This dissertation titled
Heat Transfer from Optically Excited Gold Nanostructures into
Water, Sugar, and Salt Solutions

by
ANDREW J. GREEN

has been approved for
the Department of Chemistry and Biochemistry
and the College of Arts and Sciences by

Hugh H Richardson
Professor of Chemistry and Biochemistry

Robert Frank
Dean, College of Arts and Sciences
ABSTRACT

GREEN, ANDREW J., Ph.D., December 2013, Chemistry

Heat Transfer from Optically Excited Gold Nanostructures into Water, Sugar, and Salt Solutions

Director of Dissertation: Hugh H. Richardson

Nanotechnology has introduced a wide variety of new behaviors to study and understand. Metal nanostructures are of particular interest due to their ability to generate large amounts of heat when irradiated at the plasmon resonance. Furthermore, heat dissipation at the nanoscale becomes exceedingly more complicated with respect to bulk behavior. What are the credentials for a heat carrier to move across an interface? Is it important for both materials to have similar vibrational density of states? What changes if one material is a liquid? All of these questions have open ended answers, each of which hold potential for new technologies to be exploited once understood.

This dissertation will discuss topics exploring the transfer of heat from an optically excited gold nanoparticle into a surrounding liquid. Gold nanostructures are created using conventional electron beam lithography with lift-off. The nanostructures are deposited onto a thin film thermal sensor composed of AlGaN:Er\textsuperscript{3+}. Erbium(III) has two thermally coupled excited states that can be excited with a 532nm laser. The relative photoluminescence from these excited states are related by a Boltzmann factor and are thusly temperature dependent. A scanning optical microscope collects an image of Er\textsuperscript{3+} photoluminescence while simultaneously exciting the gold nanostructure. The
nanostructure temperature is imaged which is directly related to the surrounding’s heat dissipation properties.

The first of two topics discuss the heat dissipation and phase change properties of water. A gold nanostructure is submersed under water and subsequently heated with a 532 nm laser. The water immediately surrounding the nanodot is can be superheated beyond the boiling point up to the spinodal decomposition temperature at 594 ± 17 K. The spinodal decomposition has been confirmed with the observation of critical opalescence. We characterize the laser scattering that occurs in unison with spinodal decomposition due to an increased coherence length associated with the liquid-liquid transition.

The second topic will measure the change in heat dissipation with respect to solute adhesion onto the nanoheater. A small amount of aqueous solute molecules (1 solute molecule in 550 water molecules) dramatically increases the heat dissipation from a nanoparticle into the surrounding liquid. This result is consistent with a thermal conductance that is limited by an interface interaction where minority aqueous components significantly alter the surface properties and heat transport through the interface. The increase in heat dissipation can be used to make an extremely sensitive molecular detector that can be scaled to give single molecule detection without amplification or utilizing fluorescence labels.
I dedicate this dissertation to my parents Nancy and Joe, my sister Alle and to my future wife Andrea.
First and foremost, my greatest thanks to Dr. Hugh Richardson. His dedication and passion for science has always driven me to better understand the world around me. Graduate work involves is often taxing but he was always there to lighten the mood. I have learned more in the past three years than I ever could have imagined and am eternally grateful.

I would like to thank the professors in my committee: Dr. Jeffery Rack, Dr. Martin Kordesch and Dr. Michael Jensen. The weeks leading to my defense were difficult due to my misunderstanding of the graduation process. Everyone was terribly accepting of my mistakes and sacrificed a lot to accommodate me. I also thank you for the insight brought to my research through a combination of Physical Inorganic Seminar inquiries and coffee breaks. Your guidance has been invaluable.

I would like to thank my group for their support and hard work. The Richardson group has been small historically but has lately grown into a small team. I have to admit the medium sized group brought a lot of extra life to my day and made work much more enjoyable.

Lastly I want to thank my family. My parents have offered unending support and love during the last seven years. I could not have done it without you. I want to thank my bride to be, Andrea. The patience you have shown is staggering. We have endured a lot while living apart these past two years and I promise that it will be worth it.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>Dedication</td>
<td>5</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>6</td>
</tr>
<tr>
<td>List of Figures</td>
<td>8</td>
</tr>
<tr>
<td>List of Tables</td>
<td>11</td>
</tr>
<tr>
<td>Chapter 1: Introduction</td>
<td>12</td>
</tr>
<tr>
<td>Chapter 2: Experimental Procedures</td>
<td>23</td>
</tr>
<tr>
<td>Chapter 3: Superheating Water by CW Excitation of Gold Nanodots</td>
<td>41</td>
</tr>
<tr>
<td>Chapter 4: Ultra-Sensitive Molecular Detection Using Thermal Conductance of a Hydrophobic Gold Water Interface</td>
<td>55</td>
</tr>
<tr>
<td>Chapter 5: Summary and Future Work</td>
<td>76</td>
</tr>
<tr>
<td>References</td>
<td>81</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1. Mechanism for the plasmon resonance of a metal nanoparticle. The vertical black lines represent electric field lines of light point in the k vector. The gold nanoparticle is shown as the red circle while the oscillating conduction electrons are shown in green. The electron cloud oscillates in cycle with the wavelength of light. ...................................................................................................................... 13

Figure 1.2. The temperature of the heat sink (red) decreases linearly as a function of the distance away from the heat source (grey). The temperature decay follows Fourier’s law. The heat dissipation function is linear when the heat transfer is one dimensional. The slope of the line is a function of the heat sink’s thermal conductivity. A material with high thermal conductivity will have a smaller slope. ............................................................................................................................... 17

Figure 1.3. Temperature is plotted a function of distance away from the heat source. The interfacial boundary resistance creates a temperature discontinuity between the heat source (red) and the heat sink (grey). The difference in temperature is denoted as ΔT. The relationship between the thermal boundary conductance G and ΔT is show in equation 1.10.............................................................................. 20

Figure 2.1. (A) The substrate is spin coated with a thin film positive resist composed of 950K A4 PMMA. (B) The thin film is irradiated with an SEM in dimensions specified by the L-Edit pattern. (C) A Metal layer is sputtered or evaporated over the mask (in this case a 5 nm titanium layers was first deposited as an adhesion layer followed by 60 nm of gold). (D) The residual gold/PMMA layer is removed revealing pristine gold nanoparticles matching the L-Edit design. ....................... 24

Figure 2.2. An SEM image of gold nanostructures is pictured above. The standard width of the nanostructures is 108 nm. The structures stand 64 nm tall. ........................ 26

Figure 2.3. An energy diagram of Er(III) in a solid matrix. The carrier lattice splits the symmetry of the f orbitals. The overlapping states are thermalized and their relative emission is related by a Boltzmann factor. On the left is the band structure of AlN. Due to the relatively weak oscillator strength of Er$^{3+}$, the light is absorbed into defect states of AlGaN followed by a thermal decay into the excited states of Er(III). ................................................................................................................... 29

Figure 2.4. A collected spectrum of AlGaN:Er$^{3+}$ sputtered onto a silicon substrate. The high energy peak is the $^2H_{11/2}$ while the low intensity peak is the $^4S_{3/2}$. The peak at 532 nm is the reflected laser line and the sharp peak at 547 is a silicon Raman band from the substrate. ........................................................................................................ 30

Figure 2.5. On the left, an optical diagram of the scanning microscope used collect image spectra. On the right: a cross section of the collection volume (black dotted line) and the laser spot (green shaded area). It should be noted that the laser spot has a typical Gaussian profile. ........................................................................................................ 31
Figure 2.6. Collected spectra from the AlGaN:Er$^{3+}$ thin film is shown above. The red spectrum is from a ‘cold’ spot in the image while the black spectrum is from a ‘hot’ spot.

Figure 2.7. The spectra above is collected from an AlGaN:Er$^{3+}$ thin film sputtered on silicon while excited with a 532 nm laser. The high and low energy peaks are integrated from approximate 535 → 547 and 550 → 570 respectively. This changes slightly day by day due to small CCD alignment shifts so manual choice of integration limits is necessary.

Figure 2.8. A cross section of two lithographically prepared gold nanostructures on the temperature sensing substrate. The difference between the maximum measured temperature and the background is the measured temperature.

Figure 2.9. The measured change in nanoparticle temperature is plotted as a function of incident laser intensity.

Figure 2.10. The schematic above shows the temperature decay as a function of distance away from the gold nanoheater. As shown, some ‘cold’ spectra is collected away from the nanoparticle while ‘hot’ spectra is also collected. This necessitates a temperature transfer parameter that will convolute the measured temperature to a true local temperature. The temperature transfer parameter is 12.8 using the darkfield 50x lens and is a function of numerical aperture.

Figure 2.11. Local and measured temperature is plotted as a function of intensity. The temperatures have been adjusted to convolute the ‘cold’ and ‘hot’ spectra collected during the image scan. The slope is increased by a factor of 12.8, the temperature transfer parameter.

Figure 3.1. This figure contains four images of lithographically prepared nanodots. Figure 1A shows a scanning electron microscope image of the nanodots. Figure 1B shows a temperature contour plot of the nanodots submersed in water excited with a laser intensity of 4.9 x 10$^9$ W/m$^2$. Figure 1C and 1D are integrated laser scattering images at temperatures of 333K and 806K respectively.

Figure 3.2. A plot showing the local temperature change of the nanodots in both air and water as a function of excitation laser intensity. The local temperature from four nanodots is shown with the temperature uncertainty less than the symbol size. The red dashed-line corresponds to the water SDT, whereas the black dashed-line corresponds to the melting temperature of gold. At temperatures above the SDT, the temperature variation between nanodots was dramatically increased due to the temperature instability of spinodal water.

Figure 3.3. A plot of the local temperature change (blue squares) averaging the four nanodots with laser intensity contrasted to the integrated laser scattering divided by the laser intensity (red squares). The red data points correspond to the right axis and were measured by integrating the intensity from the excitation laser relative to the baseline scattering and then scaled by the laser intensity. Both data sets were collected simultaneously. The transition in laser scattering between positive and negative scattering at a temperature change of 295 K and laser intensity around 7 x 10$^9$ W/m$^2$ is due to critical opalescence and confirms that the temperature is the SDT.
Figure 4.1. An SEM image of lithographically fabricated gold nanowires with a standard height and width of 64 nm and 108 nm respectively. The lengths from smallest to largest are 470 nm, 580 nm, 860 nm, and 1100 nm.

Figure 4.2. A 3-D thermal image of the smallest gold nanowire in figure 1 with different surroundings of air, water, 2% g/g NaCl and 2% g/g D-Glucose. The excitation intensity in every image is $3.0 \times 10^9$ W/m$^2$.

Figure 4.3. A plot that shows the change in temperature of the smallest gold nanowire as a function of incident laser intensity. The nanostructure temperature is measured while surrounded in air, water, 2% g/g, 3% g/g, and 4% g/g D-Glucose, and 2% g/g and 4% g/g NaCl solutions.

