NONLINEAR OPTICAL EMISSION AND NEAR-FIELD ENHANCEMENT EFFECTS
IN ARRAYS OF GOLD BOWTIE NANO-ANTENNAS

BY

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Mechanical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2011

Urbana, Illinois

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ABSTRACT

This thesis investigates the effects of the large near-field intensity enhancements from periodic arrays of gold bowtie nano-antennas (BNAs) after illumination by laser light. Specifically, we focus on laser-induced damage, nonlinear optical emission, and a proof-of-concept for utilizing arrays of gold BNAs to enhance the forces in an optical trapping system. From FDTD simulations, the optical response of a single BNA is demonstrated to increase the local intensity by a factor of $10^3$ in the feed-gap region by using a periodic array. Because of the high near-field intensities, inherently weak nonlinear optical processes become enhanced, and we take advantage of these favorable conditions to investigate the dependence of second-harmonic generation and two-photon photoluminescence emission intensities with respect to the array periodicity and the incident polarization. A detrimental side-effect of the efficient radiative coupling to the incident light and high near-field intensities is laser-induced damage which may alter the morphology of the BNA structures at sufficiently high laser fluences. A damage threshold is systematically determined in terms of irradiation time and average incident power after implementation of damage reduction measures including laser pulse-width optimization, a stochastic beam-scanning pattern, and the use of a chromium adhesion layer. Finally, the increased optical forces in a trapping system resulting from the field enhancement of arrays of BNAs is demonstrated. In addition, based on the exclusive behaviors of these types of systems, a new method of characterizing plasmonically enhanced optical traps is proposed.
To my family and friends
ACKNOWLEDGEMENTS

It is my great pleasure to honor and thank everyone who has helped in making this work possible. First and foremost, I am sincerely thankful to my advisor, Prof. Kimani Toussaint, Jr. for his expert guidance, critical suggestions, kind advice, and constant encouragement throughout the course of my research. He has been a mentor of infinite patience and optimism who has given me the freedom to both explore many different areas in optics and develop my own approach to research.

I would also like to acknowledge and express my gratitude to all of my colleagues which have been instrumental for the achievement and progress of this work. I would specially like to thank Brian Roxworthy, Raghu Ambekar, Dr. Kin Hung Fung, and Dr. Anil Kumar for being a part of the teams that have helped overcome many of the challenges presented in this work. My lab mates Monal Mehta, David Luedtke, Erik Misawa, and Santosh Tripathi have also been an invaluable source of encouragement and inspiration for my research. I am also greatly thankful to Prof. Nick Fang and Prof. Logan Liu for their knowledgeable guidance, lively discussions, and collaborative environment during our meetings.

I would like to thank my many friends and family. Several close friends have added great memories during my time in Champaign which I will always hold in high regard. I would like to thank Emily for being who she is, for her love and her many sacrifices. Lastly, my family has been very loving, supportive, and understanding during this time of my life, and I am forever indebted to them for what they have provided for me.
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Chapter 1

Introduction

1.1 Background & Motivation

Research on the interaction of light with metal nanoparticles has become increasingly important due to their wide range of application, potential for use in novel optoelectronic devices, and their readily realizable benefits. The fundamental phenomena of metal nanoparticles that has held the interest of researchers is the surface plasmon (SP) polariton, which for metal nanoparticles with size dimensions on the order of the incident wavelength, can interact strongly with the incident light. This strong interaction can also result in a spatial redistribution of the incident light on a sub-wavelength scale, and it is how the light is distributed that makes these optical nano-antennas the subject of numerous studies.

Over the past decade, many advancements on the characterization of the plasmon resonance in nano-antennas have been made in an effort to achieve higher coupling efficiencies with the incident light. These advancements have gone hand-in-hand with the breakthroughs in nanofabrication, which
has enabled the creation of nano-scale objects of nearly any size, shape, and composition. This has spawned an entire class of novel geometries including nano-spirals,\(^1\) nano-stars,\(^2\) nano-bouquets,\(^3\) and nano-sunglasses.\(^4\) Because of this flexibility in fabrication, many of the characteristics of nano-antennas that promote strong coupling and sub-wavelength light confinement have been identified. Structures with geometric singularities such as sharp tips or corners have been shown to exhibit localized field confinement and enhancement of the applied field.\(^5\)–\(^7\) Another method is the use of dimer structures, where particles are in close proximity (< \(\lambda\)), which allows interaction between individual SP modes of the two structures and results in further increases of the field enhancement and confinement.\(^7\)–\(^14\) An extension of this is arrays of nanoparticles which show strong long-range interactions that may considerably increase the near-field intensity enhancements of an individual nanoparticle within the array.\(^9\)\(^,\)\(^15\)–\(^18\)

One of the more promising geometries with large field enhancements is the bowtie geometry, where two triangular nanostructures are placed tip-to-tip. They have been widely studied for their favorable optical properties \(^7\)\(^,\)\(^10\)\(^,\)\(^11\)\(^,\)\(^19\) and ability to manipulate light on a sub-wavelength scale.\(^13\)\(^,\)\(^20\) They have been proposed for use in photonic circuits,\(^21\) super-resolution optics,\(^22\)–\(^25\) and tunable nano-scale emitters.\(^26\)–\(^31\) The nonlinear optical response of gold nanostructures has shown to be useful in fundamental studies of their electronic structure,\(^32\)–\(^38\) which is the source of their favorable optical properties.

The work presented in this thesis investigates the combined use of sharp-tip geometries, coupled-plasmon nanoparticle-pairs, and periodic arrays,
and studies the associated effects of the resulting near-field intensity enhancement and confinement.

### 1.2 Thesis Organization

In this thesis, the unique phenomena resulting from large near-field enhancements in arrays of gold bowtie nano-antennas after illumination by laser light are explored. The remainder of this chapter elaborates upon the linear optical properties of arrays of gold BNAs. The theoretical groundwork for optimizing the field enhancement and confinement using sharp-tip geometries and periodic arrays are established through the use of FDTD simulations. Also, details of the fabrication are presented along with a description of the advanced microscopy platform.

In Chapter 2, the laser-induced damage is described within the context of a few notable studies from literature. Several damage reduction measures are introduced, and afterwards, a damage threshold is systematically determined. The particular behavior of the laser-induced shape changes observed for the BNAs are also discussed.

Chapter 3 describes a spectroscopic characterization of the nonlinear optical emission from arrays of gold BNAs using pulsed-laser illumination. In addition to second-harmonic generation (SHG) and two-photon photoluminescence (TPPL), typical of gold nanostructures, an analysis of the emission reveals a continuum generation that cannot be attributed to a single multiphoton process. A discussion on the mechanisms of SHG and TPPL are presented with an emphasis on identifying their relationship with the near-field enhancement.
Validation of a proof-of-concept for an optical trapping application which exploits the large near-field enhancements of arrays of gold BNAs is shown in Chapter 4. Utilizing the increased optical forces provided by the BNAs, complete manipulation of both single particles and clusters of multiple particles are demonstrated. The various behaviors of an unstable trap in this plasmonically-enhanced system, not seen in conventional optical tweezers, inspired us to describe a new term, “trampolining,” which forms the basis of a new method of characterizing future novel optical trapping systems based on plasmonic nanostructures.

1.3 Linear Optical Properties

Studies in the past few years have investigated the dependence of the field enhancement, field confinement, and optical resonances on various parameters of the geometry of the BNA including gap size, antenna size, and radius of curvature of the tip. For the resonance position, in general, increasing the gap size results in a blue-shift of the resonance peak for a given antenna size, and increasing the antenna size results in a red-shift of the resonance peak for a given gap size. The field enhancement has a more complex dependence on antenna size and gap size for a given material. In gold nano-dimers, for example, decreasing the gap size results in more of an increase in the field enhancement than increasing the antenna length. Optimizing each of these parameters is an iterative process for engineering the field enhancement and optical resonances when designing a nanostructure for a particular application.

Figure 1.1 shows FDTD simulation results of the dependence of the
resonance position on the gap size of a BNA. For resonant excitation, a
decrease in the gap size results in a red-shift of the resonance peak which
is expected.\textsuperscript{7,19,20,23,29,32,39} However, this red-shift is also associated with
a decrease in field enhancement which is known to be attributed to the
overall antenna size.\textsuperscript{7} The inset of Fig. 1.1a shows the field enhancement
intensity distribution for a BNA under resonant excitation, where the field
enhancement is confined in the gap region and the outer edges of the BNA.
The inset of Fig. 1.1b shows a similar distribution for nonresonant excitation
where the field enhancement is confined to the outer corners of the BNA with very little field in the gap region. This is indicative of a lack of coupling between the two arms of the BNA and contributes to the relative insensitivity of the field enhancement to a change in the gap size in Fig. 1.1b for nonresonant excitation.

Recently, increasing the field enhancement in nano-disks and nano-spheres have been investigated by arranging them into periodic arrays.\textsuperscript{9,15–18} Generally, the increase in the field enhancement from arrays of nanostructures can be discussed in the context of the coupled dipole approximation (CDA). The electric polarizability, $\alpha$, is the tendency of a charge distribution to be polarized into an electric dipole with moment, $p$, related to the electric field, $E$, by $p = \alpha E$. This is related to the overall extinction, $\sigma_{ext}$, by the optical theorem, $\sigma_{ext} = klm(\alpha)$, where $k$ is the magnitude of the wave vector. The electric polarizability for a single nano-scale particle, in the electrostatic approximation, is defined as

$$\alpha^{static} \propto V \frac{\epsilon_m - \epsilon_d}{3\epsilon_m + 3\chi(\epsilon_m - \epsilon_d)}$$

(1.1)

where $\epsilon_m$ and $\epsilon_d$ are the relative permittivities of the material and surrounding medium, respectively, $V$ is the volume of the particle, and $\chi$ is a shape factor.

In an array of nanostructures, assume one particle, or dipole, is excited. This dipole will reradiate a scattered field proportional to its dipole moment. Then, the net field on an adjacent particle will be equal to the incident field plus to the radiation from other dipoles. This leads to a system of coupled
equations, which when solved self-consistently for an infinite array, the
electric polarizability for an indistinguishable particle within the array, $\alpha^*$, is

$$\alpha^* = \frac{1}{\left(\frac{1}{\alpha}\right) - S}$$  \hspace{1cm} (1.2)

where $\alpha$ is the single particle polarizability and $S$ is a geometric arrangement parameter described by

$$S = \sum_{dipoles} e^{ikr} \left[ \frac{(1 - ikr)(3\cos^2\theta - 1)}{r^3} + \frac{k^2\sin^2\theta}{r} \right]$$  \hspace{1cm} (1.3)

where $\theta$ is the in-plane angle between dipole locations.

In this semi-analytical approach of the CDA, $S$ is defined only by the arrangement of the particles. While the definition of $S$ is known, it is difficult to optimize as a function of the particle arrangement for increasing the field enhancement because of singularities in the function due to the contributions of the individual resonance modes of the particles. However, when the particles are arranged appropriately, strong long-range interaction or coupling occurs in the array, which results in a higher quality resonance and increased field enhancement.\textsuperscript{15–17}

Figures 1.1c and 1.1d show FDTD simulation results of the dependence of field enhancement on the array periodicity or spacing for resonant and nonresonant excitation. As expected, resonant excitation in Fig. 1.1c shows higher field enhancement than the nonresonant case in 1.1d. The field enhancement for the nonresonant case in Figs. 1.1d shows two local maxima for 525 nm x 525 nm and 575 nm x 575 nm spacings. These two maxima correspond to the individual BNA resonance ($\lambda \sim 700 \text{ nm}$) and the array
resonance ($\lambda \sim 800 \text{ nm}$). For the arrays of BNAs shown here, the individual BNA resonance remains unchanged because the antenna size and gap width is held constant while varying the array periodicity. When the array periodicity is chosen such that its resonance is near the individual BNA resonance, the result is a dramatic increase in the field enhancement.

