be evident in the uncertainty of the mean. Since all images have mean particle sizes that do not exceed 10 pixels the bias and random calibration errors will be the same for all capping layer thicknesses. Pulling values from Table 3.5 and converting to nm yields bias and random
calibration uncertainties on the mean radius of -5.08 nm and [-1.95, 1.84] nm, respectively. Combining the conversion uncertainty with the random uncertainty from calibration yields one sided uncertainties of [-5.75, 5.71] nm on the mean radius. The same analysis performed for the pitch by pulling values from Table 3.6 yields a bias uncertainty of -0.1243 nm and a combined two-sided random uncertainty from calibration and conversion of 5.41 nm. Final 95% confidence intervals on the means for random uncertainty are presented in Table 3.8.

SEM images after CNT growth can be seen in the top panel of Figure 3.9. From these images, it is clear that the addition of a capping layer to reduce NP size and spacing has engendered a much different CNT mat than the control sample. The area density of the CNTs has increased greatly, with no evidence of NP agglomeration during the growth process. Additional differences after growth come from the Raman spectra for each sample presented in the bottom panel of Figure 3.9. The most prominent feature of these spectra is the relative difference in magnitude of the disorder (D) band. The ratio of the D to G band is 1.14 for the case with no capping layer and 1.56 for the case with a 20 nm cap. These results indicate an increase in the signal from the disorder band. This could be an indication of more defects in the CNTs grown on the 20 nm cap sample, but this result could also be a by-product of there being significantly more CNTs on the capped sample.

![Fig. 3.5: The SEM image and the distributions for radii and pitch for the case with no capping layer.](image-url)
Fig. 3.6: The SEM images for all three capping layer thicknesses before and after the etches.
Fig. 3.7: The radii distributions for all three capping layer thicknesses before and after the etches.
Fig. 3.8: The pitch distributions for all three capping layer thicknesses before and after the etches.

Table 3.7: Tabulated values for the means and standard deviations of the radii and pitch distribution for each of the four capping layer thicknesses.

<table>
<thead>
<tr>
<th>Cap Thickness (nm)</th>
<th>$\bar{r}$ ($\mu$m)</th>
<th>$s_r$ ($\mu$m)</th>
<th>$\bar{p}$ ($\mu$m)</th>
<th>$s_p$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0571</td>
<td>0.0195</td>
<td>0.216</td>
<td>0.0476</td>
</tr>
<tr>
<td>5</td>
<td>0.0360</td>
<td>0.0140</td>
<td>0.145</td>
<td>0.0478</td>
</tr>
<tr>
<td>10</td>
<td>0.0348</td>
<td>0.0116</td>
<td>0.134</td>
<td>0.0345</td>
</tr>
<tr>
<td>20</td>
<td>0.0326</td>
<td>0.0117</td>
<td>0.124</td>
<td>0.0342</td>
</tr>
</tbody>
</table>
Table 3.8: Tabulated values for the 95% random confidence intervals (CI) and bias (b) uncertainties from calibration of the means of the radii and pitch distribution for each of the four capping layer thicknesses for the Ni samples.

<table>
<thead>
<tr>
<th>CI_r (nm)</th>
<th>b_r (nm)</th>
<th>CI_p (nm)</th>
<th>b_p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[52.35,62.81]</td>
<td>-5.08</td>
<td>210.6,221.4</td>
<td>-0.1243</td>
</tr>
<tr>
<td>[30.25,41.71]</td>
<td>-5.08</td>
<td>139.6,150.4</td>
<td>-0.1243</td>
</tr>
<tr>
<td>[29.55,40.51]</td>
<td>-5.08</td>
<td>128.6,139.4</td>
<td>-0.1243</td>
</tr>
<tr>
<td>[26.35,38.31]</td>
<td>-5.08</td>
<td>118.6,129.4</td>
<td>-0.1243</td>
</tr>
</tbody>
</table>

Fig. 3.9: SEM images and respective Raman spectra for an uncapped sample in the left panel and a 20 nm thick capped sample in the right panel after CNT growth.
3.3 Au-Al$_2$O$_3$ System