Figure 4.4. The temperature of a hydrophobic coated gold nanoparticle surrounded by water is measured as a function of time (black). The decrease in temperature relates to the removal of the hydrophobic layer. This increases the heat dissipation, in turn lowering the steady state temperature. The temperature is then transformed in the thermal conductance and is plotted in red.

Figure 4.5. The Absorption cross section for two gold nanowires (470 and 1100) is calculated and plotted as a function of wavelength. The absorption cross section is a function of the surrounding dielectric constants and therefore red shifts when surrounded by water. The maximum absorption wavelength also red shifts as a function of aspect ratio. The inset shows the abruption values at the excitation wavelength of 532 nm.

Figure 4.6. A plot that shows the measured thermal conductance as a function of solute concentration. The dots correspond to the 470 nm, 580 nm, 860 nm, and 1100 nm wires. The thermal conductance increases rapidly with solute molality and levels off at approximately 0.3 m.

Figure 4.7. A plot of thermal conductance as a function of adsorbed solute molecules. The number of solute molecules adsorbed onto the surface is calculated through the concentration of the solution. The error bars in this figure are three times the standard deviation. The dotted lines show the how the standard deviation decreases with the number of molecules adsorbed. The red line shows the point at which the lower limit rises above the minimum upper limit, this is the limit of detection for this nanowire (470 nm x 64 nm x 108 nm). The current detection limit of this system is 43 ± 10 molecules.
Table 4.1. A table listing the calculated absorption cross sections of the longitudinal mode for the four Au nanowires of different lengths. The cross sections are calculated with the particle sitting on a substrate of AlN and surrounded by either air ($\varepsilon b = 1$) or water ($\varepsilon b = 1.77$). The value listed is the absorption cross section at the excitation wavelength (532 nm). ..................................................... 67
CHAPTER 1: INTRODUCTION

Metal nanoparticles have received a large amount of attention in the past decade due to their unique properties. There are two particularly interesting properties of metal nanoparticles that are currently being explored for applications. The nanoparticle will enhance the electric field near the particle when irradiated with light. This has been used to increase the signal to noise on Raman spectroscopy\(^1\) with applications in imaging\(^3\). The particle also will generate large amounts of heat when irradiated.\(^4\) Heat generation has many potential applications that are currently being investigated including thermal tumor ablation\(^9\), drug delivery\(^10\), and water purification.\(^11,12\)

This dissertation will focus on the ability of gold nanoparticles to absorb large amounts of light and convert virtually all of the light energy into heat. The mechanism of this process is known as the plasmon resonance. The plasmon resonance is the collective oscillation of the conduction band electrons induced by an oscillating electric field (light). Figure 1 below shows how an oscillating electric field will induce movement of the conduction band electrons of a gold nanoparticle.
Figure 1.1. Mechanism for the plasmon resonance of a metal nanoparticle. The vertical black lines represent electric field lines of light point in the k vector. The gold nanoparticle is shown as the red circle while the oscillating conduction electrons are shown in green. The electron cloud oscillates in cycle with the wavelength of light.

The electron cloud becomes thermalized and the inelastic electron/lattice collisions transfer heat to the nanoparticle lattice. Heat will then dissipate into the surroundings. The amount of light that will be absorbed is related to the absorption cross section ($C_{\text{abs}}$). This can be calculated using Mie theory which is described below.

Heat Generation Calculations using Mie Theory

Mie theory was derived by solving Maxwell’s equations of light interacting with a spherical particle smaller than the wavelength of incident light. The absorption cross section can be calculated using Mie Theory. Once the cross section is known, the amount
of energy transferred from the irradiation can be calculated by multiplying the absorption cross section by the average light intensity across the particle.

Two types of gold structures are studied in this dissertation: a nanodot with a radius of 150 nm and a height of 20 nm, and a nanowire with a height of 64 nm, a width of 108 nm, and varying lengths from 200 nm to 1100 nm. The nanodot was modeled as a spherical shape with the same volume as the nanodot. A prolate spheroid was used to model the nanowires. The Mie Theory equations for the absorption cross section in the spherical and prolate spheroid case are shown in equations 1.1 and 1.2 below,

\[ C_{abs} = \frac{24\pi^2 r^3 \alpha_o^2}{\lambda} \left( \varepsilon' + 2\varepsilon_o \right)^2 + \varepsilon'^2 \]  
\[ C_{abs}(\lambda) = -8\frac{\pi^2}{\lambda} \sqrt{\varepsilon_o} \text{Im}[\alpha(\lambda)] \]  

where \( \alpha_j \) is the polarizability. For a prolate spheroid, \( \alpha \) is defined with the following equation:

\[ \alpha(\lambda) = \frac{V(\varepsilon(\lambda) - \varepsilon_o)}{4\pi L_j (\varepsilon(\lambda) - \varepsilon_o) + \varepsilon_o} \]  

The dielectric constant of the surrounding medium is \( \varepsilon_o \), and \( \varepsilon(\lambda) \) is the wavelength dependent dielectric constant of the gold nanowire (\( \varepsilon' \) is the real dielectric constant while \( \varepsilon'' \) denotes the imaginary part). \( L_j \) is a factor that depends on the ratio of the main axes \( a \) and \( b \) for the prolate spheroid (see below), \( r \) is the spherical radius, and \( V \) stands for the volume of the nanowire.

To calculate \( \varepsilon_o \), defined as the effective dielectric constant (\( \varepsilon_{eff} \)) in equation 1.2, we adopt the methodology of Vernon et al where the effective dielectric constant of a
nanostructure at an interface is transposed into an object immersed in a medium with
dielectric constant \( \varepsilon_{\text{eff}} \). The effective dielectric constant is given by equation 1.4
through 1.6,

\[
\varepsilon_{\text{eff}} = \varepsilon_b \left( 1 + \frac{\eta T_q^j}{1 + \gamma_q^j} \right)
\]

(1.4)

\[
T_q^j = -1/(a_j x^2 + b_j x + c_j)
\]

(1.5)

\[
\gamma_q^j = sx^p + k
\]

(1.6)

where \( x \) is the aspect ratio, \( j \) and \( q \) are the \( j \)th resonance mode of nanostructure \( q \), the
parameters \( a_j, b_j, c_j, s, p, k \) are parameters for an ellipsoid of \(-0.115, 4.977, -0.862, 1.93, -2.093, 1.072 \)
respectively.\(^2\) Also, \( \eta \) in equation S2 is given by \( \eta = (\varepsilon_b - \varepsilon_s) / \varepsilon_b + \varepsilon_s \), where \( \varepsilon_b \) is
the dielectric constant of the surrounding medium, air or water, and \( \varepsilon_s \) is the dielectric
constant of the substrate, Al\(_{0.94}\)Ga\(_{0.06}\)N.

A prolate ellipsoid has only two modes because two of the principle axes are
equivalent with the other axis being much larger. The depolarization factor \( (L_j) \) for these
two modes is given by equations 1.7 and 1.8,

\[
L_1 = \frac{1 - e^2}{e^2} \left( -1 + \frac{1 + e}{2e} \ln \frac{1 + e}{1 - e} \right), e^2 = 1 - (b^2 / a^2)
\]

(1.7)

\[
L_2 = L_3 = \frac{1}{2} (1 - L_1)
\]

(1.8)

where \( L_1 \) and \( L_2 \) represent the longitudinal and the transverse mode, respectively, and the
principle axes are given by \( a >> b = c \).
When observing the nanowires, the excitation laser is linearly polarized along the nanowire axis so only the longitudinal mode is excited. The absorption cross section for the longitudinal mode at the excitation wavelength of 532 nm in both air and water is given in Table 4.1. All measurements are conducted at steady state and thus the energy generated will be dissipated into the surroundings. In the next section, Fourier’s law will be used to model the heat dissipation into the surroundings.

Heat Transfer and Thermal Conductance

Heat can be transferred through three modes of transport: thermal conduction, thermal convection, and thermal radiation. The hot metal nanoparticles will transfer heat into the surroundings through thermal conduction. Thermal convection from a hot nanoparticle into a surrounding fluid has been thought to not occur theoretically. I have also tried to probe convection by observing the movement of 0.1 µm glass beads in solution. The beads were pulled into the laser spot using a technique called optical tweezing. The focused laser field creates a force trap that allows for the beads to be moved into specific locations. The beads were moved above a nanoparticle and if a strong convection current occurred the bead would be swept away with the current. Conversely the bead exhibited normal Brownian motion. Appreciable thermal radiation occurs with materials when they are heated to extreme temperatures (>1000K).

The particles we study will only dissipate heat through thermal conductance. The heat dissipated away from the particle will follow Fourier’s Law.

\[
q = kA \frac{dT}{dx}
\]  

(1.9)
Where $q$ is the amount of heat dissipated, $k$ is the heat sink’s thermal conductivity, and $dT/dx$ is the thermal gradient. The figure below shows the temperature gradient when heat is moving from source to sink.

Figure 1.2. The temperature of the heat sink (red) decreases linearly as a function of the distance away from the heat source (grey). The temperature decay follows Fourier’s law. The heat dissipation function is linear when the heat transfer is one dimensional. The slope of the line is a function of the heat sink’s thermal conductivity. A material with high thermal conductivity will have a smaller slope.
The temperature of the particle is regulated by the ability for the surroundings to dissipate heat. The higher the heat sink thermal conductivity, the more able the material will pull energy into the surroundings. The raised temperature of the heat source is the driving force pushing heat into the surroundings. If the surrounding material is able to remove heat efficiently, the heat sources temperature will be lower than if the material had a poor thermal conductivity.

Some material interfaces do not transmit heat well. If there is a thermal boundary resistance, or Kapitza resistance, there will be a temperature discrepancy between the heat source and heat sink. The literature will sometimes discuss the inverse Kapitza Resistance as a thermal conductance. If the thermal resistance is limiting in the transfer of heat, it acts as an insulating layer between the source and sink. There is speculation as to why some materials exhibit a Kapitza resistance when paired with a heat source while others do not. There are two models that are used to calculate the thermal boundary resistance between two materials. Both mechanisms argue that the ability to transmit a phonon through the heat sink/source interface is a result of matching material phonon spectra. If the materials have similar phonon density of states, the transmission probability of the phonon is high and would result in a low thermal boundary resistance. The alternative is also true; a low overlap of phonon spectrums will generally lead to lower phonon transmission. The Acoustic Mismatch Model assumes that the interface is perfect and transmission of heat carriers (phonons) is elastic. This relates the probably of heat carrier transmission being a function of the angle of incidence. The reflection/refraction of the heat carrier will obey Snell’s law. The Diffuse Mismatch
Model assumes the interface is perfectly scattering and the incident phonons are randomly oriented. Generally the Acoustic Mismatch Model overestimates the thermal boundary conductance while the Diffuse Mismatch Model underestimates it. True understanding of heat transfer across the interface is still widely unknown. Multiple articles and reviews can be found for a more detailed explanation\textsuperscript{17-19}.