Figure 1.2a shows the experimentally observed peak position of the resonance as the array spacing is increased. This is a different representation of the plots in Figs. 1.1c and 1.1d, where a red-shift of the resonance is associated with an increase in the array spacing. As the array spacing is increased, the BNAs in the array essentially become isolated and the resonance position will be that of an isolated BNA. Similarly, as the antenna length is increased, the general linear trend is a red-shift in the resonance position. Figure 1.2b shows FDTD simulation results of the dependence of
antenna length (triangle altitude) on the resonance position for a BNA of a given gap size. However, this trend is expected to break down for longer antenna lengths due to the presence of multiple resonances.⁷

1.4 Fabrication

Fabrication of the bowtie nanoantennas was done at the University of Illinois at Urbana-Champaign with the help of Dr. Anil Kumar, from Professor Fang’s group (ECE department), and Edmond K.C. Chow, staff member at Micro-Nano Technology Laboratory (MNTL). Fabrication of the bowtie nanoantennas was done using electron beam lithography and electron beam evaporation.⁴⁰ First, a polished float glass substrate (CEC080P, Praezisions Glas & Optik GmbH, Germany), 25 mm x 25 mm x 0.4 mm in size (width x length x thickness) with a 25-nm thick, manufacturer-applied ITO-coating, is cleaned by ultrasonic agitation in an acetone bath for 5 minutes and baked at 200°C for 2 minutes. The sample is subsequently spin-coated at 2000 RPM for 60 sec with PMMA resist (2% solution of 95k mol. Wt. in anisoline, from MicroChem Corp.) to a thickness of ~90 nm and baked again at 200°C for 2 minutes. An electron beam lithography machine is used to pattern the resist (20 nA current) which is then developed in a 3:1 solution of IPA:MIBK with ultrasonic agitation for 3 minutes. After developing the sample, electron-beam evaporation (Temescal FC-1800 at MRL) is used to deposit a 3-nm thick Cr or Ti adhesion layer and 50-nm thick layer of Au at pressures of ~5 microTorr. In the last step, lift-off is done in an acetone bath with ultrasonic agitation for 3 minutes.

Figure 1.4 shows the relative layout of the arrays of BNAs on the sub-
Figure 1.3: Dimensions of the arrays of BNAs are shown in (a) where x- and y- correspond to the array spacing in those directions. SEM image of the fabricated arrays in (b).

Arrays of BNAs, 80 $\mu m \times 80 \mu m$ in size, are fabricated in up to fourteen columns of four rows each with an 80 $\mu m$ separation between each array. Each of the columns of arrays have various x- and y- center-to-center spacings, shown in Fig. 1.3, which are 425 x 425, 475 x 475, 500 x 500, 525 x 525, 575 x 575, 1000 x 1000, 1000 x 500, 500 x 1000, 500 x 500c, and a 25-micron patch, with each of the four rows being identical. Nominal dimensions for the two equilateral triangles comprising a single BNA are 120-nm side lengths and a 20-nm gap, and are also shown in Fig. 1.3. SEM images show the radius of curvature of the tips to be $\sim$15 nm. Two crosses, composed of two long strips 1-mm long by 5-$\mu m$ wide, are used for finding the structures in the microscope, and are placed at least 80 $\mu m$ from any given array. The arrays are also numbered sequentially for identification. The numbers are 6-$\mu m$ tall by 5-$\mu m$ wide and are placed 40 $\mu m$ above the
Figure 1.4: A diagram illustrating the layout of the arrays of gold BNAs on the substrate. Array spacings are reproduced identically for each column of four dies and are identified by sequential numbering placed $\sim 40 \mu m$ above the column of each die.

1.5 Advanced Microscopy Platform

The custom-built advanced microscopy platform (AMP) is the primary tool used in the following experiments. It consists of an Olympus BX51 microscope mounted directly above the base of an Olympus IX81 microscope a floating optical table. The essential components in the AMP are shown in Fig. 1.5.

An optical train consisting of lenses and dielectric mirrors couples the output of an ultrafast, wavelength-tunable Ti:Sapphire laser (SpectraPhysics MaiTai with DeepSee, 80-MHz repetition rate, 100-fs pulse width) to the
Figure 1.5: A schematic of the Advanced Microscopy Platform (AMP) used for all experiments. The main components of the AMP are an ultrafast Ti:Sapphire laser, a galvanometer-based scanner, a microscope (outlined in gray), and an EMCCD for imaging or spectrometer for spectral measurements (outlined in blue).

IX81 microscope. A motorized filter wheel in the IX81 contains a 45-degree, 670 nm, short-pass dichroic mirror (Semrock FF670-SDi01-25x36) and a 680-nm short-pass filter (Semrock FF01-680/SP-25) for illumination of the sample and rejecting the fundamental wavelength of the laser. A linear polarizer (Edmund Optics, Glan-Thompson) and half-wave plate (Thorlabs) combination allows the incident power to be varied without altering the polarization direction. Incident power is measured at the entrance of the...
microscope and reaches a maximum average power of 75 mW.

For imaging, an electron-multiplying charge coupled device (EMCCD) from Hamamatsu (C9100-3) is used in either reflection or transmission geometries. The EMCCD is vital for controlling the Z-position of the objective since a small change in the focal plane will affect both the illumination of the nanostructures and the collection of the emission. Used in conjunction with a built-in software-based auto-focus routine in IPLab, the Z-position of the objective is varied +/- 1 µm in 100-nm increments (21 steps total) with the internal motorized focus drive function of the microscope to identify the Z-position which produces the highest contrast image. This auto-focus routine is done two to three times prior to data collection to ensure proper focusing and collection of the objective. The objective used is a 100x fully-corrected, oil-immersion objective with an NA of 1.4 (Olympus UPLSAPO 100XO). A galvanometer-based scanner is used to scan the incident beam in a suitable manner.
Chapter 2

Laser-Induced Damage

2.1 Overview

Since the demonstration of the first laser device in the 1960s, scientists have acknowledged the destructive power of lasers.\textsuperscript{41-43} Their ablative nature has been exploited for many useful applications in industry where lasers are now commonly used for material processing,\textsuperscript{44} micromachining,\textsuperscript{45} and even surgical procedures.\textsuperscript{46} Despite this wealth of knowledge, the mechanisms of laser-induced damage (LID) in nanostructures are not yet widely understood, especially at high optical energies.\textsuperscript{47,48} In nanostructures, LID is a broad term used to describe either structural damage in the form of shape changes or optical damage in terms of irreversible changes of optical properties. Investigations of LID in nanostructures in the past were met with complications due to the limited feature-sizes of fabrication techniques and control of the environment to verify theoretical models. However, recent advancements in nano-fabrication have enabled more detailed studies of LID on the nano-scale to overcome experimental obstacles of the past
to achieve a better understanding of the fundamental mechanisms involved. These studies have become especially relevant for the undeveloped, yet promising use of nanostructures in photonic devices, where the demand for maximum output of a device is easily supplied by an increase in input laser power which may ultimately degrade or damage the materials involved.

In the following study of the nonlinear optical emission of arrays of gold BNAs (see Chapter 3), high laser fluences (radiant exposure) are used to increase the signal-to-noise ratio (SNR) of measurements, thereby increasing the likelihood of LID to occur. In fact, experiments prior to any consideration of LID, have shown that a high-SNR measurement of the nonlinear emission used incident intensities and exposure times that could completely destroy the sample. Because the intensity of the nonlinear optical emission is very sensitive to the field enhancement, and therefore the particle geometry (see Section 1.3), the primary interest of this chapter is to investigate methods of minimizing or eliminating LID, while maintaining a high-SNR measurement of the emission, if possible. In addition, the arrays of gold BNAs may represent an entirely different nano-scale system than those that have been previously used for LID studies. Thus, we have taken the approach of experimentally determining the LID threshold as a function of incident power and exposure time exclusively for our experimental system.

In this chapter, the unique behavior of LID for arrays of gold BNAs and the efforts to minimize the detrimental effects are discussed. Because the mechanisms of LID at the nano-scale are not yet completely understood, a few notable results of LID studies from literature are presented to further define the context of this work. The proposed theories consistently identify
the laser pulse fluence, the pulse duration, the wavelength-dependent absorption, and size, shape, and composition of the nanoparticle as fundamental properties. Using one of the proposed phenomenological thermodynamic models, the temperature of BNAs in our experimental setup is estimated. Finally, based on the hypothesized heating mechanisms, the results of LID reduction measures are discussed and a damage threshold is defined.

2.2 Identification in Arrays of BNAs

For the purpose of reducing laser-induced shape changes of the BNAs and determining a damage threshold, high-resolution SEM images, brightfield transmission images, and the nonlinear emission spectrum were used to make observations for identifying damage. Damage is identified by comparing observations before and after pulsed-laser exposure (from MaiTai). Any change or deviation of the post-irradiation observation from the pre-irradiation observation are qualified as damage.

Identifying damage is a binary, yes or no, decision and all measures of the degree of damage are made qualitatively, e.g., slight damage, severe damage. Because of the unique behavior of the post-irradiation shapes in these experiments, defining a universal metric for quantifying the degree of damage is difficult. However, when comparing two observations showing damage, it is often adequate to describe qualitatively the amount of damage solely by visual inspection since the sole priority is determining the presence of damage.

The use of SEM images is valuable for this work due to its high resolution and large depth of field. Another advantage for using the BNAs in the SEM
Figure 2.1: SEM images of a portion of exposed arrays. (a) shows unexposed bowties where \(x\)- and \(y\)- denote the spacings of the horizontal and vertical periodicity; (b) destroyed bowties after 30 minutes of uncompensated 58 mW; bowties after GVD-compensated irradiation for 7 minutes at (c) 30 mW and (d) 50 mW. Taken by Anil Kumar, ECE Dept.

is that they are fabricated on a conductive ITO-coated substrate which is easily grounded in the SEM. This allows the sample to be placed in the SEM without any prior sample preparation. Figure 2.1a shows an SEM image of BNAs pre-irradiation and Figs. 2.1b-d show post-irradiation at several incident powers and times. The shape of the structures in Figs. 2.1b-d have clearly changed from the original BNA shape (Fig. 2.1a).

Large changes in the shape, like those in Figs. 2.1b and 2.1d, can also be seen in the microscope. A set of bright-field transmission images are
shown in Fig. 2.2, where the well-defined square-shaped regions are those which have been exposed. In Fig. 2.2a, two patches have been heavily damaged and show different image characteristics than the patches in 2.2b which were not irradiated at such high fluences. The degree of structural deformation in Fig. 2.2a is similar in nature to Fig. 2.1b, and Fig. 2.2b is similar in nature to Figs. 2.1c and 2.1d.

In addition to the imaging-based techniques, the nonlinear emission spectrum can also be used to identify structural changes. It is the only one of these methods that can identify optical damage independent of a structural change and monitor any intermediate states prior to the final state of damage. Because of the strong dependence of the nonlinear processes on the geometry of the BNAs, a change in the spectrum can indicate a change in the geometry. Figure 2.3 shows sets of two spectra taken before (solid/upper curve) and after (dotted/lower curve) 7 minutes of exposure to 30 mW of incident power. The SEM image in Fig. 2.1c was taken from the same region of the sample as the spectrum, which verifies that a
structural change has taken place. However, due to the complexity of the nonlinear optical response in these nano-scale structures and without further investigation, we must be careful in the assumption that the change in the nonlinear emission spectrum is due only to the structural change. It is known that the plasmonic response in gold can be suppressed, but this bleaching effect is recovered in less than 10 ps. Nevertheless, we have not observed a change in the nonlinear emission spectrum in the complete absence of a structural change in post-irradiation SEM images.
2.3 Damage Mechanisms in Nanoparticles

The sequence of events leading to damage upon pulsed-laser exposure is quite straightforward. When a metal nanoparticle (NP) is exposed to laser light, the energy is absorbed by conduction-band electrons and acts to heat the NP through electron-phonon coupling and scattering which results in an increase in temperature. At high optical powers, the ensuing temperature increase can cause melting or vaporization of the NP. At very high optical powers, complete photoionization without melting has been shown to occur.\textsuperscript{48}

In contrast to the melting of macroscopic shapes of bulk materials, the dependence of size on the melting temperature is much more prominent on the nano-scale. Specifically, the reduction of melting temperature with a reduction in size, also known as melting point depression (MPD),\textsuperscript{49} can greatly affect the expected behavior of a nanoparticle subject to high temperatures. Several theoretical models based on both surface chemistry and classical thermodynamics have been used to explain this unique phenomena, however, researchers frequently observe differing results for the melting temperatures of nanoparticles of a given material that cannot be explained within the construct of a single model. Several phenomenological thermodynamic theories even predict that particles below a certain size should be melted at all temperatures.\textsuperscript{50}

Metals are unique in that they can absorb many photons compared to other materials. In addition, the heat capacity of electrons in metals is two to three orders of magnitude smaller than that of the lattice,\textsuperscript{51} which
can lead to very large differences in the temperature of the two as seen in Fig. 2.4 (from numerical simulation\textsuperscript{52}). The electrons equilibrate with the lattice through electron-phonon scattering and generally occurs within a few picoseconds for gold NPs.\textsuperscript{48,51,53} Within a few hundreds of picoseconds, energy dissipation from the lattice to its surroundings occurs.\textsuperscript{51}

The temperature increase in metal NPs is directly related to the irradiated laser fluence ($J \times \text{cm}^{-2}$), the absorption coefficient at the pump wavelength, and the pulse width.\textsuperscript{54} While the laser fluence and pulse width can be accurately determined and controlled, the absorption properties of the NP may not be.