The control sample was imaged prior to its anneal to test for Ostwald Ripening. The control sample image and radii and pitch distributions can be found in Figure 3.10. SEM images after the etches for each of the four samples can be seen in Figure 3.11 with their radii and pitch distributions in Figure 3.12. From Tables 3.9 and 3.10 and a comparison of SEM images in Figure 3.10 and the top left panel of Figure 3.11, it is clear that the anneal process on the control sample had no effect on particle statistics, ruling out Ostwald Ripening as the driving force behind the increase in particle size and spacing. Tables 3.9 and 3.10 show statistics for the distributions. Due to the distributions being asymmetric, parameters describing spread will be intervals covering 95% of the data in the distribution.

Trends in radii and pitch can be seen in Figure 3.13. There is an initial increase in the size and spacing with the addition of the 5 nm capping layer, with this effect becoming less pronounced as capping layer thickness increases. Since the thickness of the capping layers is 5 nm or larger, increasing thickness should not have a significant effect in altering surface tension. The difference in the effect of the capping layer with increasing thickness indicates that factors other than surface tension could be affecting the kinetics. The Ni-Al$_2$O$_3$ system, from Sec. 3.2, did not show a trend where increasing thickness had a different effect on the final particle statistics. The main difference between the two systems is in the choice of material and in the method of dewetting (specifically the time scales involved). The differences in trends seen here is most likely a combination of the two factors, with the choice of material system causing the increase or decrease in the particle size and spacing and the dewetting method causing the difference in trends with increasing capping layer thickness.

The uncertainty of these values will be a combination of the conversion uncertainty from pixels to micron and the calibration uncertainty. The images analyzed have a scale bar of 1 µm spanning 370±1 pixels. With these parameters the control image will have particles that are ~10 pixels in radius and the experimental samples will have particles that are ~20 pixels in radius. The conversion uncertainty is 1 pixel or 2.703 nm and will only
be evident in the uncertainty of the median. Pulling values from Table 3.3 and converting to nm yields bias and random calibration uncertainties on the median radius of the control sample of $-0.346$ nm and $[-0.0935,0.1038]$ nm, respectively. Combining the conversion uncertainty with the random uncertainty from calibration yields a two-sided uncertainty of $2.71$ nm on the mean radius. The same analysis performed for the pitch by pulling values from Table 3.4 yields a bias uncertainty of $-0.057$ nm and a combined two-sided random uncertainty from calibration and conversion of $2.7$ nm. Performing the same analysis on the experimental samples yields a bias uncertainty of $-0.319$ nm and a combined two sided random uncertainty from calibration and conversion of $2.7$ nm for the radius. The results for pitch show a bias uncertainty of $-0.0724$ nm and a combined two sided random uncertainty from calibration and conversion of $2.7$ nm. The combined random uncertainty for all of the samples is approximately the same despite having different calibration uncertainties. This is because the conversion uncertainty from pixels to nm is the largest source of uncertainty for Au type samples. Final 95% confidence intervals on the means for random uncertainty are presented in Table 3.11.

Fig. 3.10: The SEM image and the distributions of the Au-Al2O3 system for radii and pitch for the case with no capping layer prior to the anneal
Fig. 3.11: The SEM images for all four samples from the Au-Al₂O₃ system after the anneal on the control sample and the etches for the experimental samples.

Table 3.9: Tabulated values for the median \( (r_m) \), intervals covering 95\% of the data \( (I_{95\%}) \), and the spread of this interval \( (S_I) \) of the radii distribution for each of the capping layer thicknesses for the Au-Al₂O₃ system.

<table>
<thead>
<tr>
<th>Cap Thickness (nm)</th>
<th>( r_m ) (nm)</th>
<th>( I_{95%} ) (nm)</th>
<th>( S_I ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (prior to anneal)</td>
<td>14</td>
<td>[7.8, 24.4]</td>
<td>16.6</td>
</tr>
<tr>
<td>0 (post anneal)</td>
<td>14.2</td>
<td>[7.25]</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>18.4</td>
<td>[7.94]</td>
<td>29.1</td>
</tr>
<tr>
<td>10</td>
<td>17.3</td>
<td>[8.6, 32.7]</td>
<td>24.1</td>
</tr>
<tr>
<td>20</td>
<td>15.6</td>
<td>[7.8, 32.5]</td>
<td>24.7</td>
</tr>
</tbody>
</table>

Table 3.10: Tabulated values for the median \( (p_m) \), intervals covering 95\% of the data \( (I_{95\%}) \), and the spread of this interval \( (S_I) \) of the pitch distribution for each of the capping layer thicknesses for the Au-Al₂O₃ system.