The thermal interface resistance acts as a thermal insulator. This results in a temperature discrepancy between the heat source and heat sink. Figure 1.3 below shows the temperature discrepancy.
Figure 1.3. Temperature is plotted as a function of distance away from the heat source. The interfacial boundary resistance creates a temperature discontinuity between the heat source (red) and the heat sink (grey). The difference in temperature is denoted as $\Delta T$. The relationship between the thermal boundary conductance $G$ and $\Delta T$ is shown in equation 1.10.

The interfacial thermal conductance, $G$, is a function of the heat flux across the interface $q$ and the discontinuous temperature at the interface $\Delta T_i$

$$q = G\Delta T_i$$  \hspace{1cm} (1.10)

The heat flux ($q$) into the surroundings can be derived from the heat generation of the nanoparticle because the system is at steady state. As discussed earlier the heat generation
can be derived from Mie Theory. Knowing the temperature of the surroundings immediately next to the particle then becomes necessary when determining the value for the interfacial thermal conductance. \( G \) can also be broken down into the thermal conductivity divided by the thermal decay length. This is the expectation value for the temperature to decay from the heat source temperature to the background temperature.

Recently, Cahill et al showed that the heat transferred from a quartz substrate through a self-assembled monolayer (SAM) into a gold thin film is strongly dependent upon the SAM’s head chemistry.\(^{20}\) The SAM head chemistry was changed from a purely Van Der Walls attractive force to a fully covalent bond structure. An increasing percentage of convalency led to a higher thermal interface conductance. This surprising result generated ideas on how to change the thermal conductance in solution. How does heat transfer from gold nanostructures into a surrounding fluid. Will solute particles on the surface of a nanoparticle change the thermal interface conductance? To further understand this question, gold nanostructures were fabricated using e-beam lithography and their heat dissipation properties were probed using a novel thermal sensor composed of AlGaN:Er\(^{3+}\). This led to multiple interesting results. The first of which was that bubble nucleation could not occur from a hot nanoparticle in steady state. A metastable state of water exists until the spinodal decomposition temperature is reached. Chapter 3 discusses these results. Once heat transfer into water was understood and characterized, solutions with different concentrations of NaCl, and D-Glucose were investigated. Surprisingly, there was a strong dependence of the thermal interface conductance on solute concentration. Even more impressive, the amount of solute molecules needed to observe
an increase the thermal interface conductance is $43 \pm 10$. This number is incredibly small and is obtained with no optimization of signal to noise, or size and shape of the nanoparticle.
CHAPTER 2: EXPERIMENTAL PROCEDURES

Lithography

Due to the strong dependence of the absorption cross section on the particle’s size and shape, isometric particles are needed for experimental reproducibility. Statistics could be collected on a large volume of data to combat the randomness of particle size and shape in colloidal gold nanoparticles, but each experiment would require a sizably larger time investment. Because of this I developed a lithography process in collaboration with the Nanotech West Institute at The Ohio State University. It should be noted that Dr. Kahn Aurangzeb developed lithography at Ohio University and it was used for the data in chapter 3.

The lithography is conducted in four steps as seen in the figure below.
Figure 2.1. (A) The substrate is spin coated with a thin film positive resist composed of 950K A4 PMMA. (B) The thin film is irradiated with an SEM in dimensions specified by the L-Edit pattern. (C) A Metal layer is sputtered or evaporated over the mask (in this case a 5 nm titanium layers was first deposited as an adhesion layer followed by 60 nm of gold). (D) The residual gold/PMMA layer is removed revealing pristine gold nanoparticles matching the L-Edit design.

The first step is to apply the 950K PMMA A4 positive resist to the substrate using a spin coater. Assuring a clean substrate is detrimental to applying a consistent thin film across the entire surface. Small dust particles have a tendency to cause hiccups in the spin coating process. To clean the substrate, first submerge the substrate into chloroform and
sonicate for 15 minutes. Afterwards submerge the substrate in a 5 minute acetone bath followed by an acetone wash and an IPA wash. Blow the substrate dry with N₂. Be sure to keep the substrate covered after blowing to ensure dust does not fall on the sample. The sample is then plasma cleaned for approximately 1 minute. The Richardson group plasma cleaner tends to have hot spots inside the container. Ensure the substrate is located inside the plasma. A dehydration bake is then preformed at 205 °C for 5 minutes.

To spin coat: pour the PMMA into a leur lock syringe with a 0.2 µm filter and purge until the solution does not come out with bubbles. If air is in the syringe it will disturb the spin coating process. Cover 75% of the substrate with PMMA and spin coat at a spin speed of 1500 rpm with an acceleration rate of 200 rpm/s for 90 seconds. After spin coating, bake the sample for 5 minutes at 205 °C. If a different resist is used a new baking point may need to be set to ensure drying. Just make sure to avoid temperature close to the melting point of the resist.

The SEM used to irradiate the sample follows a self-designed pattern that uses a program called L-Edit. Amiee Price will operate the SEM that patterns the undeveloped resist. L-Edit can be installed from a disc at the Nanotech West Institute. A copy of the pattern used in these experiments can be sent upon request. The SEM is operated at 50kV. After irradiation, the sample is developed for 3 minutes in a 3/1 IPA:MIBK solution followed by a 30 second rinse in an IPA bath and a 30 second IPA spray bottle rinse. Finally the sample is dried with N₂. It is important to inspect the resist layer after development, if there are problems with the mask a hot acetone bath can be used to remove the layer and start over.
An electron gun evaporation tool is used to sputter a thin film of gold onto the positive resist. First a 5 nm titanium adhesion layer is sputtered followed by a 60 nm layer of gold. It should be noted that the gold nanostructures created had a tendency to fall off after sonication. A 10 nm adhesion layer may remedy this.

The figures below are images taken with the SEM at the Nanotech West Institute. Other images can be obtained by request.

Figure 2.2. An SEM image of gold nanostructures is pictured above. The standard width of the nanostructures is 108 nm. The structures stand 64 nm tall.

It should be noted that in my L-Edit program, I designed the particles to be 50 nm wide but the final result was 108 nm. Most likely this was due to the drawing SEM not being
perfectly focused. If having exact size is essential to the experiment, make sure the SEM operator knows this. The program also had some difficulty interpreting circles with diameters of 100 nm and below. An error showed up while translating the L-Edit information to the drawing SEM. If this could be a problem alert the SEM operator.

AlGaN:Er(III) Thin Film Temperature Sensor

As noted earlier, the ability to generate heat using an irradiated metal nanoparticle is a unique property that has brought the new field of plasmonics and their applications to light. Measuring the heat generation and/or dissipation of said nanoparticles remains a difficult challenge. Multiple techniques have been developed to fundamentally understand the limiting factors of heat dissipation. As stated in the introduction, the heat transfer into the surroundings can limit the flow of heat. The most popular technique to measure the thermal interface conductance is known as Time-domain Thermoreflectance (TDTR). This system uses a pump-probe laser system to measure the decay of the reflected pump beam as a function of time with reference to the probe beam. The sample material’s index of refraction is a function of the material’s temperature. The decay of the temperature is a function of the interfacial thermal conductance. Inherently, the system is kinetically controlled, due to the femtosecond pump having a small duty cycle. A disadvantage to this technique is the inability to look at individual nanoparticles. A review of TDTR can be found by Cahill et al describing the process.\textsuperscript{17} Other nanothermometry techniques have been in development utilizing the temperature dependence of Raman\textsuperscript{21}, and photoluminescence\textsuperscript{22}. A recent review was published looking over multiple techniques.\textsuperscript{23}
A thermal imaging technique was developed by Carlson et al in 2011 that has the ability to measure the steady state temperature of single gold nanostructures with nanoscale resolution. The thermal sensor is based on a thin film of Al$_{0.94}$Ga$_{0.06}$N doped with Er$^{3+}$. The thin films are prepared by Dr. Martin Kordesch at Ohio University. The Er$^{3+}$ has two thermally couple excited states that can be accessed when irradiated with a 532 nm laser. The two excited states are the $^2H_{11/2}$ and the $^4S_{3/2}$ which both radiatively emit to the $^4I_{15/2}$ ground state. The excited states are close in energy and thusly the excitons can be thermally excited between the vibrational levels. An energy level diagram can be seen below. Other information regarding the electronic structure of Er$^{3+}$ can be found in reports by Porter and Garter.
Figure 2.3. An energy diagram of Er(III) in a solid matrix. The carrier lattice splits the symmetry of the f orbitals. The overlapping states are thermalized and their relative emission is related by a Boltzmann factor. On the left is the band structure of AlN. Due to the relatively weak oscillator strength of Er$^{3+}$, the light is absorbed into defect states of AlGaN followed by a thermal decay into the excited states of Er(III).

The oscillator strength of Erbium$^{3+}$ is relatively low but the luminescence signal extracted from the thin film is bright. This is most likely due to the absorption of the 532 nm laser
into defect states of the AlGaN thin film, which then vibrationally relaxes into either the $^2\text{H}_{11/2}$ or $^4\text{S}_{3/2}$ excited states. A spectrum collected using the scanning optical microscope (NSOM) can be seen in the figure below.

![Figure 2.4](Figure 2.4. A collected spectrum of AlGaN:Er$^{3+}$ sputtered onto a silicon substrate. The high energy peak is the $^2\text{H}_{11/2}$ while the low intensity peak is the $^4\text{S}_{3/2}$. The peak at 532 nm is the reflected laser line and the sharp peak at 547 is a silicon Raman band from the substrate.)

A diagram of the optical scanning microscope can be seen below.
Figure 2.5. On the left, an optical diagram of the scanning microscope used to collect image spectra. On the right: a cross section of the collection volume (black dotted line) and the laser spot (green shaded area). It should be noted that the laser spot has a typical Gaussian profile.

To focus on the sample, white light is brought in from the side of the microscope and reflected with a mirror through a lens (generally a 50x small working distance Nikon). An adjustable 532 nm laser is also brought in from the side and passed through a corner cube which then runs parallel to the white light and is focused onto the same plane. The corner cube will only pass one polarization so it is important to couple the correct polarization from the laser source into the microscope. The lens will collect light from approximately a 500 nm diameter area on the substrate, the light travels through the
microscope, past the corner cube with a protective filter (to block the CCD from harmfully high laser counts) and into either a CCD or camera.

The microscope used to collect the spectrum has a scanning capability. This enables it to measure a spectrum multiple times at different points in space for a predetermined integration time, pixel size, and image size. Generally the integration time in air is set to 0.03 s. A 3x3 µm image takes approximately 1 minute to complete at 100 nm x 100 nm pixel resolution. The lens has a large effect on the collection efficiency due to the changes in numerical aperture. It may be necessary to integrate for longer intervals to obtain data with adequate signal to noise. In my experience, Er$^{3+}$ counts should be above 1000 to obtain adequate data. This of course changes depending on the temperature being measured.