To investigate the transient absorption properties of irradiated NPs for fluences that do not induce photoionization, a commonly used technique is the pump-probe method.\textsuperscript{55} Typically, a pump laser is used to excite the NP and a probe laser at a different wavelength is used to monitor the optical properties, usually absorption, of the excitation volume at a certain delay. The idea is that the response of the electronic structure, induced by the
pump and measured by the probe, is directly related to the absorption.

Figure 2.7 shows how the change in absorbance spectra of a 0.12 mM gold colloidal suspension changes relative to its unexcited state for a 20-ps pulse centered at 355 nm. It should be noted that the absorbance of gold NPs at 355 nm is mostly independent of shape and size. The change in the absorbance is related to the perturbation of the electron distribution near the Fermi level due to heating which subsequently affects the real and imaginary parts of the dielectric constant near the interband and intraband transition wavelengths. At pump wavelengths that do not excite the collective oscillation of the plasmon band, the pump effectively excites individual electrons which quickly equilibrate with the entire distribution (in a few femtoseconds) by electron-electron scattering processes causing a broadening of the plasmon band and a resulting decrease in the maximum absorption. As electron-phonon scattering processes set in and the system reaches temperature equilibrium, the optical properties return to the
unperturbed state.

However, if the optical energies involved are large enough, shape changes due to melting may occur. In the case of gold nanorods, the pump-probe method has been applied spectroscopically by Link et al. to measure the average optical extinction, which indirectly monitors a laser-induced nanorod-to-nanosphere shape change, and arrive at a melting threshold energy.\textsuperscript{55} By varying the fluence and assuming a constant absorption during the pulse duration, it was found that an average of 60 fJ is required to melt a single nanorod. Furthermore, it was found that the energy required to convert nanorods to nanospheres, corrected for the wavelength-dependent absorption coefficient, was independent of wavelength. This suggests that once the energy is absorbed, the method of delivery is irrelevant. This led to a derivation of the melting threshold energy of the nanorod, $E_{NR}$,

$$E_{NR} = C_p \times m \times \Delta T + m \times \Delta H_{melt}$$  \hspace{1cm} (2.1)

where $\Delta T$ is the temperature difference in Kelvin between room temperature (293 K) and the bulk melting temperature (1340 K), $C_p$ is the phase-independent specific heat (0.131 J · g$^{-1}$ · K$^{-1}$), $m$ is the mass of the nanorod using a bulk fcc-gold density (1.9297 $\times$ 10$^{-20}$ g · nm$^{-3}$), and $\Delta H_{melt}$ is the heat of melting (62.8 J · g$^{-1}$); which has been shown to compare reasonably well with the experimentally determined values of melting threshold energy ($E_{NR}$) for gold nanorods in solution.\textsuperscript{55} The amount of error associated (roughly 50%) with eqn. (2.1) is due to $E_{NR}$ being the value at which all NPs in the excitation volume are changed to spheres (rather than a single
NP), estimation of the excitation spot size, and the variations in sizes of the individual NPs.

If the laser pulse is much shorter than the characteristic time for heat dissipation to the environment, such as the 100-fs pulses in the BNA experiments, Takami et al. has suggested a similar thermodynamic analysis to estimate the temperature of laser-heated NPs. If the laser energy absorbed by the gold particles per unit mass, per pulse is

$$Q = \frac{P}{RM}$$

(2.2)

where $P$ is the average incident power, $R$ is the repetition rate, and $M$ is the mass of the NP, then the temperature of the gold particle can be estimated as

$$T = \frac{Q - \Delta H_{melt} - \Delta H_{vap}}{C_p} + 293$$

(2.3)

$$T = \frac{Q - \Delta H_{melt}}{C_p} + 293$$

(2.4)

where $\Delta H_{vap}$ is the heat of vaporization (1870 J·g$^{-1}$), and eqn. (2.3) is used if the temperature is above the boiling point ($T_{\text{boil}} = 3130$ K) and eqn. (2.4) if it is above the melting point ($T_{\text{melt}} = 1340$ K). Being above the boiling point (or melting point) means that the NP has absorbed enough energy to be vaporized (or melted), resulting in a size reduction (or shape change), therefore these values represent an upper limit estimate of the lattice temperature if the associated phase changes have occurred.

In their study with 7-ns pulses it was found that if the estimated temper-
ature is lower than the melting point, no shape or size change is observed. For temperatures between melting and boiling point, only shape change is observed. At the boiling point, size reduction occurs and the diameter of the resulting particle is dependent on average incident power. Above the boiling point, the NP diameter reaches a minimum and remains constant regardless of the estimated temperature. In a separate study using the same type of analysis, the authors of Ref. 59 suggest that these estimations should be only used in the femtosecond regime as studies of ablation of bulk metal thin films have shown that plasmon bleaching eventually transforms the material into a transparent state with a high index of refraction within the first nanosecond after excitation.

Investigations by Inasawa et al. considered the liquid skin melting (LSM) mechanism to explain the sub-melting point shape changes they observed in determining the melting threshold energy. In LSM, a liquid skin of finite thickness forms over a solid core, and at the melting temperature, the solid core instantaneously changes into a liquid. If LSM is present during a laser-induced shape change, the threshold energy would be much lower as it does not require the entire volume to melt. Using 30-ps pulses and measuring the mean aspect ratio of gold nanorods with various fluences, they determined that the threshold energy required for shape change is 16 fJ, suggesting that LSM is present.

At laser fluences capable of photoionization and vaporization of material, the structural and optical damage is readily apparent. It was shown by Link et al. that ablation of gold nanorods is not correlated with the fact that the boiling point was reached, but this conclusion may be due to suppres-
sion of vaporization in a solvent. In studies of bulk metal thin films in air, ablated material is prone to redeposition.\textsuperscript{60} It was also demonstrated that a 100x reduction in laser fluence is needed to induce ablation when using femtosecond pulses compared to nanosecond pulses and can be attributed to the NP dissipating heat to the environment during the excitation, for the case of nanosecond pulses.

Furthermore, the resulting gold nanodots (from nanorods) induced by femtosecond pulses (at 10.2 J cm\textsuperscript{-2}) appeared to have more jagged surfaces compared to the smooth spherical shapes from nanosecond pulses. This observation is indicative of photoionization and implies that a different LID mechanism is responsible for photoionization since material ejection can occur with or without melting at sufficiently high fluences.

Hleb et al. has developed a method of imaging and measuring the subsequent bubble/vapor generation of the surrounding media after NPs are superheated by exposure to high laser fluences.\textsuperscript{47} They used two 10-ns pump pulses at 532-nm or 750-nm at delays of 20-ns or 150-ns and measured the bubble characteristics. The bubble diameter and lifetime is known to be linearly proportional to the amount of thermal energy released.\textsuperscript{47} It was found that the damage threshold, defined as the laser fluence that caused changes in size, shape, or structure of 50% of the population of nanorods, was 5-7 times lower at wavelengths of 532 nm than at 750 nm, which seems counterintuitive due to their absorbance spectrum (see Fig. 2.5). This is explained by the bleaching effect of the plasmon band effectively causing a “saturation point” where no more photons may be absorbed. For two 750-nm pulses 10-60 times the experimentally determined damage threshold fluence, the
gold nanorods showed nearly identical bubble generation response from the two pulses even at a delay of 150-ns. As the fluence increased to 100 times the damage threshold, the nanorods gave a decreased bubble generation response at 150-ns but at 20-ns there was no change. Because gold nanospheres have low absorbance at 750-nm (see Fig. 2.5), this implies that the longitudinal plasmon response of the nanorods are maintained for at least 20-ns at fluences 100 times above the damage threshold. This is contradictory to the other experimental results mentioned above where rod-to-sphere shape change is on the order of tens of picoseconds and thus would not be able to absorb a second pulse at the nanorod absorption peak. Although their study is focused on photothermal energy conversion by NPs, it does provide insight to the mechanisms of LID, especially for the plasmonically-enhanced trapping studies presented in Chapter 4.

2.3.1 Effects of LID in BNAs

The previous discussion on experiments from literature aim to elucidate the fundamental physics behind LID by investigating ideal shapes such as rods and spheres. While the electron dynamics and principles of optical absorption remain the same, the effects of LID in arrays of gold BNAs are not as simple as ellipsoidal shape changes due to the complexity of our system. Here, we use ordered arrays of identical nanostructures with a well-defined shape in air, compared to a population of nanorods of various sizes, randomly oriented in an aqueous solution. The arrays of BNAs represent a different plasmonic system than nanorods in solution where the field enhancement and near-field confinement of BNAs are even more sensitive to
the morphology of the nanostructure. In addition, the use of a high-NA, oil-immersion objective focuses the laser beam much more tightly leading to much higher effective fluences and power densities. As a result, the effect of LID in arrays of BNAs are quite different, in particular the behavior of the shape change, ablation, and final post-irradiation shape.

Another important feature of the damage mechanisms in arrays of BNAs is the unique dependence on incident polarization. From the FDTD simulations in Section 1.3, the field enhancement for nonresonant excitation is lower than for the resonant case and confined to the outer edges of the BNA rather than in the gap region. The effect of this polarization dependence manifests itself in the shape of the final deformation and a higher damage threshold. Figure 2.8 shows the final state of the sample, with a 2-nm thick alumina coating on Cr adhesion layer, after 50 mW at 10 minutes for resonant (2.8a) and non-resonant (2.8b) incident polarizations. Interestingly, when the excitation is resonant, the two triangles appear to merge together.
Figure 2.9: SEM images of damage tests done with a stationary beam, pre-GVD compensation: (a) wide view of damage spots, (b) 10 minutes at 23 mW, (c) 30 minutes at 23 mW, (d) 10 minutes at 48 mW, (e) 30 minutes at 48 mW, and (f) 5 minutes at 100 mW for 525 x 525 nm spacing and Ti adhesion layer.

while for nonresonant excitation the triangles spread apart.

Figure 2.9 shows SEM images of an array where damage tests were performed with a stationary beam. The beam, prior to GVD-compensation, is focused using a 100x, oil-immersion, NA = 1.4 objective and the Ti adhesion layer sample is irradiated with incident powers of 23 mW for 10 and 30 minutes (in Figs. 2.9b and 2.9c), 48 mW for 10 and 30 minutes (in Fig. 2.9d and 2.9e), and 100 mW for 5 minutes (in Fig. 2.9f). There are several important things to note from these images.

In Fig. 2.9a, the radius of the circular area affected by the laser is several times larger than the estimated spot size of \( \sim 400 \text{ nm} \) \( (\lambda/2) \) for a diffraction-limited system, and increases with incident power. Also, considering that the damage radius is relatively circular, the circular shape of the illuminating spot and coupling of adjacent BNAs both come into play. This implies
that although only 1 - 2 BNAs are illuminated, adjacent BNAs are still affected by the laser, which is expected from the array effect (see 1.3).

When increasing the irradiation time from 10 minutes to 30 minutes for 23 mW and 48 mW in Figs. 2.9b - 2.9e, the degree of deformation seen in the images are arguably the same or more for both irradiation times. This follows the results of Section 2.3, where shape changes are shown to occur after the first pulse, and a bleaching effect that reduces the amount of incident photons absorbed. However, the most striking result of the stationary beam damage tests is that in each combination of irradiation time and incident power, the samples irradiated with a stationary beam show considerably less damage than equivalent samples irradiated with a scanning beam. For example, Fig. 2.1b shows near complete destruction of the BNAs after 30 minutes at 58 mW, and the SEM images in Fig. 2.8 show much more deformation than Fig. 2.9d after 10 minutes at 50 mW.