<table>
<thead>
<tr>
<th>Cap Thickness (nm)</th>
<th>( p_m ) (nm)</th>
<th>( I_{95%} ) (nm)</th>
<th>( S_I ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (prior to anneal)</td>
<td>37.4</td>
<td>[26.4, 53.3]</td>
<td>26.8</td>
</tr>
<tr>
<td>0 (post anneal)</td>
<td>36.9</td>
<td>[25.6, 52.5]</td>
<td>26.9</td>
</tr>
<tr>
<td>5</td>
<td>56.9</td>
<td>[33.4, 87.3]</td>
<td>53.9</td>
</tr>
<tr>
<td>10</td>
<td>51.3</td>
<td>[32.9, 76.6]</td>
<td>43.7</td>
</tr>
<tr>
<td>20</td>
<td>47.2</td>
<td>[30.4, 72.8]</td>
<td>42.4</td>
</tr>
</tbody>
</table>
Fig. 3.12: The radii and pitch distributions for all four samples from the Au-Al$_2$O$_3$ system after the anneal on the control sample and the etches for the experimental samples.
Table 3.11: Tabulated values for the 95% random confidence intervals (CI) and bias (b) uncertainties from calibration of the means of the radii and pitch distribution for each of the four capping layer thicknesses for the Au samples.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>-0.01</td>
</tr>
<tr>
<td>15</td>
<td>0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>20</td>
<td>0.06</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Fig. 3.13: Trends in the median pitch and radii for each of the capping layer thicknesses of the Au-Al₂O₃ system
CHAPTER 4
CONCLUSION

Here we have presented a scalable process to alter the radii and pitch distributions of nickel and gold NPs and shown the differences in as-grown CNT mats for the Ni samples. The mean and standard deviation of the size and spacing of the Ni NPs were reduced with the addition of different thickness alumina capping layers prior to dewetting. Analysis of the final NPs shows approximately a 43% decrease in both the mean particle radii and pitch between particles for the optimum case. The standard deviation of particle radii was reduced by approximately 40% and the pitch standard deviation by approximately 28%. The mean size and spacing of the Au NPs was increased successfully with a reduced effect seen for thicker capping films. A potential explanation for the reduced effect may lie in the choice of dewetting mechanism, specifically the time scales involved. The alterations in the particle distributions presented here are only a first step towards size and spacing control of self-assembled nanoparticles. Also presented in this work is a calibration analysis of programs used to extract the radius and pitch distributions. Error distributions for varying levels of particle coverage have been created, indicating that when particles cover too many pixels, false particles can be created, leading to a significantly less accurate answer.

Future work should include an analysis of different thickness catalytic films and an analysis of the instability modes of the dewetting films. Additional analysis should also try to capture the difference between solid state and liquid phase dewetting as it applies to using capping layers, with further investigation of the time scales involved and which factors come in to play across these time scales. Additional uncertainty work would include an analysis of the bias errors from the calibration to extract a bias distribution. For the Au system this is not a problem as all calibration uncertainty can be neglected by the rule of four, but this would represent a significant improvement in the Ni system. Further work should also include an analysis of rivulets. This work only dealt with circular particles for calibration, however, the majority of real samples have particles that are not circular.
REFERENCES


APPENDICES
A.1 Au Error Distributions

\textbf{Au Error Distributions for } r=10 \\

\textbf{Mean} \\

\begin{align*}
\text{Mean} & = -0.128 \\
I_{95} & = [-0.16,-0.09]
\end{align*}

\textbf{Std. Dev.} \\

\begin{align*}
\text{Mean} & = 0.0306 \\
I_{95} & = [0.0014,0.063]
\end{align*}

\textbf{Radius} \\

\begin{align*}
\text{Mean} & = -0.021 \\
I_{95} & = [-0.053,-0.0033]
\end{align*}