If the microscope scans over a gold nanoparticle (or most other particles for that matter), the particle will generate heat and transfer that heat into the thin film, which is also being excited by the 532 nm laser. The film will emit temperature data in the form of spectra. The figure below shows an image collected with the optical scanning microscope and spectra corresponding to a ‘cold’ spot in the background and a ‘hot’ spot on the gold nanoparticle.
Figure 2.6. Collected spectra from the AlGaN:Er$^{3+}$ thin film is shown above. The red spectrum is from a 'cold' spot in the image while the black spectrum is from a 'hot' spot.

In the figure above, the cold spectrum is shown in red while the hot spectrum is shown in black. The relative intensities of each peak are directly related to the temperature by a Boltzmann factor. The high energy peak above is enhanced thermally. The figure below shows how the peaks are integrated.
Figure 2.7. The spectra above is collected from an AlGaN:Er$^{3+}$ thin film sputtered on silicon while excited with a 532 nm laser. The high and low energy peaks are integrated from approximate $535 \rightarrow 547$ and $550 \rightarrow 570$ respectively. This will slightly change day by day due to small CCD alignment shifts so manual choice of integration limits is necessary.

After an image is collected and each spectrum is transformed into a temperature, the spectral image becomes a temperature image. The measured temperature of the nanoheater is the difference between the nanoheater and the background. The figure below shows a cross section of a thermal image and how a measured change in temperature is extracted from the cross section of a thermal image.
Figure 2.8. A cross section of two lithographically prepared gold nanostructures on the temperature sensing substrate. The difference between the maximum measured temperature and the background is the measured temperature.

The error in this measurement is related to the background noise. The RMS of the background is equal to the standard deviation, and so generally the error of the measurement is roughly twice the RMS.

If the nanoheaters are excited with a stronger light intensity they reach a higher temperature. To test this, an image scan of the nanoheater is taken at different laser intensities. The laser power can be changed using a micrometer that open and closes a slit.
in the laser source. The laser is measured with a power meter and can be transformed into an intensity with the equation below:

\[
\Phi = \frac{P_{\text{laser}}(2.3546)^2}{2\pi(f\text{whm})^2}
\]  

The temperature of the particle will also be related to the heat generated and dissipated by the particle. The heat generation (from Mie Theory) and dissipation (from Fourier’s Law) terms are set equal to one another. The amount of heat generated is a function of the size and shape of the material while the amount of heat dissipated is a function of the thermal conductivity of the surroundings. It should be noted that this system is modeled using Fourier’s Law with spherical symmetry and thus the effective thermal conductivity is a weighted average of the surrounding’s thermal conductivity. Below is the heat generation and dissipation terms set equal to one other, followed by it being recast solving for temperature.

\[
C_{\text{abs}} < I > = 4\pi k_{\text{eff}} R_{\text{NP}} \Delta T 
\]

\[
\Delta T = \frac{C_{\text{abs}} < I >}{4\pi k_{\text{eff}} R_{\text{NP}}}
\]

\(C_{\text{abs}}\) is the absorption cross section, \(< I >\) is the average intensity, \(K_{\text{eff}}\) is the effective thermal conductivity, \(T\) is the change in temperature, and \(R_{\text{NP}}\) is the radius of the nanoparticle. A plot of the measured nanoparticle temperature as a function of incident laser intensity is shown below. As expected, the temperature changes linearly with laser intensity.
The measured temperature is lower than what Mie Theory coupled with Fourier’s Law would expect. This occurs due to the size of the microscope collection volume. The temperature will fall off as a function of $1/r$ away from the nanoheater, which means that the microscope is collecting ‘cold’ and ‘hot spectra simultaneously. Below is a figure depicting this concept.
The amount of heat generated from the nanoparticle can be calculated using Mie Theory. The particle temperature then becomes a solvable using Fourier’s Law. To simplify the heat transfer, the surroundings are assumed to be a homogeneous. The thermal conductivity of the material is a weighted average of substrate and air’s thermal conductivity. The thermal conductivity of the AlGaN:Er$^{3+}$ thin film is measured to be 1.5 W/m$^2$-K while the thermal conductivity for air is effectively 0. The effective thermal conductivity
conductivity of a homogeneous material when the particle is centered between the two layers becomes $0.75 \text{ W/m}^2\text{-K}$. The heat dissipation of Fourier’s law is recast using the heat generation term from Mie Theory as noted in equations 2.2 and 2.3. $\Delta T_{\text{max}}$ is calculated as the true temperature of the nanoparticle.

The ratio between the calculated temperature and the measured temperature becomes the temperature transfer parameter. The figure below shows the change in slope between the calculated temperature and measured temperature.

![Figure 2.11. Local and measured temperature is plotted as a function of intensity. The temperatures have been adjusted to convolute the ‘cold’ and ‘hot’ spectra collected during the image scan. The slope is increased by a factor of 12.8, the temperature transfer parameter.](image-url)
The temperature transfer parameter is a function of the collection volume and thus will change with the microscope lens used. The temperature transfer parameter of 12.8 was found using the Nikon 50x dark field lens. The Nikon 60x water immersion lens has been found to have a temperature transfer parameter of 10.2. This was calculated based on the change in numerical aperture. The small aperture will collect less ‘cold’ photoluminescence making the temperature transfer parameter smaller. All temperature data collected from the AlGaN:Er\(^{3+}\) must be convoluted by the temperature transfer to reflect the true temperature. The temperature transfer parameter can be avoided by creating a thermal sensor that will be in local thermal equilibrium with the nanoheater. All data will then reflect the only the nanoparticle temperature and will not obtain ‘cold’ spectra.
CHAPTER 3: SUPERHEATING WATER BY CW EXCITATION OF GOLD NANODOTS

Abstract

A temperature dependent photoluminescent thin film of Al$_{0.94}$Ga$_{0.06}$N doped with Er$^{3+}$ is used to measure the temperature of lithographically prepared gold nanodots. The gold nanodots and thin film are excited simultaneously with a CW Nd:YAG 532 nm laser. The gold nanodot is submersed under water and the dot is subsequently heated. The water immediately surrounding the nanodot is superheated beyond the boiling point up to the spinodal decomposition temperature at 594 ± 17 K. The spinodal decomposition has been confirmed with the observation of critical opalescence. We characterize the laser scattering that occurs in unison with spinodal decomposition due to an increased coherence length associated with the liquid-liquid transition.

Introduction

Photothermal heating of noble metal nanostructures is an active area of research where applications have been demonstrated in many different areas including remote release of encapsulated material$^{27}$, melting of strands of DNA$^{28}$, thermal therapy of tumors$^{29}$, and controlled manipulation of phase transitions of phospholipid membranes$^{30}$. Remote actuation in these environments by nanoscale heating utilizes the small size and large optical cross section of nanostructures to place a large temperature variation within a small space. It is presently unclear the effect that these large temperature extremes within a confined nanometer space have upon the system. Confinement effects of
metastable materials have been extensively researched due to fundamental importance and a broad range of applications from drug delivery\textsuperscript{31} to explosive cancer ablation.\textsuperscript{32,33} Do thermodynamic stabilities normally occurring at the macroscale, like water boiling at 373 K, translate to the nanoscale?

In this paper we show that the stability of liquid water can be extended to the spinodal decomposition temperature (SDT) of 594 ± 17 K by nanoscale confinement of heat transfer. We use a CW laser to optically heat a gold nanostructure immersed in water beyond the normal boiling point to the SDT without bubble formation. The local temperature at the nanostructure water interface is measured optically using the temperature dependent photoluminescence intensities of Er\textsuperscript{3+} embedded in a wide band gap III-V thin film and the SDT is characterized and confirmed by critical opalescence. This result compliments pulsed laser heating of nanoparticles in water where water superheating and bubble formation is observed.\textsuperscript{7,32-35}

Methods

The nanodots in figure 1A were created using conventional e-beam lithography with lift off. Approximately 100 nm of Poly(methyl methacrylate) (PMMA) (3% PMMA in Anisole) positive resist was spin coated onto the temperature sensing substrate. The substrate was subsequently baked in an oven for 30 minutes at 180°C. A JOEL 6400 SEM operating at ~30KV was then used to expose nano arrays into the PMMA film. The substrate was then developed with MIBK: IPA = 1:3 (volume) for 30 s and rinsed with 18.2 M\textOmega water and dried with N\textsubscript{2} gas. A thin adhesion layer of titanium was deposited
followed by a 50-70 nm layer of gold via DC sputtering. Lastly, the Ti/Au/PMMA residual layer was removed with a light sonication bath in acetone (60°C).

The thermal sensor film is cleaned by sonication in chloroform. Over time, with repeated cleanings, the height of the gold nanostructures gradually decreases. The height of the nanodots was measured with AFM with an average height of 27 ± 5 nm.

The spectral images were collected using a WITec α-SMON300s upgraded with Raman imaging, dark-field, and AFM capabilities. The temperature images of nanodots in air were collected with a 50X objective (Zeiss EC Epiplan-NEOFLUAR 50x/0.8 HD) while under water a Nikon Fluor 60x water immersion lens was used. Each pixel contained both temperature and laser scattering data as can be seen in Figure 1.