While not completely inconceivable, it is unlikely that the damage seen in Fig. 2.1b occurred instantaneously after a single pulse from the laser. A reasonable explanation for the higher degrees of deformation in the scanned samples is that this behavior is due to the dynamic nature of the system. As a region of the sample is scanned over time, it is unlikely that the beam will be rescanned at the exact same position or that the beam will be evenly illuminating BNAs at all times during the scan. Considering that the percentage of area occupied by the BNAs is roughly 10% for the densest array, the probability that the beam is partially illuminating a BNA or is centered on deformations or redepositions of ablated material is high. The end result is more deformation compared to the relatively steady-state station-
ary beam system. This also indicates that damage is dependent on both irradiation time as well as incident power.

Also worth noting, is that the lower triangles in the middle row of Fig. 2.9f show large shape changes compared with the upper triangle of the same BNA. The occurrence of the predominant shape change in the lower triangles is unclear. In addition, when using a long-working distance, 40x, NA = 0.6, air objective, the damage threshold is much lower, and damage is seen for average incident powers of 5 mW (not shown here). Whether this is due to the array effect or a larger spot size is unclear.

This discussion of BNA damage mechanisms indicates that some damage threshold, in terms of irradiation time and incident power, should exist which results in negligible laser-induced shape change of the original BNA geometry.

2.3.2 BNA Temperature Analysis

To estimate the temperature for the arrays of BNAs, the method of analysis described in Section 2.3 is used. For the case of the BNAs, a 100-fs pulsed laser with a repetition rate of 80 MHz at $\lambda = 780$ nm is used in conjunction with a 100x, NA = 1.4 fully-corrected objective. Therefore, the assumption that particle-environment heat dissipation is negligible during the pulse is valid. If the spot size is assumed to be 400-nm in diameter (diffraction-limited) and the energy distribution is uniform, then a single BNA receives approximately 13.5% of the total irradiation (ratio of BNA area to spot size).
Then at 20 mW average incident power,

\[
Q = \frac{(20 \cdot 0.135)\text{mW}}{(80\text{MHz}) \cdot (1.638 \cdot 10^{-14} \frac{\text{g}}{\text{bowtie}})} = 2.06 \frac{\text{kJ}}{\text{g \cdot pulse}}
\]  

and the temperature is estimated to be 1260 K in eqn. (2.3) and 15540 K in eqn. (2.4). These temperatures indicate that if there is enough energy to cause melting (or boiling), the temperature of the lattice would be 15540 K (or 1260 K) after the phase change(s). Since 15540 K assumes only melting and is above the boiling point, the BNA should be above the melting temperature. The estimated temperature for boiling (after two phase changes) is 1260 K, but is below the boiling point, so the BNA is considered to be at the boiling point. Following the discussion of Inasawa et al., both shape and size changes should be expected. However, by sampling portions of post-irradiation SEM images, 20 mW was experimentally determined to give no detectable structural deformation. The discrepancy may be due to deviations from the assumptions of energy absorbed or to the environment of the BNA.

At 30 mW, eqns. (2.3) and (2.4) give 9130 K and 23400 K, which are both much higher than the boiling point. This is consistent with the moderate damage seen in the SEM images (Fig. 2.1c). The lighter shade of material in the gap region is the Cr adhesion layer and the grainy appearance of the surroundings is the ITO-coated substrate. It is difficult to know whether the initial 50-nm thickness is maintained making it unclear if material has been removed.
As power is increased to 50 mW (Fig. 2.1d), we obtain 24870 K and 39100 K, and observe large deformations. It is clear that material has been removed, but it is unclear whether the lightly shaded portion of the image in close proximity to the bowties is redeposition after photoionization or diffusion of material along the substrate. The exact process would be indicative of the energy-transfer pathways at such high fluences. Because these images are taken after exposures of 7 minutes in length, it is expected that the structure is changing over this time scale, which would alter the optical absorption characteristics in a transient manner.

Even though structural damage was not observed for 20-mW incident power, the analysis above shows that the BNAs should be at the boiling temperature, but has not absorbed enough energy to transition to vapor. Whether the BNA is in a melted state for a short period of time before the temperature equilibrates with the substrate or the BNA is in a superheated state is uncertain, and the dependence of the optical properties on the phase (state of matter) is also uncertain. In addition, because of the high temperatures involved, alloying of the Au and adhesion material is a possibility and its effects are unknown. Despite the elementary assumption of absorbance and the large experimental differences for which these equations were in agreement, namely aqueous solution and particle geometry, the heat-transfer based estimated temperatures may provide a rule of thumb for the following studies. Nevertheless, the heating mechanisms discussed suggest that the LID seen in the experiments presented in this thesis may be unavoidable due to the time scales involved.
2.4 Damage Reduction Measures

In spite of the potentially unavoidable damage in our system revealed in the previous section, several basic measures were taken to combat the effects of LID. The pulse broadening, or positive group velocity dispersion (GVD), imparted by the optical train is compensated for by adding an equal amount of negative GVD. This minimizes the pulse width at the sample resulting in increased peak power per pulse, which gives an increased probability for nonlinear processes, for a given average power. The pattern scanned by the galvanometer-based scanner is modified from raster-type to stochastic-type, which results in a more even and total distribution of the irradiated scan area. Finally, to address the thermal effects, the adhesion layer is changed from titanium to chromium which has a slightly higher melting point ($1670 \degree C$ and $1863 \degree C$, respectively). Also, the usefulness of a thin layer of alumina ($Al_2O_3$), a material known to have a high melting point and high thermal conductivity, to aid in the dissipation of heat is investigated.

2.4.1 GVD Compensation

GVD is the spreading of the pulse due to chromatic dispersion in the optical train. The components in the optical train consist of lenses made of materials having a wavelength-dependent refractive index which results in the “red” and “blue” components of the pulse to travel at different velocities over time. When the pulse passes through the lens, the higher frequency components (blue) travel slower than the lower frequency components (red) and pulse is said to be positively chirped. Using the DeepSee module of the MaiTai Laser, which is essentially a prism compensator, the effect of the positive
chirp induced by the optical train is compensated for by adding an equal amount of negative chirp at the output of the laser.

From the preceding discussion on damage mechanisms (see 2.3), the principal cause of LID is the incident power density. Having the shortest pulse by GVD compensation provides an indirect means of reducing damage by reducing the needed incident power for this particular setup. Since the primary interest of the arrays of BNAs is to characterize the nonlinear optical response, two identical photons must interact with the system in a single, instantaneous quantum event. Achieving the highest peak power necessarily means having the shortest possible pulse. Increasing the peak power increases the number of photons and shortening the pulse increases the probability of simultaneous interaction of identical photons, thereby increasing the overall nonlinear emission. As a result, GVD compensation gives higher nonlinear emission intensity for a given average incident power irradiating the sample. Therefore, after GVD compensation, the average incident power on the sample can be reduced while maintaining a high signal-to-noise measurement of the nonlinear emission, and ultimately the damage is reduced.

Calculation of the amount of positive chirp induced in each component is difficult given the use of proprietary components such as lenses, polarizers, dichroic filters, and dielectric mirrors in the optical train. For this reason, the DeepSee module was calibrated by varying the motor position of the module and observing the change in two-photon fluorescence (TPF) intensity of 1-µm fluorescent beads (Duke Scientific, G0100). The motor position at which the highest TPF intensity is measured is assumed to be
compensated. Care was taken to ensure that the average incident power was kept constant while changing the motor position.

Figure 2.10 shows the TPF signal of fluorescent beads measured by the spectrometer before (red, lower curve) and after (blue, upper curve) GVD compensation for the same average incident power of 10 mW. According to the GVD compensation table given by manufacturer (see Appendix A.1), the amount of negative chirp for the default motor position is $-2800 \text{ fs}^2$, and the motor position resulting in the highest TPF intensity adds $-6483 \text{ fs}^2$ of negative chirp. The impact of GVD compensation is substantial as the TPF signal intensity is increased over 70% for the same average incident power.
2.4.2 Scanning Pattern

The galvanometer-based scanner is a vital component for illuminating large parts of the sample. A technique commonly employed in microscopy, the beam is scanned back and forth in the x-direction and stepped in one direction in the y-direction. This systematic process of progressively illuminating the entire scan area is called raster scanning.

There are several disadvantages in using a raster scan method for illumination of periodic arrays of BNAs. The signals sent to the scanner controller are digitized samples of a waveform, and given the periodic nature of both the scanning waveform and the sample itself, the overall sample coverage may become unbalanced with certain regions being exposed much more than others. In the most severe case, certain regions of the sample may not be exposed at all. This can be seen in the SEM image in Fig. 2.11,
where consecutive horizontal rows do not show similar degrees of deformation, implying that these rows were irradiated more than others. Decreasing the sampling interval of the waveform may help alleviate the uneven sample coverage by making consecutive beam positions closer. However, given that the periodicity of the densest array is 425 nm, the resolution of the scanner would ideally be $\sim 213$ nm to avoid skipping rows of BNAs during the scan. The time taken for the beam to cover the entire scan area would also be sacrificed when decreasing the sampling interval. Furthermore, a reduced sampling interval would not address the periodic nature of the waveform where specific points on the sample are repeatedly irradiated.

An alternative to a raster pattern is a stochastic pattern. In this method, the beam is positioned by sending random sets of x- and y-coordinates generated with a pseudorandom white-noise function (in LabVIEW). The image produced by a stochastic scan pattern shows less spatio-temporal artifacts and achieves relatively uniform illumination compared with the conventional raster pattern. Figure 2.12 shows a simulated output plot.
of 10,000 coordinates sent to the controller for the raster pattern (2.12a) and for the stochastic pattern (2.12b). Each coordinate is plotted with a marker radius of 0.5 units and the coordinates are integers. The color map corresponds to a histogram of the number of times each coordinate is sent to the controller with red being the maximum and blue being a minimum of zero. The distribution for the raster pattern in Fig. 2.12a has a maximum of 40 while for the stochastic pattern the maximum is 16. From this, and a visual inspection of the distribution of coordinates, it is clear that the stochastic pattern has a more uniform distribution of coordinates sent to the controller. Therefore, using the stochastic scan pattern greatly reduces the frequency of points repeatedly scanned and should result in damage reduction.

A disadvantage of the stochastic pattern over the raster pattern is related to a practical consideration for both types of scans. The inertia of the scan head, which consists of the mirror, mirror support, and motor, fundamentally limits the speed at which the beam can be scanned. When scanning at high speeds, the system can no longer control the scan head, and in our system, the scan heads return to a home position for a brief period of time before scanning resumes. In a raster pattern, the distance between consecutive scan coordinates is relatively small. However, for the stochastic pattern the distance between coordinates is random, and for a square-shaped scan area there is a small, but non-zero probability for consecutive coordinates to trace out the diagonal of that square.

The consequence of the reduced scan speed is not readily apparent when implemented because of the much faster fill rate of the stochastic scan.62
Figure 2.13: TPF images of fluorescent beads taken with 20 ms exposure and 16x accumulation for (a) raster scan and (b) stochastic scan. Raster scan sampled at 10 kHz, 200 Hz.

Figure 2.13 shows TPF images of fluorescent beads after 320 ms of exposure (sum of 16 20-ms exposures). Both scan patterns were scanned in a 0.5 V scan window, with the raster scan sampled at 10 kHz for the x-mirror, 200 Hz for the y-mirror, and 0.01 V step size, and the stochastic scan was sampled at 7.5 kHz for both mirrors. Comparing Figs. 2.13a and 2.13b, the stochastic scan does appear to fill more of the scan area than the raster scan for the same time frame.

With regards to damage reduction, figure 2.14 shows post-irradiation SEM images of the 425 x 425 nm array with Cr adhesion layer after an exposure of 6 minutes at 65 mW for both types of scan patterns. By visual inspection of the images, the raster scan image (Fig.2.14a) shows more deformation than the stochastic scan image (Fig.2.14b), particularly in the lower three rows. While not completely conclusive, combined with the experimental comparison presented here and the results of Jureller et. al.\textsuperscript{62}
the stochastic scan pattern is a suitable technique for damage reduction.

2.4.3 Materials

For the sake of brevity, post-irradiation SEM images of both Cr and Ti adhesion layer samples have been shown without a discussion on the choice of material. An adhesion layer is used in fabrication of these structures to aid in the adhesion of gold to the substrate. The most widely used adhesion layers for gold are chromium (Cr) and titanium (Ti). Prior to knowledge of LID in our structures, the first choice of Ti as the adhesion layer material was arbitrary, although it was recently reported that adhesion layer material plays a crucial role in plasmonic nanostructures.