\textbf{Pitch} \\

\begin{align*}
\text{Mean} & = -0.0167 \\
I_{95} & = [-0.065,0.0059]
\end{align*}

\textbf{Error [Pixels]} \\

\begin{align*}
\text{Mean} & = -0.08 \\
I_{95} & = [-0.06,0.04]
\end{align*}

Fig. A.1: Gold error distributions in mean and standard deviation of radii and pitch for \( r=10 \)
Fig. A.2: Gold error distributions in mean and standard deviation of radii and pitch for r=15

Fig. A.3: Gold error distributions in mean and standard deviation of radii and pitch for r=20
Fig. A.4: Gold error distributions in mean and standard deviation of radii and pitch for \( r=30 \)
A.2 Ni Error Distributions

Fig. A.5: Nickel error distributions in mean and standard deviation of radii and pitch for \( r=10 \)

Fig. A.6: Nickel error distributions in mean and standard deviation of radii and pitch for \( r=15 \)
Fig. A.7: Nickel error distributions in mean and standard deviation of radii and pitch for $r=20$

Fig. A.8: Nickel error distributions in mean and standard deviation of radii and pitch for $r=30$
A.3 Computer Code

General Program

% Defining the number of pixels in each direction
imageSizeX = 1536;
imageSizeY = 1103;

nx = 16; ny = 11;

nP = nx*ny;

% Defining how many pixels in a radius
mean_rad = 30;

std_rad = 5;

true_radius = mean_rad + std_rad*randn(nP,1);

radius = round(true_radius);

% Making a folder to put data and image in
fold = ['Radius',num2str(mean_rad,3),'/'];

 [~,~,~] = mkdir(fold);

% Determining the mean center for all points

distx = (imageSizeX-4*mean_rad-50)/(nx-1);


disty = (imageSizeY-4*mean_rad-50)/(ny-1);


distx = disty;

centerx = round([75,75+(1:1:nx-1).*distx]);

centery = round([75,75+(1:1:ny-1).*disty]);

% Creating a noisy background

bckgnd = 0.5 + (0.15)*randn(imageSizeY,imageSizeX);

% Normalizing the background

bckgnd = bckgnd/max(max(bckgnd));

% Adding randomness to the pitch

xpitch_rand = round(5*randn(nP,1));
ypitch_rand = round(5*randn(nP,1));

% A counting variable
n = 0;
for i = 1:length(centerx)
    for j = 1:length(centery)
        n = n+1;
    end
end

% making a single particle with a radius of radius and an intensity
% standard deviation of std_dev
std_dev = radius(n)/1.5;
gaussPart = make_particle(radius(n),std_dev);

% Setting the x and y positions of the particle centers
yindex(i,j) = centery(j) + ypitch_rand(n);
xindex(i,j) = centerx(i) + xpitch_rand(n);

% Placing a particles on image
temp = bckgnd(yindex(i,j)-length(gaussPart)/2+1:yindex(i,j) +...  
    length(gaussPart)/2,xindex(i,j)-...  
    length(gaussPart)/2+1:xindex(i,j)+length(gaussPart)/2);
temp = temp + gaussPart;
bckgnd(yindex(i,j)-length(gaussPart)/2+1:yindex(i,j) +...  
    length(gaussPart)/2,xindex(i,j)-...  
    length(gaussPart)/2+1:xindex(i,j)+length(gaussPart)/2) = temp;
end

% Normalizing the image again
bckgnd = bckgnd/max(max(bckgnd));
img = uint8(mat2gray(bckgnd)*255);

% Creating the image and saving it
% figure('WindowStyle','Modal');
% imshow(img);
imwrite(img,[fold,'image.tif'])
% Collecting the actual pitch data
pitch = [];
for i = 1:size(xindex,1)
    for j = 1:size(xindex,2)
        temp1(1:3) = Inf;
        % Playing indexing games
        if(i==1)
            lbi = i;
            ubi = i+1;
        elseif(i==size(xindex,1))
            ubi = i;
            lbi = i-1;
        else
            lbi = i-1;
            ubi = i+1;
        end
        if(j==1)
            lbj = j;
            ubj = j+1;
        elseif(j==size(xindex,2))
            ubj = j;
            lbj = j-1;
        else
            lbj = j-1;
            ubj = j+1;
        end
% Determining minimum two nearest neighbor distances
for ii = lbi:ubi
    for jj = lbj:ubj
        if(ii==i & jj==j)
            continue
        end
        temp1(3) = sqrt((xindex(i,j)-xindex(ii,jj))^2+...
                        (yindex(i,j)-yindex(ii,jj))^2);
        if(temp1(3)<=temp1(1) & temp1(3)~=0)
            temp1(2) = temp1(1);
            temp1(1) = temp1(3);
            temp1(3) = Inf;
        elseif(temp1(3)<=temp1(2) & temp1(3)>temp1(1) &...
            temp1(3)~=0)
            temp1(2) = temp1(3);
            temp1(3) = Inf;
        else
            continue
        end
    end
end
pitch = [pitch;temp1(1);temp1(2)];
end
end

% Printing useful output to files
fID = fopen([fold,'Image_param.txt'],'w+');
fprintf(fID,'# Particles	%3.0f',nP);
fprintf(fID,'
# x,y	%2.0f	%2.0f',nx,ny);
Particle Making Function

function gaussPart = make_particle(radius, std_dev)

[columnsinPart, rowsinPart] = meshgrid(1:round(2*radius), 1:round(2*radius));
circlePix = (rowsinPart - radius).^2 + (columnsinPart - radius).^2 <= radius.^2;

if(std_dev~=0)
    gauss_filt = fspecial('gaussian', [2*radius, 2*radius], std_dev);
    gauss_filt = gauss_filt/max(max(gauss_filt));
    gauss = zeros(round(2*radius), round(2*radius));
    for j = 1:size(circlePix, 2)
        for i = 1:size(circlePix, 1)
            if(circlePix(i,j))
                gaussPart(i,j) = gauss_filt(i,j);
            end
        end
    end
end
gauss(i,j) = gauss(i,j) + gauss_filt(i,j);
else
    continue
end
end
end
else
gauss = circlePix;
end

gaussPart = gauss./max(max(gauss));
B.1 Solid State Dewet Ni-Al$_2$O$_3$ System

Presented in Figure B.1 are images of the four different solid state dewet Ni-Al$_2$O$_3$ samples. The magnifications for each of these images is the same except for the bottom right image. The key points to observe here are that the case with a 10 nm cap appears to have hole formation beginning in the alumina film as it is dewetting on top of the Ni film. This causes there to be smaller particles in the holes that have formed in the film but larger particles where there are no holes. This heterogeneity indicates that this will not be an ideal system for adjusting NP size and spacing. The image in the bottom right of this figure only shows a crystallized alumina film.

![Image](image_url)

Fig. B.1: Results for the solid state dewet Ni-Al$_2$O$_3$ system. From left to right, top to bottom the images have the following capping layer thicknesses: 0, 5, 10, 20 nm. Also note the magnification of the image in the bottom right is less than that of the other images.
B.2 Au-Si System

Shown below, in Figure B.2, are some images of the results from the Au-Si samples. The top right image was taken at a different magnification than the other two because it exhibits much different final morphology. If the etch process were to only etch the capping layer rather than the capping layer and the substrate, these samples may exhibit a decrease in size and spacing as evidenced in the very small size of particles shown in the top left and bottom images. This would only be the case if in fact the islands that appear to be underneath the Si film are gold particles.

Fig. B.2: Results for the Au-Si system. From left to right, top to bottom the capping layer thicknesses are 5, 10, 20 nm. The magnification of the top right image is different from the other two.
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Benjamin C. White

Published Journal Articles


Journal Articles in Progress


Published Conference Papers


Conference Presentations


• B. White, and N. Roberts. The Effect of Different Thickness Al$_2$O$_3$ Capping Layers on the Final Morphology of Laser Pulse Induced Dewet Ni Films. nanoUtah. October, 2015, Salt Lake City, UT, USA. First Place Award in Student Poster Competition

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