The temperature sensing substrate is composed of Al$_{0.94}$Ga$_{0.06}$N embedded with Er$^{3+}$ ions. Approximately 270 nm was deposited onto a silicon substrate using a RF magnetron sputtering process. The film’s temperature dependent photoluminescence has been previously characterized in our earlier works. The film will emit from two electronic states whose emission intensity is related by a Boltzmann factor. The laser will simultaneously heat the gold nanoparticle and cause the film to emit temperature dependent spectra that when collected in a scanning manner will produce a temperature image. The optically measured temperature can be converted into a local temperature by multiplying by a factor (temperature transfer parameter) that relates the measured diffraction-limited temperature to the local non-resolution limited temperature. The temperature transfer parameter (ttp) is 12.8 if the measurement is made in air with the 50X objective (NA = 0.8) while the factor becomes 10.2 ($ttp = \frac{12.8 \times 0.8}{1.0}$) when the
temperature measurement is made with the substrate immersed in water and using the water immersion objective (60 X, NA = 1.0). This factor allows us to scale the measured temperature, a convoluted temperature within the measurement volume, to the local temperature at the surface of the nanodot. Generally there is a small effect of the temperature transfer parameter with temperature, but we observe the effect to be small enough that to a first approximation the parameter is independent of temperature.\textsuperscript{36}

The laser fluence can be calculated by knowing the laser power and the full width at half max of its Gaussian profile. The laser power is controlled by a micrometer set screw that blocks a set amount of light through the fiber. The power was measured at different micrometer settings using an optical power meter (gentec TPM-300). The spot size (890 nm) was optically imaged and characterized using image J. The equation below allows for the calculation of intensity (\(\Phi \, (W/m^2)\)) using the laser power (\(P(W)\)) and full width at half max (fwhm (nm)) of the two-dimensional Gaussian laser profile.

\[
\Phi = \frac{P(2.3546)^2 10^{18}}{2\pi (fwhm)^2}
\]  

(3.1)

Results and Discussion

SEM images of the nanodots (figure 1A) show that the nanodots are asymmetrical with the pristine nanodots having on an average a long axis of 550 nm and a short axis of 380 nm. The optical properties change with the gradual degradation of the particles over time. We have previously characterized the temperature variation of the nanodots as seen here.\textsuperscript{36} The spacing between nanodots is 3000 nm which is large compared to the laser spot size and thermal profiles when the nanodots are heated with the laser. The optical set up uses a 532 nm laser to scan the surface producing photoluminescence spectra of
the temperature sensing film. The laser will simultaneously probe the temperature on the film while heating the gold particle by light absorption of the nanodot. The thermal contour plot from four nanodots immersed in water for a laser intensity of $4.9 \times 10^9$ W/m$^2$ is shown in figure 1B. The local temperature change of the nanodots in water was determined by multiplying the measured temperature change by a factor of 10.2 to relate the diffraction-limited composite temperature collected by our optical system to the local temperature of the heated nanostructure.$^{36}$ This factor also takes into account the change in the numerical aperture of the different objectives used between air and water (see methods section). Figures 1C and 1D show integrated laser scattering intensities at 333K (below the SDT) and $\sim 806$ K (above the SDT). The significance of these images to the SDT will be discussed later.
Figure 3.1. This figure contains four images of lithographically prepared nanodots. Figure 1A shows a scanning electron microscope image of the nanodots. Figure 1B shows a temperature contour plot of the nanodots submersed in water excited with a laser intensity of $4.9 \times 10^9 \text{W/m}^2$. Figure 1C and 1D are integrated laser scattering images at temperatures of 333K and 806K respectively.

Figure 2 shows the maximum local temperature change for optically excited nanodots as a function of laser intensity. This measurement is made with the nanodots under air and water represented by the red (circles and squares) and blue (triangles) data respectively. When the nanodot is surrounded by air, the only channel for heat dissipation is through the temperature sensing substrate. There is a negligible amount of heat dissipated radiatively at extreme temperatures.\textsuperscript{37} We have previously shown that the optical properties of gold will change once the particles change from solid to liquid
phase.\textsuperscript{36} We do not include these data points in the following model due to this reason.

When the nanodot is immersed in water, heat can be dissipated into both the substrate and water. The heat dissipation can be expressed using Fourier’s law:

\[ q = \sum_i k_i A_i \left( \frac{\partial T}{\partial x} \right) \]  \hspace{1cm} (3.2)

where \( q \) is the total heat dissipation (also total heat generation because the system is at steady state), \( A_i \) is the surface area where heat dissipation occurs, \( k_i \) is the thermal conductivity of the material at surface \( A_i \), and \( \frac{\partial T}{\partial x} \) is the thermal gradient. The maximum thermal gradient is at the nanodot where the maximum change in temperature is measured. The substrate interface should be the same temperature as the nanodot. We have previously explored the thermal resistance and found that there is little expected difference in temperature between the nanodot and the surrounding medium. This can be confirmed by the fact that spinodal decomposition occurs at the expected temperature.

Theory also predicts that the thermal resistance is not large enough to have a discontinuous temperature at the interface.\textsuperscript{36} This means that the slope in figure 2 is directly proportional to the sum of the total surface area of the dissipating surface multiplied by the thermal conductivity for that surface. When the nanodot is submersed in water, heat can dissipates both into the substrate and into water. This causes a decrease in the slope of temperature with laser intensity when comparing heating of nanodots in water to air. The expected ratio of air and water slopes can be calculated using equation 2 if the thermal conductivity of water is known.
Figure 3.2. A plot showing the local temperature change of the nanodots in both air and water as a function of excitation laser intensity. The local temperature from four nanodots is shown with the temperature uncertainty less than the symbol size. The red dashed-line corresponds to the water SDT, whereas the black dashed-line corresponds to the melting temperature of gold. At temperatures above the SDT, the temperature variation between nanodots was dramatically increased due to the temperature instability of spinodal water.

The static thermal conductivity of water is 0.6 W/m-K. The localized heating of nanodots in water might induce fluid convection during illumination. This effect should increase the thermal conductivity of water. We probed water convection around the nanodot during optical excitation by placing small polymer beads (~100 nm in
diameter) in the water. The beads were trapped by the laser and could be released when the laser was turned off. The motion of the beads with respect to trapping and release was not affected by heating the nanodot optically and from these measurements we conclude that there is no evidence of convection. This observation is supported by theory, where dissipation through convection compared to diffusive heat flow for a similar sized system is negligible,\textsuperscript{16} and by our experimental data shown in figure 2. We measure a ratio for the slope of air to water of 2.01. Our simple model using Fourier’s law (equation 2) gives this measured ratio when an elliptical shape is assumed for the nanodot shape having a long axis of 550 nm, short axis of 380 nm and a height of 25-30 nm.

The temperature change of the nanodots immersed in water scales linearly with laser intensity until a temperature of 594 K ± 17K is reached (296 K+298 K= 594 K). This matches the expected SDT of water that has been extrapolated in previous works.\textsuperscript{38-41} Spinodal decomposition is a phase transition that takes place without the presence of nucleation. The phenomenon creates a distinct mixture of two phases throughout the unstable region. The transition at the spinodal decomposition temperature has been described as a liquid-liquid phase transition where nucleation of the new liquid with different density grows in time.\textsuperscript{42} This results in small density fluctuations over a large spatial area and can be discriminated between bubble formation where a large density fluctuation is observed over a small region. The small density fluctuations scatter light when the coherence length of the spinodal is comparable to the laser excitation wavelength. (critical opalescence).\textsuperscript{38,39} Optically heating the nanodots above the spinodal
decomposition temperature instabilities that are observed as an increase in the
temperature variability over time between nanodots. The instability occurs because
scattering of the excitation light causes a decrease in the amount of light reaching the
nanodot, which lowers the temperature until the coherence length of the spinodal
decrease below 532 nm (the excitation wavelength) where the scattering decreases and
light absorption increases. This causes a dramatic increase in temperature which starts
the cycle again.
Figure 3.3. A plot of the local temperature change (blue squares) averaging the four nanodots with laser intensity contrasted to the integrated laser scattering divided by the laser intensity (red squares). The red data points correspond to the right axis and were measured by integrating the intensity from the excitation laser relative to the baseline scattering and then scaled by the laser intensity. Both data sets were collected simultaneously. The transition in laser scattering between positive and negative scattering at a temperature change of 295 K and laser intensity around $7 \times 10^9$ W/m$^2$ is due to critical opalescence and confirms that the temperature is the SDT.

Part of the laser is backscattered into the detector during the temperature measurements. Figure 1C and 1D was created by integrating the scattering peak in the spectra at each pixel. A cross section across the nanodot in the scattering image was then integrated to give a relative scattering efficiency. This was divided by the incident laser intensity for normalization then plotted against laser intensity to show the red data in figure 3 above. Laser scattering images for a laser intensity of $5.6 \times 10^8$ W/m$^2$ (corresponding to a temperature change of 35K) and $1.33 \times 10^{10}$ W/m$^2$ (corresponding to
a temperature change of ~ 508K) is shown in panel 1C and 1D respectively. The temperature change of 35K is below the normal boiling and SDT of water while the temperature change of ~508 K is above the SDT. All the scattering images of the nanodot for temperatures below the SDT showed a positive scattering integrated intensity relative to the background while scattering images for temperatures above the SDT showed negative scattering relative to the background. This trend is shown in figure 3 for different laser intensities as red squares and is compared to the average local temperature of the four nanodots (blue squares). The transition between positive and negative scattering is due to critical opalescence and occurs at a temperature change of 296 K. Incident light is scattered away from the detector creating negative peaks in comparison to the background. The observation of critical opalescence is a strong indicator for critical phenomena and the measured absolute temperature of 594 K ± 17K, is in good agreement with the expected normal pressure SDT of water near 587 K.

The water surrounding the nanodot is superheated because homogeneous bubble nucleation is an activated process where a free energy barrier must be surmounted to convert liquid to vapor. If there is insufficient energy to overcome this barrier, then the metastable liquid is trapped even though the chemical potential of the vapor is lower than the chemical potential of the liquid. Normal boiling relies on heterogeneities within the liquid to catalyze nucleation of vapor bubbles. If these heterogeneities are not present, then nucleation of vapor bubbles must occur from a vapor embryo that exceeds a critical radius to grow spontaneously. As the temperature increases toward the SDT, the free energy barrier and critical radius are reduced with a dramatic rise in nucleation rate. At
the SDT, the free energy barrier disappears and the liquid undergoes a liquid-liquid phase transition. Each pixel in the image contains a spectrum that has been collected for 0.03 s. The distance between pixels is 100 nm; this gives a residence time across the nanodot of 0.24 s. For the time scales in our measurements bubble nucleation does not occur and the metastable liquid is not converted into vapor.

The SDT is reached without bubble formation because the lifetime for homogeneous bubble nucleation is much longer than the measurement optical excitation and collection time of 0.2 s. The space, size and amount of water heated are restricted by the small size of the nanodot heater and relatively small thermal conductivity of water. This confinement limits access in water to cavities of dissolved gas or other heterogeneities in the liquid that facilitate bubble nucleation. Surprisingly, the gold nanodot is not capable of initiating bubble nucleation even though the size of the nanodot is larger than nanoparticles (diameters less than 100 nm) where bubble nucleation is observed with nanosecond pulsed laser excitation. Bubble formation is not observed with longer excitation pulses. The size of the nanodot heater compared to smaller nanoparticle heaters suggests that curvature effects are not what inhibit bubble formation. The critical radius of the bubble embryo is much smaller in size than the nanodot (expected to be between 10 and 100 nm within 100 K of the SDT) and still, the nanodot heater is not capable of nucleating the vapor.