From the phase diagrams shown in Fig. 2.15, the melting temperatures for Ti and Cr are shown to be 1670 °C and 1863 °C, respectively. Although the calculations in Section 2.3.2 show potential temperature changes much higher than the melting points of either adhesion layer material, every attempt to reduce damage and shape deformation should be taken.
Figure 2.15: Phase diagrams of the (a) Ti-Au system, and (b) Au-Cr system. Melting temperature for Ti and Cr is 1670 °C and 1863 °C, respectively.

The images of samples prepared using a chromium adhesion layer are figures 2.14b, 2.8, 2.1c, and 2.1d. The images of samples prepared using a titanium adhesion layer are figures 2.14a, 2.11, 2.9, 2.2, and 2.1b. In each case, for a similar irradiation time and average incident power, the Cr adhesion layer samples exhibit less shape deformation and damage.

In addition to changing the adhesion layer material, the effects of a thin layer of Al$_2$O$_3$ was also investigated. The excellent thermal properties of alumina is well known. Upon heating, it maintains its phase as a crystalline solid up to its melting point of $\sim 2050^\circ$C, has a high heat capacity per unit volume, and has high thermal conductivity.

A conformal alumina coating of 1-nm or 2-nm thickness was applied to the BNA sample using atomic layer deposition (ALD). At these thicknesses, the coating should have a very small effect on the optical properties of the BNAs. The main idea is that the coating should increase heat dissipation away from the BNAs and reduce damage. Also, should melting occur, the rigidity of the coating would serve to maintain the shape of the BNAs after
Damage tests were performed on arrays of BNAs with a Cr adhesion layer for samples with and without an alumina coating. The average incident power, incident polarization, and thickness of the coating were varied for exposures of 10 minutes. After the samples were irradiated, post-irradiation SEM images were taken and measurements of the area of the triangles were compiled.

Figure 2.16 shows a plot of average incident power versus triangle area for the various experimental conditions. Each point on the graph is an average of the areas of 8 adjacent triangles (4 bowties). To estimate the
area of a triangle, the altitudes of 8 triangles are measured \((h_1, \ldots, h_8)\), averaged and used in the formula for the area of an equilateral triangle defined as

\[
A = \frac{\sqrt{3}}{3} \left( \frac{\sum_{i=1}^{8} h_i}{8} \right)^2
\]  

(2.6)

where \(A\) is the area. For damaged BNAs that no longer resemble a triangle, the length of the longest distance between two points lying on the edge (chord) is used.

For a given incident power, samples with 1-nm thick alumina coating show less decrease in the triangle area compared with uncoated samples. Samples with a 2-nm thick alumina coating show the similar final triangle areas after irradiation by 45-55 mW compared with uncoated samples irradiated by only 30-40 mW. The results of these damage tests, shown in Fig. 2.16, indicate that the use of an alumina coating improves the damage resistance in terms of minimizing the change in triangle area. However, Section 2.3 discussed the temporal evolution of the energy transfer and dynamics of an irradiated NP. If the particle–environment heat transfer (hundreds of ps) is an order of magnitude longer than the particle thermalization (tens of ps), then no amount of surface additive can enhance heat transfer when a 100-fs pulse is used.

2.5 Summary

The sole purpose of the experiments presented above is to determine what average incident power does not result in damage. After unexpectedly observing laser-induced damage (LID) in post-irradiation SEM images of ar-
rays of BNAs, damage mechanisms and reduction measures were investigated. Post-irradiation SEM images were heavily used for identification and qualification of LID.

Proposed theories of damage mechanisms from literature have generally identified several important parameters influencing damage. These are the laser pulse fluence, pulse duration, and the optical absorption properties of the NP being irradiated. In the studies presented here, the pulse duration is optimized and held constant, while the laser pulse fluence is varied by controlling the average incident power irradiating the sample. In addition to the dependence on incident power, it was determined that other factors unique to our experimental system also influence the LID.

The attempts to combat the effects of LID may not have been ideal based on the discussion of damage mechanisms in Section 2.3. The addition of the alumina layer may help in distributing the heat evenly in a nanosecond or greater time scale, but on the femtosecond time scale of absorption and thermalization of the BNAs, the alumina may have no effect in terms of preventing LID. Similarly, changing the adhesion layer material to one with a higher melting point may also have no effect due to the short time scale. However, the studies of transient thermal mechanisms of Au nanorods were performed in aqueous solution where the solvent has significantly higher heat transfer coefficient and heat capacity than air, where studies of BNAs were done. A repetition rate of 80 MHz corresponds to a delay of 80 µs between pulses, which may be long enough for the BNA to cool completely in solution, but when supported by a substrate in air, an increase in temperature over several pulses may be present. The follow-up experiments of
alumina-coated BNAs indicate a damage resistance in terms of preventing shrinkage of the triangle area.

Damage reduction measures included changes to the adhesion layer, scan pattern, and optimizing the laser pulse width. The effect of changing each of these parameters also aided in gaining insight to the specific LID mechanisms in arrays of BNAs. Not only was a dependence of LID on incident power found, but also the extent of damage was found to be dependent on both irradiation time and scanning pattern.

The discussion here merely highlights the complexities of LID, and the difficulties in verifying the hypotheses presented are the same as those in literature. The experimental system and conditions are very difficult to control well enough to characterize the fundamental phenomena. However, through a systematic study, guided by the results of a few notable publications, we have been able to implement damage reduction measures and determine a damage threshold based on incident power and irradiation time for our specific experimental system of arrays of BNAs. These results will prove useful in any future experiments involving arrays of gold BNAs.
Chapter 3

Nonlinear Optical Emission

3.1 Overview

Research on the optical response of bowtie nano-antennas (BNA) has gained attention in the scientific community due to their favorable optical properties and ability to manipulate light on a sub-wavelength scale. They have been proposed for use in photonic circuits, super-resolution optics, and tunable nano-scale emitters. In particular, the nonlinear optical response of gold nanostructures has shown to be useful in fundamental studies of their electronic structure, which is the source of their favorable optical properties.

Here, the exceptional field enhancement in arrays of gold BNAs are exploited for the study of its nonlinear optical response. The theory presented in section 1.3 elaborates on the linear optical properties of BNAs. Essentially, the large electric-field intensity enhancement arises from a combination of the localized surface plasmon resonances (LSPR) in sharp-tip geometries and the electrodynamic coupling of LSPR modes in dimer nanostruct-
tures, which results in a confinement of the applied field to a subwavelength gap. This antenna effect has also been shown to enhance nonlinear processes such as second-harmonic generation (SHG), third harmonic generation (THG), two-photon photoluminescence (TPPL), and continuum generation. The large electric-field enhancements and nonlinear emission from nanostructures can be further enhanced by arranging them in periodic arrays. However, the optical response of a nano-scale system combining the array effect with the inherently large field enhancements of coupled-plasmon resonant-nanoparticle pair geometries has not yet been investigated. Since the nonlinear optical response has a polynomial dependence on field intensity, the effects of field intensity should play an important role in the nonlinear emission. Characterizing the nonlinear optical response is a crucial first step in engineering their design for next-generation devices.

3.1.1 Additional Theory

Second-harmonic generation (SHG) is a special case of sum-frequency generation (SFG) and typically only occurs on non-centrosymmetric systems. When two identical photons simultaneously interact in a non-centrosymmetric system, SHG can occur and the result is the emission of a single photon with twice the energy of the incoming photons. A simplified schematic of this process is depicted in Fig. 3.1a. For example, two interacting photons at $\lambda = 800$ nm ($\nu = 375$ THz) result is an emission of a single photon at $\lambda = 400$ nm ($\nu = 750$ THz) when SHG occurs. In arrays of gold BNAs, the non-centrosymmetry exists at the gold-air and gold-substrate interfaces.
Two-photon photoluminescence (TPPL) is the emission of a photon due to the relaxation and recombination of an electron-hole pair after two-photon absorption. A diagram of the electronic structure for gold is shown in Figs. 3.1b and 3.1c. When the system is illuminated, electrons in the occupied $d$-type band below the Fermi level are excited by two-photon absorption into the unoccupied $sp$-type conduction band. The excited electrons lose energy in the conduction band due to intraband scattering processes until they approach the Fermi level and recombination occurs. Radiative recombination after the previously described process is termed TPPL. The energy of a TPPL photon is related to the interband separation between the ground and excited states, but due to competing non-radiative pathways and processes, such as heat, TPPL is observed as a broadband emission.

In gold, the TPPL process is most efficient when the incident wavelength, or incident photon energy, matches the $d$ to $sp$ transition energy for two-
photon absorption. If the linear optical response of a gold nanostructure is designed to also be resonant with this transition energy, then the TPPL emission can be resonantly enhanced due to the increased electrodynamic coupling of the incident light. The term “plasmon-assisted” is also widely used.

It was recently suggested that a similar enhancement mechanism occurs for SHG and THG in gold nanostructures as well. A more common view of the enhanced SHG emission attributes the enhancement to increased local field intensities and confinement in plasmonic nanostructures. However, it should be noted that the exact mechanisms of SHG in nanoscale structures, particularly the sources of the second-order nonlinearity, are still a subject of research.

3.2 Experimental Setup

Characterization of the nonlinear optical response of the arrays of BNAs is carried out using the advanced microscopy platform (see Section 1.5) after implementation of damage reduction measures (see Section 2.4). Briefly, an ultrafast near-infrared laser with a 100-fs pulse is used to illuminate arrays of BNAs with various spacing. The arrays of BNAs with a Cr adhesion layer are fabricated by e-beam lithography on an ITO-coated glass substrate (see Section 1.4). Using a stochastic scan pattern (see Section 2.4.2) and a fully-corrected oil-immersion objective (100x, NA = 1.4), an unexposed region of the sample ~ 25 x 25 µm is illuminated for a maximum of 120 seconds. The average incident power for these experiments is set to 10 mW (peak power density ~ 10^{12} W/cm^2, peak fluence ~ 32 mJ/cm^2) by a half-wave
plate and linear polarizer combination, where incident polarization is set to excite the BNAs in a resonant or nonresonant fashion. The optical emission is collected in reflection geometry by the same objective and coupled to either a CCD spectrometer for spectral analysis or an EMCCD for imaging. A majority of the experimental process is automated with a script written using AutoHotKey, an open source program used under GNU General Public License.

A spectrometer was custom-built to address the unique difficulties in measuring the spectrum of the nonlinear optical emission from arrays of gold BNAs. Due to the nature of the emission, several design considerations were made which required the use of a specialized spectrometer. The emission from the BNAs is expected to have low intensity and contain both narrow- and broad-band components over a wide range in the visible spectrum. In addition, long periods of illumination are not preferred due to potential damage of the structures (see Chapter 2), which makes a typical monochromator design with rotating elements disadvantageous. Thus, a high sensitivity, high resolution, high throughput, spectrograph (or polychromator) is needed.

The custom-built spectrometer consists of two primary components, the grating and the detector. For the grating, an aberration-corrected concave holographic grating (Jobin Yvon CP140-103) was chosen due to its high throughput (f/2) and wide spectral range (190 nm – 800 nm) while maintaining a low dispersion (24.2 nm/mm) for relatively high-resolution measurements. The configuration of the CP140 is favorable since a single component serves as a dispersive element, collimating mirror, and focusing
mirror. It has a two-dimensional focal plane of 25 mm x 8 mm in size and is used with a 500 µm entrance slit.

For the detector, a full-frame CCD camera (Andor iDus DU420A-BU) was chosen for its large sensor area, large pixel size and high quantum efficiency throughout the UV-Vis spectrum. The back-illuminated CCD sensor is 1024 x 255 pixels with 16-bit digitization. The image area of the sensor is 26.6 mm x 6.7 mm, which is slightly larger than the length of the spectrum at the focal plane of the grating (25.2 mm). This ensures that the entire spectrum is detected by the sensor. The relatively large pixel size (26 um x 26 um) gives high sensitivity with low noise in low-light conditions. The camera is also equipped with a thermoelectric cooler which is able to cool the sensor down to -60° for increased noise attenuation.

Because the focal plane of the grating extends 25.83 mm outside of its housing and the focal plane of the CCD sensor is -10 mm from the entrance window, a spacing plate was used to maintain the proper separation be-
tween the two components. The plate was fabricated from an aluminum
block (6061-T6) in the MechSE Machine Shop by Kyle Cheek, Staff Me-
chanic (see Appendix A.3 for drawing). Two views of the plate are shown
in Fig. 3.2 In addition to matching the focal planes of the camera and grating,
the spacing plate securely mates the two components together in a
light-tight manner.

Proper entrance optics for the spectrometer ensure that the image is
properly relayed into the grating which minimizes stray light, maximizes
throughput, and optimizes resolution of the measurement. The entrance
optics were chosen based on the microscope output and limited space on
the optical table for spectrometer placement. WinLens3D basic, a free ray-
tracing program, was used to simulate various lens combinations for use as
entrance optics.

The primary design consideration for selecting the entrance optics is
NA-matching, where the NA of the grating and the NA of the entrance
optics are identical. Using the 100x oil-immersion objective, a 25 x 25 µm
area of a fluorescent bead sample was illuminated and the image size at
the output of the microscope was determined to be \( \sim 5 \) mm in diameter.
The placement of the spectrometer was extremely limited due to size of the
instrument and other optics already on the table. Because of the low-light
application, the use of mirrors and relay optics should be kept to a minimum
to avoid unnecessary losses. The spectrometer was placed with a distance
of \( \sim 545 \) mm between the microscope image plane and the spectrometer
entrance slit plane.

Based on the spectrometer input NA of 0.25, an object-to-image distance
of $\sim 545 \text{ mm}$, and an entrance slit width of $500 \text{ µm}$, several lens combinations were analyzed in the ray-tracing program. Selection of the lenses is complicated by the availability of commercially available lenses, which are limited to 5 mm increments for focal lengths between 30 and 60 mm, and 50 mm increments for focal lengths greater than 100 mm. The final design of the entrance optics included two lenses with focal lengths of 35 mm and 400 mm. A summary of the final design parameters, including distances between lenses, is shown in Fig. 3.3 along with a schematic of the layout. These lenses placed at the correct distances provide proper relaying of the microscope output and proper illumination of the grating.

Given the high sensitivity of the spectrometer and need to detect weak
Figure 3.4: Spectra of the Mercury-Argon calibration source after alignment. The yellow doublet of the Mercury emission lines is clearly resolved at $\lambda = 576.96\ nm$ and $\lambda = 579.07\ nm$

signals, the system is shielded from ambient light. Prior to shielding, appreciable levels of ambient light were detected even with all overhead lights turned off. The majority of the ambient-light noise is due to the computer monitor and various “on/off”-type LEDs on other instruments. Light shielding was done on two sub-systems of the setup, one containing components outside the microscope and the microscope itself. To test the effectiveness of the light-shielding measures, the system was tested with a relatively long 5-second exposure using the highest sensitivity setting (33kHz, 64.25 µsec) in full vertical binning (FVB) mode.

Shielding of the first sub-system, the region from the output of the microscope to the input of the spectrometer, was done with blackout cloth (Thorlabs, BK5). The blackout cloth was stiffened by gluing a sheet of
common printer paper to the cloth and rolling it up into a tube so that the white printer paper is on the outside. These tubes were placed at the interface of each entrance optic such that this system is light tight. Upon testing the first sub-system, no light was detected (flat line at noise floor), verifying that this portion of the system is light-tight. Shielding of the second sub-system, the region from the laser output to the microscope output. The primary means of ambient light coupling to the spectrometer system is through the high-NA objective. Various pieces of blackout cloth were draped around the microscope and a long exposure measurement was again performed to verify that the system was light-tight.

After aligning the entrance optics and light shielding the system, the spectrometer system was calibrated using the low-pressure gas discharge lines of a Mercury-Argon source (Ocean Optics Hg-1). The output of the calibration source was coupled into the microscope using a 50-µm fiber optic cable placed at the focal plane of a NA = 0.25 objective (low-NA). The output of the low-NA objective was focused into the high-NA 100x oil-immersion objective in the advanced microscopy platform. Figure 3.4 shows the raw spectrum of the calibration source prior to wavelength correction. The yellow Hg doublet at 576.96 nm and 579.07 nm are clearly resolved in the spectra, which verifies proper alignment of the system.

3.3 Results & Discussion

3.3.1 Array Periodicity

Figure 3.5a shows the nonlinear emission spectra for several arrays of BNAs. Each curve shows a narrowband emission at the second harmonic
Figure 3.5: In (a): nonlinear emission spectra for arrays of gold BNAs with 500 x 500 nm (green), 1000 x 500 nm (purple), 500 x 1000 nm (black), and 1000 x 1000 nm (pink) array spacings. In (b): field intensity enhancement in several arrays of gold BNAs, from FDTD simulation.

(\(\lambda \approx 780\) nm) and a broadband continuum emission that extends to \(\lambda \approx 660\) nm, the cut-off frequency of the laser-blocking filter (see Section 1.5, Fig. 1.5). The small fluctuations in the spectra are due to a possible Fabry-Perot resonance between the sample substrate and the protective cover slip. An apparent discontinuity in the spectra can be seen at \(\lambda \approx 525\) nm as well as a slight curvature of the between the narrowband peak and the discontinuity. A broadband emission that extends over such a large region is unexpected for gold nanostructures.\(^{12,13,19,34}\)

A general trend can be identified by comparing the rank order of the
emission intensity in Fig. 3.5a with the rank order of the magnitude of field enhancement at $\lambda = 780$ nm in 3.5b. For both incident polarizations, the arrays with highest and lowest emission intensities are 500 x 500 nm and 1000 x 1000 nm, respectively, which also correspond to the highest and lowest field intensity enhancement from the simulation. For non-resonant polarization, the small difference in field intensity enhancement for 1000 x 500 nm (purple) and 500 x 1000 nm (black) spacings (in Fig. 3.5b) also appear as small emission intensity differences in Fig. 3.5a. This rank-order comparison of the emission intensity and field intensity enhancement from simulations is consistent with the theory presented earlier (see section 3.1.1), where higher nonlinear emission intensities are observed for structures with higher near-field intensity enhancements.

3.3.2 Power Dependence

Because of the spectral location of the narrowband emission peak at the second harmonic of the incident wavelength, this portion of the spectrum can be attributed to SHG. The region of the spectrum between the SHG peak and the discontinuity at $\lambda \sim 525$ nm can initially be assigned to TPPL based on its spectral location.\textsuperscript{12,13,19,34} However, a test of the power dependence of the emission intensity is needed, in addition to consideration of their spectral location, for conclusively identifying these two regions as SHG and TPPL. The power dependence test is informative because of the quadratic dependence of SHG and TPPL on pump intensity ($I_{2\omega} \propto I_{\omega}^2$), which will appear as a linear trend with a slope of two on a log-log scale.

Figure 3.6 shows the results of a power dependence test of signal versus
Figure 3.6: A power dependence test of the various spectral regions of the nonlinear optical emission for an array of gold BNAs with 500 x 500 nm spacing. On a log-log scale, the mean intensity of three samples are shown as points with an ordinary least-squares fit line. The calculated slopes for the sets of points are shown with 95% confidence intervals, and coefficients of determination in the legend. Inset: Spectra of a set of power dependence measurements. The left black-dotted line shows the central wavelength for the TPPL region, and the right black-dotted line shows the upper wavelength of the CG region.

incident power on a log-log scale for the 500 x 500 nm array spacing at $\lambda = 780$ nm with resonant excitation. The average incident power was varied between 700 $\mu$W and 11 mW and the emitted spectra was captured. An example of a set of emitted spectra for this experiment is shown in the inset of Fig. 3.5. The spectra for the power dependence test were performed in three independent trials and averaged before sampling. Samples for the SHG region were taken at the narrowband emission peak, while samples
for the TPPL region were taken at $\lambda = 440$ nm, 463 nm, and 486 nm, and for the rest of the continuum, samples were taken at $\lambda = 550$ nm, 600 nm, and 635 nm. Each of these samples were then averaged for the regression analysis. For calibration and reference, several power dependence tests of the two-photon fluorescence from fluorescent beads yielded slopes of 2.00 (see Appendix A.2).

The result of the power dependence test for each of the three regions, with 95% confidence intervals, were $2.01 \pm 0.02$, $2.04 \pm 0.03$, and $1.70 \pm 0.02$ for the regions indicated as SHG, TPPL, and continuum generation (CG) in Fig. 3.5a, respectively. The $\sim 2$ slope at the second harmonic wavelength further verifies the narrowband emission as SHG. For the region between the SHG peak and the discontinuity at $\lambda \sim 525$ nm, a slope of 2.04 suggests that this is indeed TPPL. A slope of 1.70 for the region where $\lambda > 525$ nm is unexpected because it cannot be attributed to a single multiphoton process, which to our knowledge, has not been observed for gold nanostructures.

### 3.3.3 Incident Polarization Dependence

Polarization along the BNA axis is known to promote strong coupling between the two arms of the nanoantenna, which also allows collective plasmon modes along the entire antenna. This property manifests itself in the large field enhancement values from simulation for resonant excitation shown in Fig. 3.5b. Also, the spectral profile of the broadband continuum, including the TPPL, in Fig. 3.5a appear to be unique to the incident polarization. For resonant excitation, the underlying shape of the spectra is flat, whereas for nonresonant excitation, the shape is upward sloping. In addi-
tion, this occurs for all array spacings for a given polarization, even though each array is associated with a different field enhancement strength. Referring back to the inset of Fig. 3.6, the low power measurements for resonant excitation also show an upward sloping shape, it is not as prominent due to the scale of the axes. The unique correlation of the spectral profile with incident polarization indicate that the nonlinear mechanisms may be a characteristic of the individual particle geometry and allowed plasmon modes rather than the field enhancement itself.

It was established in section 3.1.1 that both SHG and TPPL can be resonantly enhanced and have a strong correlation with the near-field intensity enhancement. In fact, the authors of Ref. 19 derive a quantitative formula for the relationship between experimental TPPL signal and the local intensity enhancement values from simulation. Therefore, both TPPL and SHG signals (Fig. 3.5a) should be associated with the field enhancement values obtained in simulation (Fig. 3.5b).

To further investigate this relationship in our experiments, where SHG and TPPL emission occur together in the same system, we propose the use of a nonlinear emission ratio, $\gamma$, representing the relative emissions of SHG and the broadband continuum. It is defined as

$$\gamma_{TPPL} = \frac{\lambda_{SHG}}{\lambda_{463nm}}$$  \hspace{1cm} (3.1)

$$\gamma_{635nm} = \frac{\lambda_{SHG}}{\lambda_{635nm}}$$  \hspace{1cm} (3.2)

where $\lambda_{SHG}$, $\lambda_{463nm}$, and $\lambda_{635}$ are the signals at the wavelengths corresponding to SHG, TPPL, and CG, respectively.
Figure 3.7 shows the two nonlinear emission ratios for each array separated by incident polarization. By isolating the key components from the rest of the spectra, a few informative conclusions can be made about the mechanisms for each type of nonlinear emission. First, for resonant excitation, the trends in $\gamma_{TPPL}$ and $\gamma_{635nm}$ for each array is very similar with the 500 x 500 nm array showing the lowest ratio and the 500 x 1000 nm array showing the highest ratio. A similar comparison of $\gamma_{TPPL}$ and $\gamma_{635nm}$ for nonresonant excitation do not show a similar trend. In addition, comparing the magnitudes of $\gamma_{TPPL}$ for each incident polarization, resonant excitation gives $\gamma_{TPPL} < 1$ and $\gamma_{TPPL} > 1$ for nonresonant excitation. A direct implication of this analysis is that a stronger local field does not necessarily yield stronger SHG in these structures, which differs from previously proposed theories relating field enhancement to enhanced SHG emission. Furthermore, combined with the independence of the spectral profile on incident polarization, the nonlinear emission ratio indicates that the nonlinear mechanisms for one or both of SHG and TPPL may be independent of field enhancement.

3.3.4 Polarization of Emission

Figure 3.8 shows several spectra which have been normalized. In this case, the array spacings are 500 nm x 500 nm (Figs. 3.8a and 3.8b) and 475 nm x 475 nm (Figs. 3.8c and 3.8d). The magnitude of the measured intensity at the second harmonic can be varied by rotating an analyzer placed in front of the spectrometer. At a given excitation wavelength, and resonant excitation, the relative intensity is a maximum when the analyzer transmission axis is
oriented parallel to the bowtie axis (Fig. 3.8, solid line), and a minimum when it is perpendicular (Fig. 3.8, dash-dotted line). As observed in the figure, the amount by which this intensity can be varied is much larger for resonant excitation than nonresonant.

In addition, the dipolar nature of SHG emission is shown in the polar plots in the insets of Fig. 3.8 for 780-nm incident wavelength, where the SHG emission was isolated from the total emission by subtracting the expected TPPL emission at the second harmonic. Note that for BNAs excited resonantly, the measured SHG dipole emission pattern is also along the long axis. However, for BNAs excited nonresonantly, there is a rotation of the dipole pattern relative to the long axis, suggesting some form of elliptically polarized light.