Conclusions

In summary, we optically excite gold nanodots on a thermal sensor film immersed in water. The surrounding water is trapped in a metastable state far above its normal
boiling point. The water temperature rises until the SDT of 594 K ±17 K is reached where a liquid-liquid phase transition occurs. The onset of this transition is detected with critical opalescence where a transition from positive to negative laser scattering relative to the background is observed. The measured SDT agrees with the expected SDT for water.\textsuperscript{38-41} The nanodot heats a small volume of water that is void of nucleation sites and this temperature confinement traps the metastable liquid to the SDT where a liquid-liquid transition occurs.\textsuperscript{42}
CHAPTER 4: ULTRA-SENSITIVE MOLECULAR DETECTION USING THERMAL
CONDUCTANCE OF A HYDROPHOBIC GOLD WATER INTERFACE

Abstract

The thermal conductance from a hydrophobic gold aqueous interface is measured with increasing solute concentration. A small amount of aqueous solute molecules (1 solute molecule in 550 water molecules) dramatically increases the heat dissipation into the surrounding liquid. This result is consistent with a thermal conductance that is limited by an interface interaction where minority aqueous components significantly alter the surface properties and heat transport through the interface. The increase in heat dissipation can be used to make an extremely sensitive molecular detector that can be scaled to give single molecule detection without amplification or utilizing fluorescence labels.

Introduction

Single molecule detection is essential for pharmaceutical applications where even small transcription errors lead to a large heterogeneity in molecular ensembles assumed to be identical.\textsuperscript{44, 45} Additionally, understanding heat transfer at a solid water interface is critical to develop medical therapies where nanoscale heaters are used for photothermal therapy,\textsuperscript{29, 46-48} drug delivery,\textsuperscript{49, 50} water sterilization,\textsuperscript{21} imaging,\textsuperscript{3} and biological actuation.\textsuperscript{51} Electrolyte adsorbates also show a significant effect on a gold nanoparticle’s plasmon properties.\textsuperscript{52, 53} Many current single molecule techniques require amplification and labels to boost sensitivity to reach the single molecule level. Recently, molecule
detection, approaching a single molecule, has been realized from a specially designed array of nanodots that exhibits zero reflection. This approach benefits both from plasmonic field enhancement and phase properties of reflected light to enhance sensitivity to the single molecule level.\(^5\) Optical measurements utilizing reflection or scattering have a polarizability squared dependence while absorption measurements are proportional to polarizability.\(^14\) Polarizability scales with the nanostructure volume and as a result, scattering measurements fall off as the volume squared while absorption measurements only decrease linearly with volume. As a result, absorption measurements have the potential to be inherently more sensitive than scattering measurements for smaller nanostructures.

The effect of chemical bonding on heat transport across a gold quartz interface has been elucidated,\(^2\) and remarkably, a change in a single bond at the interface affects the heat transport through the interface. This suggests that thermal transport through the interface is facilitated or impeded on length scales that are on the order of chemical bonds. Also, ligands on a gold nanorod surface immersed in water have been shown to alter the interface thermal conductance.\(^5\) A totally different picture emerges if the region that affects thermal transport is many monolayers thick. This effect could be especially pronounced in solid liquid interfaces where the surface properties alter the properties of interfacial water. The local density of interfacial water is affected by the wettability of a gold surface. Hydrophilic surfaces tend to have a higher water density compared to the bulk\(^5\) while hydrophobic surface have a thin layer of low density water near the surface.\(^5\) The interface thermal conductance depends upon how well water adheres to a
surface,\textsuperscript{20,57-59} and the adhesion energy of water on gold surfaces can be tuned with self-assembled monolayers (SAMs) with different end groups. Hydrophilic surfaces facilitate heat flow into the surroundings while hydrophobic surfaces impede heat dissipation to the surroundings.\textsuperscript{59} In this paper we show that an extremely small amount of aqueous solute molecules (1 solute molecule in 550 water molecules) increases the heat flow through a hydrophobic gold water interface. This result is consistent with an extremely localized interfacial interaction where minority aqueous components significantly alter the surface properties and thermal transport through the interface. Previous work has shown changes in solution viscosity at the ion solution/gold film interface. We also show that this property can be used to make an extremely sensitive molecular detector that is capable of single molecule detection without amplification or utilizing fluorescence labels.

\textit{Materials and Methods}

The optical measurements and characterization of the thermal sensor film has been described in detail previously.\textsuperscript{24} We use 532 Nd:YAG CW laser to excite a thin film (~270 nm thick) of Al\textsubscript{0.94}Ga\textsubscript{0.06}N embedded with Er\textsuperscript{3+} ions on a silicon substrate. The thin film acts as a thermal sensor film by measuring the relative photoluminescent intensities of the \( ^2H_{11/2} \rightarrow ^4I_{15/2} \) and the \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) energy transitions of the Er\textsuperscript{3+} ions. These intensities have been shown to be temperature dependent\textsuperscript{25,60} and are related by a Boltzmann factor (exp(-\( \Delta E/kT \)) where \( \Delta E \) is the energy difference between the two levels, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. The optical temperature measurements were made with a WITec \( \alpha \)-SNOM300s. The same Nd:YAG laser with adjustable power is focused with a 50X objective (Zeiss EC-Epiplan-
NEOFLUAR 50X/0.8 HD) onto the thin film thermal sensor. If the data is collected with the sample submerged in water, a Nikon 60X water immersion lens is used. The emitted light from the thermal sensor is collected with the same objective and sent to the CCD spectrograph with a collection fiber. The laser will simultaneously excite both the thermal sensing thin film and the gold nanowire. The nanostructures can be seen using bright field microscopy, once found, the thermal sensor film is translated with nm control under the objective during laser excitation. An image is collected by storing the full photoluminescence spectrum at pixel locations within the image (100 nm x 100 nm pixel size). A temperature image is constructed from the photoluminescence spectra at each pixel location. The collected spectra is smoothed using Savitzky-Golay fourth order and sacrificing 10 data points at the end of the spectrum. The scanning rate moves 100 nm every 0.03 seconds. The long time scales ensure the thin film temperature is in equilibrium with the nanowire. The maximum temperature measured minus the background temperature gives the change in temperature of the nanoparticle. Dynamic temperature measurements were also taken by monitoring the spectra over time. A survey spectral image was first taken to locate the particle. Spectra were then taken while focused on the particle over a period of time.

The gold nanowires are fabricated using conventional e-beam lithography with lift-off. The height of the nanowires is 64 nm measured with a Nanoscope IIIA Multimode AFM. The nanowires have a standard width of 108 nm and vary in length from 470 nm to 1100 nm. The width and length was measured with a JEOL JSM-5300 Scanning Electron Microscope. A single layer of around 100 nm of Poly(methyl
methacrylate) (PMMA) (950K A4 PMMA in Anisole) positive resist was spin coated onto the $\text{Al}_{0.94}\text{Ga}_{0.06}\text{N: Er}^{3+}$ thin film on Si. The PMMA was filtered through a 0.2 um frit to remove bubbles. The PMMA coated samples were baked on a hotplate at 205°C for 5 minutes. After baking, electron beam irradiation ($\sim$50 kV) was performed to draw the desired pattern/dots arrays with a resolution of $\sim$ 10 nm. The samples were then developed with MIBK: IPA= 1:3 (Volume) for 30 s and rinsed/cleaned in isopropyl alcohol (IPA) and dried with $\text{N}_2$. A thin adhesion layer of Ti (5nm) was first deposited then followed by a thicker (60 nm) layer of Au using DC sputtering. The residual layer was removed with warm a (60°C) acetone bath. All subsequent cleaning was done with a sonicication bath in IPA.

Results

Figure 1 shows SEM image of the lithographically fabricated gold nanowires. The standard width and height of the nanowires is 108 nm and 64 nm respectively with lengths of 470 nm, 580 nm, 860 nm, and 1100 nm.
Figure 4.1. An SEM image of lithographically fabricated gold nanowires with a standard height and width of 64 nm and 108 nm respectively. The lengths from smallest to largest are 470 nm, 580 nm, 860 nm, and 1100 nm.

3D thermal images of 470 nm long nanowire excited with $3.0 \times 10^9$ W/m$^2$ laser intensity surrounded by air, water, 2% g/g sucrose and 2% g/g NaCl are shown in figure 2. The maximum measured temperature decreases when the sample is submerged in water and continues to decrease with increasing solute molality. It should be noted that the solute molality of 2% g/g NaCl and 2% g/g D-Glucose is 1.3 $m$ and 0.11 $m$ respectively. The ionization factor for sugar and NaCl is 1 and 1.9 respectively.
Figure 4.2. A 3-D thermal image of the smallest gold nanowire in figure 1 with different surroundings of air, water, 2% g/g NaCl and 2% g/g D-Glucose. The excitation intensity in every image is $3.0 \times 10^9$ W/m$^2$.

Figure 3 demonstrates the temperature change of the 470 nm nanowire as a function of laser intensity. We measured the change in temperature of the nanostructure in air, water and varying solutions of glucose and NaCl. The heat slope decrease when the particle is submerged in water. More heat is dissipated when the sample is immersed in water compared to air and a lower steady state temperature is observed at the same laser intensity. The substrate is immersed with five different solutions of varying solute concentration. The three solutions are 2% g/g, 3% g/g, and 4% g/g of D-Glucose with two more solutions of 2% and 4% by mass NaCl. As seen in figure 3, the heat slopes deflect further with increasing solute concentration.
Figure 4.3. A plot that shows the change in temperature of the smallest gold nanowire as a function of incident laser intensity. The nanostructure temperature is measured while surrounded in air, water, 2% g/g, 3% g/g, and 4% g/g D-Glucose, and 2% g/g and 4% g/g NaCl solutions.

Figure 4 depicts the temperature change as a function of time for a 250 nm long nanowire.
Figure 4.4. The temperature of a hydrophobic coated gold nanoparticle surrounded by water is measured as a function of time (black). The decrease in temperature relates to the removal of the hydrophobic layer. This increases the heat dissipation, in turn lowering the steady state temperature. The temperature is then transformed in the thermal conductance and is plotted in red.

A survey temperature scan was imaged to locate the nanowire on the substrate. The temperature was then monitored as a function of time with a constant laser intensity of $1.6 \times 10^{10}$ W/m$^2$. The nanowire has a monolayer of chloroform on the surface that is displaced with water over time when heated. The local temperature change (shown as black dots) decreases with time as the heat dissipation into the surrounding liquid increases.
Discussion

The temperature of the nanoparticle is directly related to how well heat transfers into the surroundings. The following section details our method for determining how much heat is dissipated per second from each surface of the nanostructure. The temperature profile at all points in the nanowire is the same because the thermal conductivity of the gold nanowire is much larger than the thermal conductivity of the surroundings. The nanowires become thermalized with a temperature equivalent to the temperature maximum. The maximum measured temperature change is observed when the nanowire is irradiated at the center of the nanowire. A steady state temperature is obtained when the amount of heat generation is equal to the amount of heat dissipation. The heat generation is the product of absorption cross section and average laser intensity. The heat dissipation depends upon whether the nanowire is immersed in air or water. In air, heat only dissipates into the substrate and is given by equation 1.

\[ q_{\text{gen}}^{\text{air}}(W) = C_{\text{abs}}^{\text{air}} I_{\text{avg}}^{\text{air}} = q_{\text{diss}}^{\text{air}} = 12.8h_{\text{sub}}^{\text{air}} \Delta T_{\text{max}} \int_{x,y} dxdy \] (3.3)

The parameter \( h_{\text{sub}} \) is the heat transfer coefficient into the substrate and \( x \) and \( y \) are dimensions along the width and length of the nanowire respectively. The factor 12.8 in the heat dissipation term relates the local temperature of the nanowire to the measured temperature. This factor takes into account that our optical measurement of temperature is resolution limited and needs to be convoluted with the collection volume of our microscope and the true thermal image in the substrate. The thermal transfer parameter is a function of the numerical aperture of the objective used to make the measurement. The temperature measurements in air and water use different objectives
with numerical apertures of 0.8 and 1.0 respectively. The thermal transfer parameter relates the measured temperature (convolution of the sampled substrate temperature with the microscope point spread function) to the local temperature of the substrate at the nanowire. The thermal transfer parameter in air is 12.8 using an objective with a numerical aperture of 0.8 and a collecting fiber with an internal diameter of 25 µm.\textsuperscript{24} When the water immersion lens is used, the thermal transfer parameter is scaled by the ratio of the numerical apertures and becomes 10.2, i.e., \( 10.2 = \frac{12.8 \cdot 0.8}{1.0} \). The absorption cross section at 532 nm is calculated for different nanowire lengths in both air and water (see section below). Once the absorption cross section and two-dimensional temperature profile are known, then a substrate thermal transfer coefficient of 82 MW/m\(^2\)-K is determined using equation 1. This value is in reasonable agreement with gold sputtered films on SiO\(_2\) substrates.\textsuperscript{62} The heat dissipation per second for the nanowires immersed in water adds a new dissipative channel where heat can dissipate into water at the gold/water interface. The total heat dissipation per second when the nanowire is immersed in water is given by equation 2.

\[
q^{\text{water}}_{\text{diss}} (W) = 10.2 \left( h_{\text{sub}} \Delta T_{\text{max}} \int_{x,y} dx dy + h_{\text{water}} \Delta T_{\text{max}} \int_{x,y} dx dy + 2h_{\text{water}} \left( \Delta T_{\text{max}} \int_{y,z} dy dz + \Delta T_{\text{max}} \int_{x,z} dx dz \right) \right) \\
(3.4)
\]

The parameter \( h_{\text{water}} \) is the thermal transfer coefficient for heat dissipation from the gold interface into water and \( z \) is the dimension along the height of the nanowire. This model assumes that the lithographically prepared nanowire is a rectangular box having dimensions \( x,y, \) and \( z \) corresponding to the width, length and height respectively.
At steady state, $\dot{q}_{\text{water}} = C_{\text{water}} I_{\text{avg}} = \dot{q}_{\text{disss}}$, and $h_{\text{water}}$ is determined using the calculated absorption cross section in water and assuming that the heat transfer coefficient to the substrate does not change when the sample is submerged in water.

The laser intensity is given by a two-dimensional Gaussian profile that depends upon the full width half maximum (FWHM) of the laser spot. The laser intensity is not constant over the gold wire but varies along the wire. $I_{\text{avg}}$ is the average laser intensity illuminating the nanostructure. The average laser intensity is determined by first integrating the laser intensity over the two-dimensional dimensions of the nanowire and then restricting the length dimension to where half of the integrated intensity is obtained. The laser intensity at this restricted dimension is a constant and set to $I_{\text{avg}}$. The product of $I_{\text{avg}}$ and $C_{\text{abs}}$ gives the total heat generation.

Mie theory is used to calculate the absorption cross section for the four nanowires (see supporting information). Briefly, a prolate spheroid shape was used to approximate the rectangular shape of the nanowire. The absorption cross section $C_{\text{abs}}$, is given by equation 3 where $\varepsilon_{\text{eff}}$ is the effective dielectric constant of the surrounding medium, $\lambda$ is the wavelength, and $\alpha_j$ is the polarizability. The polarizability is a function of the particle’s size, shape, and dielectric constant. The effective dielectric constant is determined using a theoretical model for particle–substrate interactions and how these interactions influence the localized plasmon resonances of spheres and nanowires.\(^{15}\)

\[
C_{\text{abs}} = -8 \frac{\pi^2}{\lambda} \sqrt{\varepsilon_{\text{eff}}} \, \text{Im} \left( \alpha_j \right) \tag{3.5}
\]
The nanowire is excited with the laser polarized along the nanowire axis where only the longitudinal mode is excited. The absorption cross sections for the longitudinal mode of the different nanowire lengths, in both air and water, are presented in Table 1.

Table 4.1.

A table listing the calculated absorption cross sections of the longitudinal mode for the four Au nanowires of different lengths. The cross sections are calculated with the particle sitting on a substrate of AlN and surrounded by either air ($\varepsilon_b = 1$) or water ($\varepsilon_b = 1.77$). The value listed is the absorption cross section at the excitation wavelength (532 nm).

<table>
<thead>
<tr>
<th>NW length (nm)</th>
<th>$\sigma_{abs}$ in Air (m$^2$)</th>
<th>$\sigma_{abs}$ in Water (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>$2.40 \times 10^{-13}$</td>
<td>$1.06 \times 10^{-13}$</td>
</tr>
<tr>
<td>470</td>
<td>$1.49 \times 10^{-13}$</td>
<td>$9.24 \times 10^{-14}$</td>
</tr>
<tr>
<td>580</td>
<td>$1.51 \times 10^{-13}$</td>
<td>$9.96 \times 10^{-14}$</td>
</tr>
<tr>
<td>860</td>
<td>$1.77 \times 10^{-13}$</td>
<td>$1.27 \times 10^{-13}$</td>
</tr>
<tr>
<td>1100</td>
<td>$2.09 \times 10^{-13}$</td>
<td>$1.53 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Figure 5 shows the calculated absorption cross section as a function of wavelength for the 470 nm (black and green) and 1100 nm (blue and red) nanowire. The region around the excitation wavelength of 532 nm has been enlarged by a factor of 10 for clarity in this region.
Figure 4.5. The Absorption cross section for two gold nanowires (470 and 1100) is calculated and plotted as a function of wavelength. The absorption cross section is a function of the surrounding dielectric constants and therefore red shifts when surrounded by water. The maximum absorption wavelength also red shifts as a function of aspect ratio. The inset shows the abruption values at the excitation wavelength of 532 nm.

The transfer coefficients for heat dissipation of nanowires into aqueous solutions of different concentrations are shown in figures 6 and 7. Figure 6 plots the thermal conductance for all the nanowires of different lengths while figure 7 shows the thermal conductance for the 470 nm long nanowire as a function of number of adsorbed molecules.
Figure 4.6. A plot that shows the measured thermal conductance as a function of solute concentration. The dots correspond to the 470 nm, 580 nm, 860 nm, and 1100 nm wires. The thermal conductance increases rapidly with solute molality and levels off at approximately 0.3 m.

There is a slight difference between thermal conductance from nanowires of different lengths with only a slight increase with nanowire length. Pure water (zero molality) has an extremely low thermal conductance around $11 \pm 7$ MW/m$^2$-K. The thermal conductance for a hydrophobic gold water interface has been measured to be around 50 MW/m$^2$-K and 100 MW/m$^2$-K for a hydrophilic gold water interface.\textsuperscript{59} Our result is surprising as a much higher heat transfer coefficient is expected.\textsuperscript{63} An extremely low value for thermal conductance into water suggests that the gold water interface is hydrophobic.\textsuperscript{57, 59} Wettability of electrolyte solutions above metal interfaces have been
studied both experimentally and theoretically.\textsuperscript{64-68} We believe that sonication in IPA leaves a residual hydrophobic layer on the gold resulting in the low thermal conductance. The solution specific heat, density and viscosity change very little with solute concentration in the range of this study (4\% by mass). The behavior of solvated ions with at a gold interface have been studied previously.\textsuperscript{69, 70} This implies that the solution effusivity changes little for all aqueous solutions and, consequentially, the solution heat dissipation properties should be invariant to addition of solutes to the solution. A Kapitza length of 55 nm is calculated from \( \frac{\Lambda_f}{h_{\text{water}}} \) where \( \Lambda_f \) is the thermal conductivity of water of 0.6 W/m-K and \( h_{\text{water}} \) is the thermal conductance of 11 MW/m\(^2\)-K. Adding solutes to the solution increased the thermal conductance from \(~10\) MW/m\(^2\)-K to a saturation value of \( 50 \pm 20 \) MW/m\(^2\)-K. The increase in thermal conductance implies a reduction in the Kapitza length from 55 nm to 12 nm. These values for the Kapitza lengths are in good agreement with thermal conductance measurements\textsuperscript{59} and boundary slip measurements on hydrophobic surfaces.\textsuperscript{71} The addition of salt to aqueous solutions interacting with hydrophobic surfaces has been shown to increase the wetting properties of the solution.\textsuperscript{72} This suggests that solutes in the water increase the adhesion energy between the aqueous solution and hydrophobic surface. Recently, it has been shown that an increase in adhesion energy,\textsuperscript{20, 57, 58} causes an increase in heat transfer across the interface. This effect is most likely responsible for the observed increase in thermal conductance with increasing solute molality.

An alternative mechanism that could explains the decrease in temperature with increasing solute molality involves elevation of the solvent boiling point with increasing
solute molality. This mechanism, involving the colligative properties of water, is attractive because recent results suggests that solar heated nanoparticles in water can be used to generate vapor. Increasing the solute molality will increase the boiling point. If there is vapor surrounding the nanowires then heat transfer to the surrounding liquid will be inhibited and the temperature into the substrate will be increased. When the boiling point is increased, vapor generation is suppressed and heat transferred to the surrounding increased resulting in a lower substrate temperature. We do not believe that this is the mechanism because the range of laser intensity used in our measurements insured that the local temperature of the nanostructures was below the boiling point of water.