This could be due to multipolar contributions which we believe to arise from retardation effects$^{30,37,68}$ due to the optical response of the arrays of BNAs having different surface plasmon coupling behavior$^{11,20,25,75}$ for resonant and nonresonant excitation. The resonant excitation promotes strong coupling of the two triangles that comprise a single BNA, where the charge density distribution becomes highly polar for the antenna as a whole. This results in collective plasmon modes along the entire antenna$^{20}$ and the emission being dominated by a dipolar response. In the nonresonant case, the coupling between the two triangles is reduced, and the multipole contribution becomes more pronounced, which along with retardation effects due to the gap, results in an elliptically polarized emission pattern. The exotic behavior of the nonlinear emission warrants further investigation into identifying the governing parameters.
3.3.5 Relation to Damage

At this point in the discussion it is suitable to combine the previous discussion on the mechanisms of SHG and TPPL with the discussion from Chapter 2 on laser-induced damage. Here we refer to the spectra in Fig. 2.3 (pg. 19), where the measurements were taken before and after 7 minutes of irradiation, and the SEM image in Fig. 2.1c (pg. 17), where a post-irradiation image of the same region is shown. Assuming that the initial spectra in Fig. 2.3 are representative of undamaged BNAs and the final measurement is representative of the damaged BNAs shown in Fig. 2.3, some inferences about the mechanisms of SHG and TPPL in relation to the morphology of the BNAs can be made.

By associating these spectra with the post-irradiation SEM image in Fig. 2.1c of the same area, the geometry of the BNA is relatively unchanged, but a large change in the measured spectra is observed. The TPPL intensity is heavily quenched after exposure while the intensity of the SHG is only slightly reduced. Optical damage, such as plasmon-band bleaching or other structure-independent changes in optical properties, are known to occur in gold nanostructures under pulsed-laser irradiation. However, regardless of the specific processes leading to the decrease in TPPL intensity, this comparison provides further indication that the source of the SHG enhancement differs from that of the TPPL enhancement.

3.4 Summary

Through a detailed spectroscopic study of the nonlinear optical emission from arrays of gold BNAs, several interesting, yet unexpected results are
observed by using the array periodicity and incident polarization as additional degrees of freedom in manipulating the optical response. The arrays of BNAs are shown to exhibit a remarkably uniform emission over a wide spectral region. Increases in the nonlinear emission intensity for various spacings were found to be correlated with near-field intensity enhancements from simulation. A power dependence test conclusively identified the presence of SHG and TPPL in the emitted spectrum, but also revealed a portion of the emission that cannot be attributed to a single multiphoton process. The polarization dependence of the nonlinear optical response is discussed with a specific focus on the mechanisms for SHG and TPPL, which were previously thought to be enhanced by the same mechanism. With the use of a nonlinear emission ratio, representing the relative emission intensities of the different components in the nonlinear signal, it was determined that the enhancement of SHG and TPPL emission are independent of each other with a strong indication that one or both of the SHG or TPPL mechanisms may also be independent of field enhancement. Further evidence of this was provided in a comparison of the spectral changes before and after laser-induced damage, where a slight deformation in the geometry of the BNAs resulted in a large decrease in TPPL intensity while the SHG intensity was relatively unchanged. In conclusion, this characterization of arrays of gold BNAs identifies several new parameters influencing the nonlinear optical response and serves as an important first step for the controllable design of nanoantennas in future applications.
Figure 3.7: Nonlinear emission ratio calculated at 463 nm and 635 nm which are representative of TPPL and the rest of the continuum. An incident wavelength of 780 nm was used. Resonant excitation is shown in (a) and (c); Nonresonant excitation shown in (b) and (d).
Figure 3.8: Normalized SHG and TPPL emission spectra from gold BNAs with (a,b) 500 nm x 500 nm, and (c,d) 475 nm x 475 nm array spacings. The double-headed arrow indicates the incident polarization direction. The red, blue, and black curves correspond to excitation by 780-nm, 800-nm, and 820-nm wavelength. Solid (dash-dotted) curves correspond to the polarization analyzer’s transmission axis oriented parallel (perpendicular) to the bowtie axis. Inset: the SHG emission as a function of polarization analyzer position for 780-nm incident wavelength. Note that normalization suppresses the relative magnitudes of each spectra.
Chapter 4

Near-Field Optical Forces

4.1 Overview

Conventional optical tweezers make use of large numerical aperture lenses (NA ~ 1.2-1.4) to tightly focus an input laser with powers on the order of tens of milliwatts to achieve stable, three-dimensional (3D) trapping of sub-micron particles. Recently, the use of nanostructures such as dipole antennas, nanodisks, and nanostrips for optical trapping applications have been investigated. Their use for optical trapping is favorable due to the field enhancement and confinement properties of plasmonic nanostructures which have the potential to greatly relax the constraints of conventional optical trapping. However, to this date, studies of plasmonically enhanced systems have been restricted to trapping by isolated nanostructures.

In the present work, the excellent near-field intensity enhancement and confinement properties of arrays of gold BNAs (see Section 1.3) are exploited to achieve low-NA (NA = 0.25, 0.6), low power (<1 mW) optical trapping of polystyrene (PS) spheres. The exceptional trapping ability of
the BNA system enables straightforward manipulation of the trapped particles when using a galvanometer-based scanner to steer the input beam. Full manipulation of both single spheres and clusters of multiple PS spheres over a large area ($\sim 80 \times 80 \, \mu m$) is demonstrated. Because of the vast differences of this trapping system and conventional tweezers, several new parameters are proposed for use in characterizing future systems based on plasmonic nanostructures. Although the work presented here is a proof-of-concept, it is a significant advancement for plasmonically enhanced optical trapping systems due to the dramatically relaxed conditions of power density and focusing compared with similar studies.
4.2 Experimental Setup

The experimental setup for these studies is very similar to the setup described in Section 1.5 with the exception of a 660-nm continuous-wave laser which replaces the pulsed laser. The $\lambda = 660 \text{ nm}$ beam is coupled into the advanced microscopy platform and a 40x, NA = 0.6 (or 25x, NA = 0.25) objective is used to focus the laser onto the sample. The average incident power at the sample is kept under 5 mW and the polarization is set for either resonant or nonresonant excitation of the BNAs. The sample is illuminated for imaging using the built-in lamp of the microscope. The sample is prepared using a diluted solution of polystyrene beads (Duke Scientific, PS0100), 9-mm diameter rubber gasket (0.5-mm thick), and a cover slip (Corning No.1). A schematic of the prepared sample is shown in Fig. 4.1, where the BNAs are immersed in a solution of particles with gravity pointing downwards. The arrays of gold BNAs are described in Section 1.4. In conventional optical tweezers setups, the stage is moved relative to the beam. Here, the use of a galvanometer-based scanner is used for moving the beam relative to a fixed stage and for manipulation of trapped particles.

4.3 FDTD Simulation

Several FDTD simulations (performed by Dr. Kin Hung Fung, ECE Dept.) were done to simulate the field enhancement of the arrays of BNAs in air. Figure 4.2 shows the spatial distribution of the normalized field enhancement in the center of the gap region for both resonant and nonresonant excitations. Although the simulation limits only extend 10-nm above and below the BNA, the field intensity above the BNA is expected to scale with
Figure 4.2: FDTD simulations of field intensity enhancement plotted in two cross-sections taken at the gap for (a) resonant excitation, and (b) nonresonant excitation.

the inverse of distance \( (E \propto 1/D) \), and at distances greater than 100 nm the field is expected to be very small.

The case of arrays of BNAs in water with a trapped PS bead directly above it is also simulated. Figure 4.3 shows a schematic of the simulation system, where a PS sphere is approximated as a flat surface interface, 10 nm above the BNAs. The field enhancement values for the 425 nm x 425 nm and 475 nm x 475 nm arrays are plotted in Fig. 4.4a, and a plot of the integrated force on a dielectric interface 10 nm above the BNAs is shown in Fig. 4.4b. Figure 4.4c shows the simulation results of field enhancement for BNAs in water only, and shows that the effect of a dielectric interface 10 nm above the BNA is a small blue-shift combined with a small increase
in field enhancement.

These simulation results of arrays of BNAs in water indicate that \( \lambda = 660 \, nm \) is not at the resonance peak and the field enhancement is on the order of \( 10^2 \). In addition, the field is expected to decrease with a \( 1/D \) dependence with distance, which implies that particles must be extremely close to the surface to experience an enhanced near-field force. Interestingly, as we will show, the trapping ability of these arrays of BNAs is considerably better than a conventional optical trap under the same conditions, and particles are attracted to the trap center at distances of over several bead diameters.

### 4.4 Plasmonically Enhanced Optical Trapping

#### 4.4.1 Manipulation

Figure 4.5 shows snapshots of a 1-\( \mu m \) bead traveling in a circular pattern at 11.2 \( \mu m/sec \). This particular video was taken near the center of an array so the boundaries of the array cannot be seen. Using only 780 \( \mu W \) of average
Figure 4.4: FDTD simulation results for the various array spacings and incident polarizations for arrays of BNAs in water and for the trapped-particle configuration shown in Fig. 4.3. For the trapped-particle configuration, the field enhancement is shown in (a), and the integrated optical force on the particle is shown in (b). The field enhancement for arrays of gold BNAs in water is shown in (c).

incident power and the 0.6-NA objective, the particle is tightly trapped, and full control of its motion is established.

Besides single particle manipulation, when the concentration of particles in the solution is high enough, clusters of particles become trapped and can also be manipulated. Figure 4.6 shows snapshots of a cluster of trapped 1-µm beads as they are moved off of the array. In this video, an objective of NA = 0.25 was used with 2.4 mW of average incident power. The frames in the bottom row of the figure show that the beads are no longer trapped. This is not the result of interrupted illumination or turning off the laser, but a result of the beam no longer illuminating the BNAs. This is a particularly important point because it demonstrates that the system cannot successfully trap without the field enhancement of the BNAs.
4.4.2 Trapping Behavior

The trapping behavior observed in figs 4.5 and 4.6 are not without limits. In conventional trapping systems, increasing the input power will typically result in a stronger trap. However, in arrays of BNAs increasing the power can destabilize the trap, resulting in loss of the particle. Several distinct types of destabilizing behavior, unique to the BNA-trapping system, are observed.

Figure 4.7 shows representations of the types of behavior as the power is increased past a certain threshold value for single particle trapping. Multiple particle trapping is shown in Fig. 4.7a where the input power is large enough to trap particles, but multiple particles must arrive at the trap center at the same time for a stable trap to be achieved. At this multiple particle
trapping power, localized heating of the fluid induces a convective flow due to the high coupling efficiency of the BNAs to the incident light. If a single particle is unaccompanied by another particle as it approaches the trap center, the trapping force is not able to overcome both the momentum of the incoming particle and the convective flow due to the thermal gradient. The result is observed as a particle being accelerated towards the trap center and then accelerating away from the trap center. This common type of unstable behavior, shown in Fig. 4.7b, is termed “trampolining”, because of its distinctive motion resembling the action of a trampoline. As the power is further increased (< 35 mW), heating of the BNAs and solution by the laser (see Section 2.3.2) can cause the particles to fuse to the surface after being pulled into the trap, as shown in the SEM image in Fig. 4.7c. Illuminating the system with the maximum laser output power (∼ 35 mW) results in
bubble/vapor generation seen as the dark circular area in Fig. 4.7d. Similar to the results of Hleb et al.\textsuperscript{47} discussed in Section 2.3, the size of the bubble reaches a maximum diameter and then quickly collapses. Whether this is due to the plasmon-band bleaching effect is uncertain since we also observe fusing of the beads to the surface which will also influence the optical absorption properties of the BNAs.

Another interesting feature of large clusters of trapped particles is shown in Fig. 4.8 where the laser focus is positioned at a point near the corner of the array, but the cluster of particles extends beyond the boundary of the array. It was shown in Fig. 4.6 that the system does not achieve the necessary trapping conditions without illuminating the BNAs. However, the system is able to exert a force on particles at distances of several particle diameters to form a stable cluster of trapped particles.