In order to determine if the thermal conductance is limited by the interface conductance at the gold liquid interface, a chloroform layer was deposited onto the gold through a sonication bath. The particle is then heated with the laser to displace the hydrophobic chloroform monolayer with water. The temperature was monitored during constant laser excitation of $1.5 \times 10^{10}$ W/m$^2$. As seen in Figure 4, the local temperature change decreases gradually over time from 295 K until a saturation temperature change of 190 K. The chloroform molecules at the surface are displaced by water molecules with a corresponding change in surface wettability. The interface wettability changes from hydrophobic to hydrophilic. The hydrophilic gold surface dissipates heat more readily than the hydrophobic surface. Because more heat is being dissipated into the surrounding liquid and less into the Al$_{0.94}$Ga$_{0.06}$N film the temperature drops. At the saturation temperature, further chloroform displacement does not change the dissipation rate into the liquid and no further temperature change is observed. The local temperature change is
converted into a thermal conductance (heat transfer coefficient) using equation 2. The
time dependent thermal conductance is shown as the red dots in figure 4. The saturation
thermal conductance agrees with the interface thermal conductance for a gold hydrophilic
surface\textsuperscript{59} confirming that the thermal conductance is limited by the interface conductance
of the gold liquid interface. As a further check, a 1-dodecanethiol (C\textsubscript{12}) self-assembled
monolayer was adsorbed on a clean sample and a thermal conductance of 50 ± 3 was
measured for heat dissipation into water. This value is in agreement with the interface
thermal conductance of a 1-octadecanethiol (C\textsubscript{18}) modified hydrophobic gold surface.\textsuperscript{59}

\textit{Molecular sensor detection limit.}

The largest sensitivity to molecular detection is observed when the gold surface is
hydrophobic. The interface conductance is smallest under these conditions. This leads to
the largest change in slope for temperature change with light intensity with the smallest
uncertainty. A change in this slope is easily observed when molecules bind to the
surface. In contrast, a hydrophilic surface has the highest thermal conductance where the
heat slope is the lowest and is inherently insensitive as a molecular detector. The
detection limit where the change in interface conductance due to molecular binding is
greater than the three times the standard deviation for pure water thermal conductance is
43 ± 12 sugar molecules (see figure 7).
Figure 4.7. A plot of thermal conductance as a function of adsorbed solute molecules. The number of solute molecules adsorbed onto the surface is calculated through the concentration of the solution. The error bars in this figure are three times the standard deviation. The dotted lines show how the standard deviation decreases with the number of molecules adsorbed. The red line shows the point at which the lower limit rises above the minimum upper limit, this is the limit of detection for this nanowire (470 nm x 64 nm x 108 nm). The current detection limit of this system is 43 ± 10 molecules.

Interestingly, the smaller thermal conductance for pure water improves the detection limit because the slope of temperature change versus laser intensity is inversely proportional to thermal conductance. The larger slope has the lowest uncertainty in the measurement and the best limit of detection. This detection limit is for a 470 nm long nanowire with an integration time of 0.03 s per pixel. The detection limit can be lowered by increasing the integration time of the measurement and decreasing the size of the
nanostructure. A longer integration time reduces the noise by the square root of the integration time and the smaller nanostructure reduces the size of the interface. The interface conductance from the hydrophobic gold nanowires appears to be relatively invariant with size (see figure 6). Smaller nanostructures, compared to larger nanostructures, have fewer interface molecules and should have a larger proportional change in the interface thermal conductance when displaced by target molecules such as sugar. This scaling law is confirmed by measuring the thermal conductance from 200 nm and 100 nm long nanowires covered with a 1-dodecanethiol (C₁₂) self-assembled monolayer immersed in pure water and 0.5% by mass solution of D-glucose. This data is shown in the supporting information. Also, smaller nanostructures have smaller absorption cross sections. Larger laser intensities can be used on the smaller nanostructure to generate the same change in temperature as larger nanostructures with smaller laser intensities. Larger laser intensity reduces the temperature uncertainties because the counts of Er³⁺ photoluminescence are proportional to laser intensity. Presently, the lowest sugar molality that can be detected on the 470 nm nanowire is 0.00193 moles/kg (43 sugar molecules/ 1.3 x 10⁶ water molecules). Increasing the integration time to 1 second should decrease this detection limit to 0.000334 moles/kg and single molecule detection becomes viable from a single nanocylinder, 40 nm diameter and 40 nm high. This size nanodot can be fabricated with e-beam lithography and easily probed with our molecular detection method.
Conclusions

The heat dissipation and thermal conductance from single gold nanowires immersed in aqueous solutions of D-glucose and sodium chloride are examined using a thermal sensor composed of a thin film of Al$_{0.94}$Ga$_{0.06}$N with incorporated Er$^{3+}$. A CW 532 nm laser was used to excite the nanowire and the thermal sensor simultaneously. The measured temperature of the nanowire is a direct function of the thermal conductance at the gold interface. The thermal conductance into the substrate is 82 MW/m$^2$-K, in agreement with previous measurements. When the sample is immersed in pure water, the thermal conductance into the water is low (~ 10 MW/m$^2$-K), indicating a hydrophobic surface interaction with water. The thermal conductance into the aqueous phase increases when solute molecules are bound to the surface. A saturation value of 50 MW/m$^2$-K is observed. The smallest number of solute molecules attached to the surface giving a measured detectable signal three times the standard deviation of the background signal is 43 ± 10 molecules. This occurs on a nanowire 470 nm long, 108 nm wide and 64 nm high. Because the thermal conductance does not change with nanostructure size, single molecule detection becomes viable for a single nanocylinder 40 nm in diameter and 40 nm high.
CHAPTER 5: SUMMARY AND FUTURE WORK

The first results using AlGaN:Er$^{3+}$ were published in 2012 and since then four more publications and two dissertations have been generated using this technology. I believe that we have just seen the tip of the iceberg with respect to the potential to publish using this technique. Heat transfer affects most everything we interact with; the ability to measure this on a local, nano scale is an incredible technique limited only by imagination.

The fundamental mechanisms of solid/liquid heat transfer are still largely not understood. In this work, gold nanostructures were used heated and measured simultaneously to probe the heat dissipation with respect to changes in the surroundings. Chapter 3 investigated the role of phase change when heating an extremely small volume of water. I observed the ability to superheat water past the boiling point via confinement. The water continued to rise in temperature until the spinodal decomposition temperature, 594 ±17 K. At this point, the system behaves chaotically. The temperatures measured at high laser intensities have a large amount of variance. The reason for this can be found within the laser scattering. Once the spinodal decomposition occurs, the laser is scattered away from the optics, the increased scattering causes in less nanoparticle excitation, the nanoparticle cools, and spinodal decomposition ceases. Once the spinodal fluid cools, the particle super heats the surrounding water and the spinodal decomposition cycles again. The nanoparticle cycling between spinodal decomposition and cooling results in the measurements appearing chaotic at high intensities.
Measurements were made to investigate how different solutions change heat dissipation of a nanoheater. To achieve a change in the solution properties, D-Glucose and NaCl solutions were made in 1%, 2%, 3%, and 4% w/w concentrations. I observed a strong dependence on the nanoparticle temperature (and thus heat dissipation properties) on solute concentration. The surrounding solution was better able to dissipate heat which larger amounts of solute present. This was incredibly surprising because at these low concentrations, the bulk properties such as thermal conductivity, dielectric constant, and density change very little. This yields the conclusion that the interfacial thermal conductance is changing as a function of adhered solute molecules on the surface of the gold structure. To test this, a layer of hydrophobic isopropyl alcohol is applied to the nanoparticle via a sonication bath. The temperature is then measured as a function of time. The nanoparticle temperature was found to decreases over time. This means the hydrophobic layer is slowly removed and the interfacial thermal conductance changes respectively. Interestingly, the molecular detection limit of our system is 43 ±10 molecules. This can be improved by increasing the signal to noise when collecting the data. Another option for optimization is to reduce the particle size. This will create a larger change in the thermal dissipation per molecule resulting in a lower detection limit.

Currently there are two projects that can be pursued by the Richardson group with nanoscale thermal sensing in mind. The first of which is probing the ability for nanoparticles to induce phase change in water. Secondly, can the ultra-sensitive molecular detector be optimized to a single molecule detector? Both of the projects will be discussed below.
Nanoparticles Inducing Phase Change

As detailed in chapter 3, inducing phase change with nanoheaters seems to be a complex process. To create a vapor, the surface tension of the water must be broken which is an intrinsic barrier to the transition. We observe the inability to cross this barrier at the nanoscale. Generally the barrier can be avoided by nucleating the vapor on a surface. It has been observed by Halas et al\textsuperscript{12,21} that bubble nucleation occurs from excited gold nanoparticles occasionally. I expect this means that nucleation of a vapor bubble using a nanoheater is a stochastic process. The superheated water phase is thermodynamically unstable but the nucleation barrier removes the ability to create a vapor phase.

A question then presents itself: How big is the barrier to nucleation. If the transition to the vapor phase is kinetically controlled, then the amount of time to create the bubble should be a function of the barrier’s magnitude. Theoretically the barrier to nucleation should also decrease with the temperature of the solution. The rate of bubble nucleation can then be tested at a multitude of different laser intensities (water temperatures) to measure how the kinetic barrier decreases experimentally.

The biggest challenge of this experiment will be amount of data needed. Although it is unknown how long it takes for a bubble to form using a nanoheater, the NSOM has only ever recorded a scattering event that could possibly be a bubble once. To collect enough data to model the thermal dynamics of the nucleation barrier would prove to be difficult.
Bubble nucleation at the nanoscale, if optimized could yield great prospects for chemical separation and water purification. The key to optimization is to retain the hot particle that will dissipate heat quickly into the surroundings but will also favor the nucleation of a bubble. My first thought into optimizing bubble nucleation is to change the ligand chemistry of gold nanoparticles. The ability to transport heat from the nanoparticle to the surroundings is a function of the wettability of the interface. Bubble nucleation can also be optimized by creating a non-adhering surface. To get the best of both situations a nanoheater must be engineered with half hydrophobic and half hydrophilic ligands. This will promote heat transfer into the surroundings and may possible create a nucleation site in immediate proximity to the nanoheater.

Creating a half hydrophobic half hydrophilic nanoparticle can be achieved multiple ways. I believe the easiest method would be to sputter the particles with a very thin layer of hydrophobic material while leaving the second half blank (hydrophilic). This creates an asymmetric nanoparticle with potential to create vapor bubbles fore efficiently.

*Molecular Sensor*

The second attractive topic to explore involves optimizing the molecular detector. Chapter 4 discussed the large change in heat dissipation properties when solute particles adhere to the surface. The simplest project is to monitor the binding of a protein to the gold structure through the change in thermal conductance. A large protein should have a significant effect on the heat transfer properties, particularly if the molecule has a large molar mass. Furthermore, multiple binding events could be observed in one experiment if
concentrations are controlled appropriately. I would expect the temperature to decrease in
discrete values over time as each binding event occurs.

The basic molecular detector still has avenues that can be pursued to improve the
detection limit. The particles can be optimized by changing the size, and shape. The
instrument methods could also be optimized by using a longer integration period. A new
lithographic sample will need to be fabricated to reduce nanoparticle size. Aside from
making the new sample, this should prove to be a relatively straightforward experiment.
A follow-up piece to Cahill’s nature paper\textsuperscript{20} could also be an possibility. SAMs can be
applied to multiple different gold nanostructure samples. The nanoparticle temperature
can be easily measured as function of SAM’s interaction with the surrounding fluid.
Different solvent/SAM interactions can be investigated by not immersing the lens into the
solvent (this will retain a good focal plane). This leads to many degrees of freedom that
can be explored to further understand heat transfer at a solid/liquid interface.
REFERENCES

64. Despa, F.; Fernandez, A.; Berry, R. S. *Phys. Rev. Lett.* **2004**, *93*, (22), 228104.