4.4.3 Trapping Regimes

The behavior of the BNA-trapping system is quite different from that of conventional optical tweezers. As such, we have taken a novel approach for characterizing the BNA-trapping system in terms of defining trapping regimes, where each regime represents a characteristic behavior of the particle in the system which is associated with a certain incident power. Figure 4.9 shows a representation of the trapping regimes along with several results of the trapping efficiency (Q). The behavior of the particles in this system are hypothesized to be governed by three primary factors: Brownian motion, thermally-induced convective flow, and optical forces.

When there is very low power, the relative effect of optical forces is not
enough to overcome Brownian motion which destabilizes the trap. This is termed the “no trapping” regime. At a moderate input power, the “single particle” regime is attained, and stable optical traps are achieved due to the relatively high optical forces compared with Brownian motion and convective flow. It is in this region where tests of the trap efficiency are performed, with methods analogous for characterizing conventional optical traps.\textsuperscript{79} Here, a linear fit of the maximum trapping force versus the input power gives the trap efficiency, which is calculated to be a maximum of $Q = 0.150$ for the 425 nm x 425 nm array with horizontal polarization. This magnitude of $Q$ can only be achieved in the best conventional optical trapping systems using hundreds of mW of input power and high-NA focusing.\textsuperscript{79}

Increasing the input power even further, leads to larger localized thermal gradients which induce larger convective flows. In this “multiple particles” regime, a stable trap can only be achieved when multiple particles enter the trap such that their momentum is minimized upon collision. For single particles at these input powers, trampolining occurs because the destabilizing actions of Brownian motion and convective flow are much higher relative to the optical forces.

While each of these regimes appear to be independent of each other as a function of input power only, they are in fact closely related to the fundamental ability of the system to achieve a stable trap, which ultimately affects the scalability of this system for trapping nano-scale particles. Furthermore, we believe that our particular choice of laser wavelength, particle size, particle material, BNA geometry, and array spacing was unexpectedly well-suited for these initial experiments. Each of the regimes are hypothe-
sized to be governed by Brownian motion, convective flow, and the optical forces, which are not easily isolated in this trapping system.

In general terms, the optical force on the particle is determined by the input power. If Brownian motion of a particle in solution is characterized by the temperature of the environment and the size of the particle, then there exists a certain amount of optical force which can overcome Brownian motion to trap the particle. Also, if the thermal gradient and associated convective flow is determined by the input power and field enhancement of the BNAs, then there also exists a certain amount of optical force which can overcome the flow to trap the particle. Since the input power defines each of these three phenomena (Brownian motion, thermal gradient, optical force) for a given system, there exists a possibility that the input power which provides adequate optical force to overcome Brownian motion does not provide enough optical force to also overcome the convective flow (and vice versa). In relation to the trapping regimes from Fig. 4.9, this means that the “no trapping” regime and the “trampolining” regime may become overlapping, with no possibility for a stable optical trap. Furthermore, our hypothesis of the trapping dynamics also implies that some systems may contain a very small range of powers for which a stable single-particle trap may be achieved.

For this reason, our particular choice of laser wavelength, particle size, particle material, BNA geometry, and array spacing was unexpectedly well-suited for these initial experiments. If the incident wavelength was chosen to be on resonance for the particular array spacing or BNA geometry, higher convective flows may have been produced without an associated increase
in trapping force. If the particle size was chosen to be smaller, the optical trapping forces may not have overcome Brownian motion.

These are the types of considerations that should be taken into account for designing future systems. The value of using the trapping regimes method for characterization comes from the ability to visualize the different trapping behaviors present in the system, rather than a binary model of success or failure. It also provides a fundamental groundwork for justifying why certain systems may not successfully achieve a stable trap even when large optical forces are present.

4.5 Summary

The use of arrays of gold BNAs for plasmonically enhanced optical trapping is a successful proof-of-concept advocating their use in future trapping systems. Preliminary analysis from field enhancement simulations for the specific system of BNAs in a solution of water showed that a blue-shift in resonance and increase in field enhancement occurs when a polystyrene bead is located 10-nm above the surface. Although the incident wavelength is not at the resonance peak for the arrays, stable optical trapping is achieved and full manipulation of single and clusters of 1-µm polystyrene beads is demonstrated using low-NA objectives (NA = 0.25, 0.6) and low incident power (<3 mW). Several new characteristic trapping behaviors are also identified in relation to the fundamental parameters governing the system. In particular, the most common behavior of the particles resembled the action of a trampoline, which we have termed “trampolining”. A new approach for visualizing the unique behaviors of this system is developed by
defining specific trapping “regimes” that represent the various trapping behaviors. The results presented here provide the initial foundation for engineering plasmonically enhanced trapping systems for specific applications.
Figure 4.7: Several of the unique behaviors exclusive to this plasmonically enhanced optical trapping system. Clusters of multiple particles are trapped in (a). A schematic of the trampolining behavior is shown in (b). An SEM image of particles fused to the surface after high-power illumination (< 35 mW) is shown in (c). Bubble generation (dark spot) in the solution of beads after high-power illumination (∼ 35 mW) is shown in (d).
Figure 4.8: Image of trapped cluster of particles after 30 minutes of illumination. The beam is situated near the corner of the array however the cluster extends beyond the boundary of the array (indicated by white arrows).
Figure 4.9: A schematic showing the trapping-regime based method for characterizing the plasmonically enhanced optical trapping system. Conventional efficiencies (Q) of trapped 1 µm polystyrene beads for resonant and nonresonant excitation for each of the array spacings are tabulated to the left of a plot showing maximum force on the beads as a function of incident power. Each of the trapping regimes are highlighted in gray, and the associated, relative magnitudes of Brownian motion, thermally-induced convective flow, and optical forces are indicated in the table below.
Chapter 5

Conclusions

The work presented in this thesis addresses several important areas of current research related to the large near-field intensity enhancements of arrays of coupled-plasmon resonant-nanoparticle pairs. Arrays of gold bowtie nano-antennas were used as a model system for the experimental characterization of the unique phenomena that arise from the near-field enhancements. Specifically, this work focuses on laser-induced damage, nonlinear optical emission, and near-field optical forces. Each of these phenomena provide a different piece of the nano-optics puzzle for controllably manipulating light on a sub-wavelength scale.

Because of the significant gap between theory and experiment for light-matter interaction at the nano-scale, research in this area is very active. However, one of the primary reasons for the absence of nano-antennas in current devices is their weak response due to their small size. The efforts to boost the response have come from two directions. One of these considers engineering the properties of the nano-antenna either by material, geometry, or arrangement to increase the field enhancement, which is typ-
ically the optimized metric. The other seemingly simpler way to increase the output is to increase the input.

Chapter 2 discusses the various aspects of laser-induced damage for arrays of gold BNAs. The results of numerous damage tests indicated that damage is a function of both irradiation time and incident power. Several damage reduction measures were implemented, and included changes to the adhesion layer material, beam-scanning pattern, and optimizing the laser pulse width. Because of the disparity in theory and experiment in this particular field, the damage threshold was experimentally determined for the arrays of gold BNAs.

A popular idea for future applications of nano-antennas is frequency conversion by nonlinear processes. However, by using the incident polarization and array spacing as experimental variables, the spectroscopic study of arrays of gold BNAs in Chapter 3 shows that field enhancement should not be the sole metric for increasing or optimizing the nonlinear response. A power dependence test confirmed the presence of second-harmonic generation and two-photon photoluminescence in the emitted spectrum, but also revealed a portion of the emission that cannot be attributed to a single multiphoton process.

Another popular idea for future applications of nano-antennas is plasmonically enhanced optical trapping which is successfully demonstrated in Chapter 4. A stable optical trap and manipulation of particles was demonstrated for low-NA objectives and low incident powers. Because of the large differences in trap behavior of the BNA-trapping system and conventional optical tweezers, a new method of characterizing the trap was developed.
This method employs the use of defining trapping regimes which are based on the unique behaviors of an unstable trap at various input powers.

5.1 Future Work

While the work presented here focuses on only a few key aspects of the effects of near-field enhancement for a specific class of optical nano-antennas, our results can both be applied to future studies of similar systems and aid in investigations of more fundamental problems at the nano-scale. Furthermore, the proof-of-concept for an optical trapping application asks more questions than it answers. As we have shown in Chapter 4, it represents an entirely new type of trapping system that deserves to be characterized further.

In Chapter 1, the near-field enhancement in arrays of gold BNAs were shown to not only be dependent on array periodicity and incident polarization, but also the antenna length and gap size. Nonlinear optical emission studies investigating varying all four of these parameters, including the thickness of the nanostructures (not previously mentioned), can help in identifying more precisely the role of the near-field enhancement on both SHG and TPPL. In addition, by adding more degrees-of-freedom to the tuning of the field enhancement, the nonlinear optical emission may be better optimized. This has an important implication for frequency-conversion applications such as solar cells and photonic switches.

The intimate relationship between the nonlinear emission and the electronic structure can be exploited to elucidate the complex nature of laser-induced damage. The identification of the governing parameters that affect
optical absorption and nonlinear emission, and specifically, the role of these
same parameters on the electronic structure would be invaluable to the sci-
entific community because it is essentially a combination of numerous fun-
damental problems at the nano-scale. One potential approach is the use of
the nonlinear optical emission spectrum in addition to the well-established
pump-probe method for investigating optical absorption and laser-induced
shape change.

A stable optical trap produced by arrays of BNAs is a delicate balance
between Brownian motion, thermal effects, and optical forces. The cru-
cial relationship of the near-field enhancement and confinement with laser-
induced heating should be investigated further to identify potential methods
of improving the trapping efficiency and widening the single-particle trap-
ning regime. Future work may be aimed at minimizing heat generation by
increasing non-thermal pathways for the energy to dissipate. Some possi-
bilities include introducing radiative pathways, decreasing electron-phonon
scattering, or using a heat sink. This could ultimately extend the trappable
particle size to true nanometer-scale dimensions.

The plasmonically enhanced optical trapping system could also be used
for assembling micro- or nano-structures with high precision. The clusters
of multiple particles form a close-packed structure which has the potential
to be used in applications such as 3-D colloidal photonic crystals (PCs).
Current techniques for these types of structures, known as synthetic opals,
involve self-assembly of particles from an entire colloidal solution resulting
in PCs that are on the order of millimeters. The trapping system based
on arrays of BNAs have shown to trap clusters of multiple particles on the
order of tens of microns in Fig. 4.8.

The bubble generation by the BNAs is an interesting effect that was seen at a relatively low power of 35 mW from a continuous-wave laser. If the bubble generation behavior can be properly characterized, the use of these bubbles for nano- or micro-scale fluidic valves or actuators can allow a variety of new applications in the NEMS/MEMS field. For example, if the top cover slip of the trapping sample in Fig. 4.1 is instead replaced by some thin PDMS layer, bubble generation would cause expansion of the volume resulting in an elastic deformation of the PDMS. The particular advantage of using an optically-actuated device is the relative fabrication simplicity because seals and channels for conventional actuation will not be required.
Bibliography


Appendix A

A.1 DeepSEE Group Velocity Dispersion Table
A.2 Power Dependence Calibration
A.3 Spacing Plate Dimensions
A.4 LabVIEW Diagrams
  A.4.1 Stochastic Scan
  A.4.2 Spiral Scan

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## Figure A.1: DeepSee motor position versus group velocity dispersion data from manufacturer.

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Figure A.2: Power dependence of fluorescent beads.
Figure A.3: Front panel of the stochastic scan VI.
Figure A.4: Block diagram of the stochastic scan VI.
Figure A.5: Front panel of the spiral scan VI.
Figure A.6: Block diagram of the spiral scan VI.
AUTHOR’S BIOGRAPHY

Kaspar Ko received his Bachelor of Science degree in Mechanical Engineering, with a minor in Applied Statistics, from the University of Illinois at Urbana-Champaign (UIUC) Urbana, Illinois, United States of America in May 2009. While an undergraduate, he completed an Undergraduate Independent Study Project (ME497), titled “Modeling the Optical Properties of Nanoparticles”, under the guidance of Prof. Toussaint in Fall 2008, which resulted in a publication. He joined Prof. Toussaint’s research group, Photonics Research of Bio/nano Environments (PROBE) Lab, as a Master’s candidate in the Department of Mechanical Science and Engineering in Fall 2009. His work at PROBE Lab, in collaboration with Prof. Liu (Liu NanoBionics Lab, ECE) and Prof. Fang (Nanophotonics/3D Nanomanufacturing Lab, MechSE), focused on the spectroscopic characterization of the nonlinear optical response of bowtie nano-antennas and the use of bowtie nano-antennas for optical trapping applications. His publications include: