Localized Surface Plasmon Resonance Induced Structure-Property Relationships of Metal Nanostructures

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LOCALIZED SURFACE PLASMON RESONANCE INDUCED STRUCTURE-PROPERTY RELATIONSHIPS OF METAL NANOSTRUCTURES

by
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A Dissertation submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
Department of Physics
Western Michigan University
April 2013

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The confluence of nanotechnology and plasmonics has led to new and interesting phenomena. The industrial need for fast, efficient and miniature devices which constantly push the boundaries on device performance tap into the happy marriage between these diverse fields. Designing devices for real life application that give superior performance when compared with existing ones are enabled by a better understanding of their structure-property relationships. Among all the design constraints, without doubt, the shape and size of the nanostructure along with the dielectric medium surrounding it has the maximum influence on the response and thereby the performance of the device. Hence a careful study of the above mentioned parameters is of utmost importance in designing efficient devices.

In this dissertation, we synthesize and study the optical properties of nanostructures of different shapes and size. In particular, we estimated the plasmonic near field enhancement via surface-enhanced Raman scattering (SERS) and 2-photon Photoemission electron microscopy (2P-PEEM). We synthesized the nanostructures using four different techniques. One synthesis technique, the thermal growth method was
employed to grow interesting Ag and Au nanostructures on Si. The absence of toxic chemicals during nanostructure synthesis via the thermal growth technique opens up myriad possibilities for applications in the fields of biomedical science, bioengineering, drug delivery among others along with the huge advantage of being environment friendly. The other three synthesis techniques (ion implantation, Electrodeposition and FIB lithography) were chosen with the specific goal of designing novel plasmonic metal, metal hybrid nanostructures as photocathode materials in next generation light sources. The synthesis techniques for these novel nanostructures were dictated by the requirement of high quantum efficiency, robustness under constant irradiation and coherent unidirectional electron emission. Two designs, (i) partially exposed metal nanostructures in an oxide matrix (ii) metal nanorod arrays, couple with incoming light at particular wavelengths which leads to plasmonic near field enhancement from the nanostructures. This plasmonic response is expected to lead to enhanced photoemission and thereby enhanced quantum efficiency. Moreover, the plasmonic enhancement and the shape of the nanostructure enable coherent unidirectional electron emission. Such an in depth study of the structure-property relationship, particularly the near field enhancement of novel metal, metal-metal oxide nanostructures will lead to applications as photocathode materials in next generation light sources.
ACKNOWLEDGEMENTS

Matha, Pitha, Thunaivi, Guru, Deivam – I dedicate this work to Mother, Father, Guru, Thunaivi who are verily “deivam manushya roopena” and to God. Words cannot express my gratitude and love for my mother Srimathi Pushpa Ganapathy and my father Sri V.S. Ganapathy for giving me this human birth and providing me with a loving and caring home during my formative years and all the sacrifices they have made along the way. My love and gratitude to my wife Smt. Meenakshi Subramanian who just by her presence makes my life beautiful. My humble salutations to the padha kamalam of my pujya Guru Sri Sri Sri Muralidhara Swamigal whose infinite grace guides my life including this work.

I would also like to express my gratitude to my dissertation advisor Dr. Asghar Kayani who took me into his research group and for all the help and advice he has given over the course of my research. I would also like to specially thank Dr. Suntharampillai Thevuthasan for giving me the opportunity to work in his group and for his constant support and advice. I really treasure the freedom he gave me to pursue my experiments. This dissertation would not be possible without them. I would also like to thank Dr. Dean Halderson for the wonderful physics lectures. I really appreciate the help he provided during the qualifiers, without which I might not be here today. I thank Dr. Sung Chung for agreeing to be in my committee and for his help and suggestions.
I would like to acknowledge Dr. Wayne Hess for his help and guidance. I would like to thank my friends and colleagues Dr. Weidong He and Dr. Patrick El-Khoury for our collaborations and for the scientific and philosophical discussions. I would like to thank Dr. Arun Devaraj for taking the time to train me on the FIB/SEM and for his help. To all the other people who have helped me along the way a big thank you!

Subramanian Vilayurganapathy
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1. INTRODUCTION

1.1 Introduction to nanotechnology and nanoscale materials

“There is plenty of room at the bottom”.

This insightful statement by Nobel laureate Dr. Richard Feynman inspired the conceptual beginnings of the field of nanotechnology. Nanotechnology deals with manufacturing nanoscale devices for real world applications. The field has witnessed exponential growth in the last few years, owing to the industrial need for smaller, faster and more efficient devices. These devices find applications in diverse fields such as medicine, semiconductor physics, molecular biology, computing and energy materials. Research in this field can be broadly subdivided into two categories: (i) nanostructure synthesis (improving existing techniques or developing new techniques to synthesize high quality nanostructures with reduced costs and environmental compatibility) (ii) nanostructure characterization (to gain a fundamental understanding of the structure-property relationships which will enable better device performance).

Nanostructures denote a class of materials whose dimensions are in the nanoscale. As the dimension of a bulk material is reduced, the density of states and the spatial length scale available for electronic motion is also reduced. As a result, these nanostructures exhibit unique optical, electronic and chemical properties when compared to their bulk counterparts.[1] In particular, metallic nanoparticles have garnered significant attention
owing to their unique optical response to incoming radiation.[2] Throughout history humans have exploited this optical response of metal nanoparticles to create brilliant colors, striking examples of which are the stained glass windows of renaissance Europe and the Lycurgus cup from roman times (see Figure 1). However, the physics behind such brilliant optical displays was not understood until Faraday’s work on colloidal gold nanoparticles[3] followed by Mie solving Maxwell’s equations for a sphere of arbitrary size.[4]

Figure 1. Clockwise from left: stained glass window from the Charters cathedral, Lycurgus cup, stained glass window from Loch chapel. The brilliant colors are due to surface plasmon resonance exhibited by Ag and Au nanoparticles embedded in glass.
When light is incident upon a metal nanostructure with size comparable to or less than the wavelength of incident light, the conduction band electrons in the metal oscillate in resonance at specific wavelengths. This phenomenon dominates the optical response of the nanostructure and is called the localized surface plasmon resonance (LSPR). The penetration depth of electromagnetic waves in metals is 30 nm and hence incident light is able to penetrate the nanoparticles and spatially shifts the conduction electron with respect to the positive lattice ions.[5] This generates a restoring force between the electrons and the positive ions and this restoring force causes the electrons to oscillate in resonance with particular wavelengths of the incident light. This resonant response depends strongly on the size, shape and dielectric medium surrounding the metal nanoparticle.[6] Investigations into the above led to the birth of the dynamic and vibrant field of plasmonics which encompasses the science and engineering of optical interaction with nanostructures.

![Figure 2. Schematics of the LSPR process. The electron cloud is displaced relative to the positive nuclei in response to the incoming E-field. The displacement of the electron cloud is greatly exaggerated for clarity.][6]
Figure 3. The LSPR frequency depends strongly on the shape and size of the nanoparticles. The image on the left shows the size dependence of gold nanoparticles while the image on the right shows the shape dependence of the LSPR frequency. [7]

Depending on the shape, size and desired device application various techniques including ion implantation, wet chemical synthesis and nano-lithography have been employed to synthesize metallic nanostructures. Ion implantation followed by subsequent annealing is a method of choice to synthesize metallic nanoclusters inside a dielectric matrix whereas electrochemical deposition is favored to grow one-dimensional periodic nanostructures over a large area. Lithographic techniques are preferred when an excellent size and shape control over a small area is required. In this dissertation, an understanding of the structure-property relationships of nanostructures synthesized by the above mentioned techniques is undertaken. Such a study is of paramount importance for the development
of new and exciting materials for specific applications, which help push the boundaries of device performance.

We synthesize:

(i) Ag nanoparticles in MgO by ion implantation followed by subsequent annealing.
(ii) Ag, Cu and Au nanorod arrays by electrochemical deposition of the corresponding metal into porous anodic alumina template (AAO).
(iii) Ag nanorod arrays using focused ion beam (FIB) lithography.
(iv) Solid and hollow Ag and Au nanostructures on Si <111> by a new thermal growth technique.

We undertake a detailed characterization of the microstructure and optical properties of the above synthesized nanostructures. In particular, we estimate the LSPR near field enhancement from the aforementioned nanostructures and study their optical response as a function of size, shape and surrounding dielectric environment.

1.2 Nanostructure synthesis techniques

1.2.1 Ag nanoparticles in MgO by ion implantation followed by subsequent annealing

Metallic nanoparticles embedded in various dielectric materials have generated considerable interest in the fields of opto-electronics and nonlinear optics due to their
strong coupling to incident electromagnetic fields. [8-15] The optical response of these substrates is dominated by the LSPR’s, which lead to an electric field enhancement which can be used to boost molecular optical responses such as surface-enhanced Raman scattering (SERS).[16] The spectral width and position of the plasmon resonance strongly depends on the type of metal and the surrounding dielectric as well as the size, shape, distribution and concentration of metal particles.[6, 7, 17, 18] Embedding metal ions in a dielectric by means of ion implantation and subsequent annealing provides a degree of control over particle size, concentration, and implantation depth. An important advantage of ion implantation over other synthetic methods is the ability to reach a high metal filling factor, beyond the metal solubility of the target matrix.[19] However implantation will also induce matrix structural defects in the form of vacancies, interstitials and dislocation loops. Several studies have focused on Au and Ag ion implantation into oxides like MgO, TiO2 and SrTiO3.[20-25] MgO is widely used in optics because it is hard, durable and transparent in the 170 - 3000 nm spectral region.[26-29] Past studies have examined Ag nanoparticles formed in MgO by ion implantation, at room temperature over energies ranging from keV to MeV, followed by annealing in vacuum or air. Implantation of Ag in MgO leads to the creation of oxygen and magnesium vacancies, which are termed as F and V centers, respectively.[26, 30] Subsequent annealing leads to the formation of Ag nanoparticles and vacancy clusters.[26, 31] The depth and distribution of Ag nanoparticles is correlated to the implantation energy and substrate temperature during the ion implantation. Abouchacra et al. [31] obtained Ag nanoparticles embedded in MgO that exhibited a surface plasmon resonance with optical
absorption peaking between 420 nm to 498 nm. They noted that the Ag concentration peak moved towards the surface upon annealing and concluded this to be an assisted diffusion because of the defect clusters formation in the region between the peak Ag concentration depth and surface during implantation process. Qain et al. [26] after 1.5 MeV implantation at room temperature followed by subsequent annealing in air reported 0.8 nm–3 nm Ag nanoparticle formation in MgO.

To create size selectable Ag nanoparticles embedded in a dielectric matrix, we have used Ag ion implantation energy of 200 keV incident on the single-crystal MgO (001) placed on a temperature-controlled substrate holder followed by high temperature annealing. Low energy of 200 keV was selected to maximize the near-surface implanted particle concentration. Followed by the ion implantation, UV-Vis optical spectroscopy and a detailed analysis of the microstructure and Ag nanoparticle distribution was performed as a function of annealing time, using Rutherford backscattering spectrometry (RBS), X-ray micro-diffraction (micro-XRD), cross-sectional scanning and conventional transmission electron microscopy (STEM and TEM) and atom probe tomography (APT).

1.2.2 Electrochemical deposition of Ag, Cu and Au nanorod arrays

Owing to their unique optical, electronic and magnetic properties,[32, 33] periodic one dimensional nanostructures have gained a lot of attention in the field of nanoscale research. Recently, vertically aligned metallic nanorod arrays have attracted interest due
to their plasmonic and photo catalytic properties.[34-36] To yield the aforementioned structures, various deposition and lithographic techniques have been employed to date, including oblique angle deposition,[37] vapor-liquid solid growth,[38] chemical vapor deposition,[39] molecular beam epitaxy[40] and e-beam lithography.[41] Template-assisted electrodeposition is highly favorable because it is a non-catalytic process with (i) excellent scalability, (ii) low operating cost, and (iii) reasonable size control. Using this technique, Sulka et. al.[42] synthesized Ag and Sn nanorod arrays in anodized aluminum oxide (AAO) templates sputter coated on one side with a thin layer of Ag to provide an electrical contact, yielding nanorods of approximately 4 µm in length. Chen et. al.[43] fabricated Cu nanorod arrays with an average nanorod length of 4 µm on a copper disc under potentiostatic conditions. Another report by Moon and Wei[44] features 1.5 µm Au nanorods, obtained using AAO templates as the cathode in the electrochemical deposition process. Notably, the AAO templates were coated with polyethyleneimine (PEI) to ensure proper adhesion between the template and the sputtered Au contact layer. Recently, increasing attention has been paid to the synthesis of well-aligned ultra-long (above 10 µm) nanostructures, since such constructs exhibit practical advantages in a number of applications including photoelectrodes, photocatalysis, fuel cells and batteries.[45-48]

To enable the growth of ultra-long nanorod arrays with uniform size distribution over a large area a superior electrical contact between the AAO template and the electrochemical cell is necessary. We achieved this by applying a layer of metal paste on
top of the sputtered metallic layer. This allowed us to grow ultra-long Ag, Cu and Au nanorod arrays. The top surface morphology, cross-section, crystal structure, as well as the preferred growth orientation of the nanorod arrays were probed using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and grazing incidence X-ray diffraction GIXRD, respectively. Moreover, the optical response and plasmonic properties of the reported nanorod arrays were studied using surface-enhanced Raman spectroscopy (SERS).

1.2.3 Ag nanorod arrays by Focused ion beam lithography

In the previous section we introduced electrochemical deposition as a technique to synthesize metal nanorod arrays. This technique allows for the fast growth of ultra-long metal nanorod arrays with uniform coverage over a large area. However, with electrodeposition, a very precise control of the aspect ratio and inter-rod distance, which is required for fundamental studies on the optical response of various plasmonic device designs, is very difficult to achieve. Traditionally lithographic techniques are employed to overcome these shortcomings. Various kinds of lithographic techniques including e-beam lithography (EBL) [49], nanosphere lithography (NSL) [50], optical lithography [51] and FIB lithography [52] are employed to create highly ordered periodic patterns of nanostructures with well controlled aspect ratio on a substrate. This property is highly desirable to synthesize reproducible arrays of nanostructures with tunable optical
properties. In EBL, a beam of focused electrons is incident upon a thin sacrificial layer of radiation-sensitive polymer in a raster scan pattern. This makes the exposed regions of the resist more/less soluble in an organic developer solution when compared with the unexposed regions. The patterned resist is removed in a subsequent etching /deposition process to generate nanostructured metallic patterns with well controlled aspect ratios and inter-pattern distance. In NSL, a nanoscale sphere of material like silica is deposited on a substrate. This creates voids of specific shape depending on the arrangement of the spheres in relation with their neighbors. Metal deposition techniques are used to deposit metal onto the substrate. The nanospheres are finally removed by ultra-sonication leaving behind metal patterns which assume the shape of the voids.

We introduce FIB lithography as an alternative to the above techniques. FIB uses a focused beam of Ga\(^+\) ions to create patterns on a substrate by ion-assisted etching. Various metallic nanostructures including nanoholes, gratings and slits have been patterned using the FIB. The advantage of FIB over other lithographic techniques like EBL lies in the fact that it does not require organic resists to create patterns. However, Ga contamination of substrates patterned with FIB might be an issue for some device applications. This could be overcome by employing emerging technologies like helium ion microscopy to pattern nanostructures. In this dissertation, we estimate the near field enhancement from Ag nanorod arrays patterned using FIB lithography. The PEEM was employed to obtain an estimate for the near field enhancement. To the best of our knowledge, this is the first study of the kind in this context.
1.2.4 Ag and Au nanostructures on Si <111> by thermal growth

In the previous two sections we introduced ion implantation followed by annealing and electrochemical deposition as two possible routes to synthesize nanostructures which are vastly different in their shapes, sizes and surrounding dielectric medium. Colloidal synthesis is another technique which is commonly employed to synthesize nanostructures of various shapes and sizes by controlling the experimental parameters. For example, using colloidal methods, a number of metal nanostructures have been synthesized, such as nanospheres, nanorods, nanotubes, nanosheets and hollow nanocages.[53-55] The colloidal methods have opened up the opportunity to investigate the fundamental plasmonic, drug-delivery, sensing and bio-imaging properties of the hollow metal structures.[56, 57] Although colloidal methods exhibit pronounced advantages including scalability and size/surface controllability, the applicability of the colloidal routes to nanostructure synthesis has some shortcomings.[58, 59] The most notable one is the frequent use of hazardous chemicals in colloidal synthesis.[60, 61] For instance, in the colloidal synthesis of Au and Ag nanocages, the nanocages are typically synthesized through reaction, where acids are employed as necessary reagents.[62] Undoubtedly, more environmentally benign routes to synthesize high-quality multi-faceted, core-shell, solid and hollow nanostructures would largely enhance the applicability of these structures in basic research and real-life applications, particularly in drug delivery and other biomedical applications. Such hollow structures are expected to exhibit intriguing optical properties due to their nonlinear structure and their size effect in micrometer and
A method to synthesize Ag and Au nanostructures that does not involve wet chemical techniques is introduced.

Ag nanostructures can be synthesized by annealing a nanoscale Ag film under inert gas environment. The synthesis does not involve chemical reaction and thus is highly environmental friendly. In addition, the size of the nanostructures can be well controlled by adjusting the thickness of the Ag films. Our subsequent SERS measurements have shown that these Ag nanostructures exhibit substantial plasmonic near-field enhancement.

A rapidly developing approach for the fabrication of gold nanostructures involves a combination of lithographic and thin film deposition techniques, like the high-temperature annealing of lithographically patterned thin films of gold, which exploits the high mobility of gold on substrates to reorganize into gold particles. Recent research efforts have demonstrated that solid gold nanostructures of various shapes and sizes could be produced from uniform gold films after thermal annealing. Specifically, solid gold particles of different diameters were realized by annealing patterned gold films, fabricated by nanosphere lithography. However, a technique to synthesize hollow gold nanoparticles is lacking. We introduce a technique wherein both solid and hollow gold nanostructures have been synthesized via thermal annealing of patterned gold films. The nanostructures were shown to be hollow via FIB milling of the nanostructure followed by cross section SEM images. To illustrate their potential application, the optical response and near field enhancement of the synthesized gold

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particles were studied using PEEM. Our studies reveal a promising method to fabricate well-arranged hollow gold particles of tunable and predictable diameter which may lead to myriad potential applications in plasmonics. In particular, due to the absence of toxic chemicals, nanostructures synthesized by this technique find potential application in biosensing, drug delivery and energy conversion.

1.3 One potential application: New photocathode designs for next generation light sources

Among the myriad applications possible for nanostructures synthesized by the above techniques we introduce one such application: New photocathode designs for next generation light source, which clearly illustrates how the marriage between nanotechnology and the field of plasmonics might possibly push the boundaries of device performance in real life applications. Photocathodes are devices that emit electrons when light is incident upon them. A good device design is one which addresses the following constraints: (i) The photocathode should be robust enough to withstand constant irradiation with light (ii) it should have high quantum efficiency (which is the number of electrons emitted per photon) over its operational lifetime (iii) unidirectional coherent electron emission at appropriate laser wavelengths (reduced work function).

Traditionally, research in photocathode materials is constrained to coating a nanoscale layer of alkali, alkali-halides like Cs, CsBr on the surface of a metal like Nb and Cu. A quantum efficiency enhancement by a factor of ~200 when compared to pure metals has been reported.\[68\] This substantial increase in quantum efficiency has been attributed to
CsBr reducing the work function of Cu along with the formation of intraband absorption states. [69] An alternate route that is currently being explored is to coat a few monolayers of metal oxide like MgO on the surface of a metal like Ag. The metal oxide serves to reduce the work function of Ag leading to enhanced photoemission.[70] Even though the results from these routes are very promising and these materials are already used in real life applications, they have certain drawbacks. The electrons emitted by these materials are not unidirectional and possess an energy spread.[71] Moreover, there is scope for improving the quantum efficiency. One way to overcome these drawbacks is to design new materials, which taps into the unique properties of nanostructures. In particular, enhanced coherent photoemission is expected if we allow for the coupling of incident radiation with the LSPR modes of the nanostructure. The requirement of unidirectionality can be addressed by careful choice of the nanostructure shape. Based on the factors mentioned above, we introduce new photocathode material designs that employ novel plasmonic mixed metal and hybrid material structures. The schematic of the enhanced photoemission mechanism along with the novel material designs are shown in Figure 4. The first design requires the synthesis of metal nanoparticles in a metal oxide matrix. The ion implantation technique introduced earlier is ideally suited to realize this design. The advantage of this design lies in the fact that the individual nanoparticles distributed in the oxide matrix resonate at particular wavelengths with incoming light and hence are expected to assume the role of enhanced electron emitters. Moreover, the size of the nanoparticles along with the surrounding oxide matrix serves to confine the electrons leading to unidirectional photoemission. The working principle is similar for the metal
nanorod arrays which respond to irradiation with light at particular wavelengths by setting up longitudinal and transverse plasmonic resonances, with the longitudinal mode expected to lead to enhanced photoemission. The rod like shape of the nanostructure ensures the majority of electrons are emitted from the tips of the individual nanorods in the array and hence the collective electron emission is highly directional. Electrochemical deposition and FIB lithography may be used to synthesize nanostructures with the above mentioned geometry. In this dissertation, we synthesize and characterize nanostructures including the above two designs. We show that these nanostructures indeed resonate with particular wavelengths of light depending on their shape, size and surrounding dielectric medium. However, testing the viability of these materials in photocathode system as photocathode is beyond the scope of this dissertation and will be undertaken in the near future.

The outline of the dissertation is as follows: to enable a better understanding of the physics behind light interaction in the above mentioned nanostructures, a mathematical framework containing important results from Mie’s theory, Mie-Gans theory and the electrostatic approximation are presented along with a brief introduction to LSPR of metallic nanostructures. Next, a basic introduction to two phenomena which we will use extensively to estimate the near field enhancement from the aforementioned nanostructures namely surface enhanced Raman scattering and two photon photoemission mechanisms will be given. Finally, a discussion on ion interaction with matter which is the basic mechanism behind the synthesis and patterning of nanostructures via ion
implantation and FIB lithography will close this chapter. This is followed by an experimental section which provides a detailed synthesis procedure followed by brief descriptions of instrumentations used in characterizing the nanostructures. A new technique for synthesizing metal nanostructures which is non-chemical and non-lithographic is discussed. The results and discussion of the LSPR near field enhancement and the dependence of the plasmonic properties on the size, shape and surrounding dielectric environment form the main part of the dissertation. Finally we conclude the dissertation by summarizing the completed work and discuss future experiments.

Figure 4. Schematic of novel photocathode material designs. Top left: metal nanoparticle in metal oxide matrix, Top right: metal nanorod arrays. Bottom: schematic of enhanced photoemission mechanism form the metal nanorod arrays. Light of particular wavelengths sets up plasmonic resonance in the individual nanostructures which leads to enhanced photoemission.
1.4 Theoretical background

In this section, we present a brief theoretical framework for the absorption and scattering of light by a sphere developed by Gustav Mie in the year 1908. We then consider the electrostatic approximation to derive the extinction cross sections of particles of radius small compared to the wavelength of incident light. Both spherical and spheroid shaped particles are considered. We have to resort to numerical methods to exactly solve for the optical response for non-spherical particles of arbitrary shapes and sizes.

Absorption and scattering of light by a sphere: Mie Theory

The solutions to Maxwell’s equations for a sphere of arbitrary size were developed by Gustav Mie in 1908.[4] We derive the necessary steps and present the important results from a more rigorous derivation of Mie theory that can be found elsewhere.[72] Consider a sphere of arbitrary radius embedded in a homogenous, linear, isotropic electric field. The scalar wave equation is given by

\[ \nabla^2 \psi + k^2 \psi = 0 \quad (1) \]

Where \( \psi \) is a scalar function, \( k \) is the wavenumber. Since we are deriving the E field inside and outside a sphere we choose spherical polar coordinate system. The scalar wave equation then becomes

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + k^2 \psi = 0
\quad (2)
\]
We seek solutions of the form,

\[ \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \]

Substituting the above into Eq. 2 yields three separated equations:

\[ \frac{\partial^2 \Phi}{\partial \phi^2} + m^2 \Phi = 0, \quad (3) \]

\[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \left[ l(l + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0, \quad (4) \]

\[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + [k^2 r^2 - l(l + 1)] R = 0, \quad (5) \]

We now have three separated differential equations. The solutions to Eq. 3 are:

\[ \Phi = e^{\pm im\phi}, \; m = 0,1,2, \ldots \quad (6) \]

For \( \Phi \) to be single valued over the entire range \( m \) must be an integer. Thus the linearly independent solutions for the azimuthal equation is

\[ \Phi_{e(even)} = \cos m\phi, \quad \Phi_{o(odd)} = \sin m\phi \quad (7) \]

The solution to Eq. 4 that are finite at \( \theta = 0 \) and \( \theta = \pi \) are the associated Legendre polynomials of the first kind \( P_l^m \cos \theta \). The linearly independent solutions to Eq. 5 are the spherical Bessel function and any linear combination of them. Therefore we have

\[ k_l^{(1)} = j_l(\rho) + iy_l(\rho) \quad (8) \]
Hence the generating functions that satisfy the scalar wave equation in spherical polar coordinates is

$$h_i^{(2)} = j_i(\rho) - iy_i(\rho) \quad (9)$$

Where $Z_n$ is any of the four Bessel functions $h_i^{(1)}, h_i^{(2)}, j_i(\rho), y_i(\rho)$.

The incident electromagnetic plane wave can be written in spherical coordinates as,

$$E_i = E_0 e^{ikx} = E_0 e^{ikr\cos\theta} \hat{e}_x \quad (12)$$

Since we are concerned with the problem of scattering of plane wave by an arbitrary sphere, we expand the Eq. 16 in vector spherical harmonics which are generated from $\psi_{eml}, \psi_{oml}$. The final solution for the expansion of a plane wave in spherical harmonics is

$$E_i = E_0 \sum_{l=1}^{\infty} i^l \frac{2l+1}{(l+1)} \left( M_{01n}^{(1)} - iN_{el}^{(1)} \right) \quad (13)$$

where,

$$M_{eml} = \nabla \times (r \psi_{eml}) \quad (14)$$

$$M_{oml} = \nabla \times (r \psi_{oml}) \quad (15)$$
\[ N_{elm} = \frac{\nabla \times M_{elm}}{k} \quad (16) \]

\[ N_{oltm} = \frac{\nabla \times M_{oltm}}{k} \quad (17) \]

At the interface between the sphere and the surrounding medium we impose the following boundary condition,

\[ (E_i + E_s - E_1) \times \hat{e}_r = (H_i + H_s - H_1) \times \hat{e}_r \quad (18) \]

Where the subscripts \( i \) and \( s \) stand for the incident and scattered field and \( 1 \) denotes the field inside the sphere. The expansion for the field inside the sphere and the scattered field now becomes,

\[ E_1 = \sum_{l=1}^{\infty} E_0 i^l \frac{2l+1}{l(l+1)} \left(c_l M_{01l}^{(1)} - id_l N_{e1l}^{(1)}\right) \quad (19) \]

\[ H_1 = \frac{-k_1}{\omega \mu_1} \sum_{l=1}^{\infty} E_0 i^l \frac{2l+1}{l(l+1)} \left(d_l M_{e1l}^{(1)} + ic_l N_{01l}^{(1)}\right) \quad (20) \]

\[ E_s = \sum_{l=1}^{\infty} E_0 i^l \frac{2l+1}{l(l+1)} \left(ia_l N_{e1l}^{(3)} - b_l M_{e1l}^{(3)}\right) \quad (21) \]

\[ E_s = \frac{-k_1}{\omega \mu_1} \sum_{l=1}^{\infty} E_0 i^l \frac{2l+1}{l(l+1)} \left(ib_l N_{01l}^{(3)} + a_l M_{e1l}^{(3)}\right) \quad (22) \]

Therefore for a given value of \( l \) there are four unknown coefficients \( a_l, b_l, c_l, d_l \) which can be obtained by solving the four independent equations from the four boundary conditions at \( r=a \):

\[ E_{i\theta} + E_{s\theta} = E_{1\theta} \quad (23) \]
The coefficients for the field inside the sphere are,

\[ c_l = \frac{\mu_j j_l(x)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[xj_l(x)]'}{\mu_j j_l(mx)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[mxj_l(mx)]'} \]  \hspace{1cm} (27)

\[ d_l = \frac{\mu_j m_j(x)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[xj_l(x)]'}{\mu m^2 j_l(mx)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[mxj_l(mx)]'} \]  \hspace{1cm} (28)

The scattering coefficients are given by,

\[ a_n = \frac{\mu m^2 j_l(mx)[xj_l(x)]' - \mu_j j_l(x)[mxj_l(mx)]'}{\mu m^2 j_l(mx)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[mxj_l(mx)]'} \]  \hspace{1cm} (29)

\[ b_n = \frac{\mu_j j_l(mx)[xj_l(x)]' - \mu j_l(x)[mxj_l(mx)]'}{\mu_j j_l(mx)[xh_i^{(1)}(x)]' - \mu_j h_i^{(1)}(x)[mxj_l(mx)]'} \]  \hspace{1cm} (30)

where \( x = k \alpha = \frac{2 \pi N a}{\lambda} \) is the size parameter and \( m = \frac{k_1}{k} = \frac{N_1}{N} \) is the relative refractive index. \( N_1 \) and \( N \) are the refractive index of the particle and the medium respectively and the prime indicates differentiation with respect to the argument in the parentheses.
The classical Mie theory, whose important results are enumerated above, is still used to calculate the extinction spectra of nanoparticles, since a vast majority of nanostructures synthesized by colloidal methods are roughly spherical. In addition, the uniqueness in shape and size of the nanoparticle is averaged in the spectra collected by optical methods since they probe an ensemble of particles. This allows Mie theory to provide a reasonable fit to the experimental spectra. Moreover, Mie Theory is the only simple, exact solution to Maxwell’s equations relevant to particles. However, increasingly, nanostructures are being synthesized using non-colloidal methods like lithography which provides excellent control over the shape and size of the nanostructure. Moreover, they can be patterned with specific inter-structure distances which allow for optical study on single nanostructures or an array of nanostructures with similar features. Obviously, classical Mie theory cannot be applied in these situations and we have to resort to numerical simulations. Excellent simulation techniques like the discrete dipole approximation (DDA), [6, 73] finite difference time domain (FDTD) [74, 75] have been extensively employed when the nanostructures are non-spherical. Having said that, we can still obtain an analytical solution for non-spherical particles in the limit that, the nanostructures are much smaller compared to the wavelength of incident light. This limit, known as the electrostatic approximation, is discussed below. Thus the choice of the applicable solutions is determined by the shape and size of the nanostructure which is depicted pictorially in Figure 5.
Figure 5. A schematic showing the applicability of theoretical techniques as a function of shape and size of the nanostructure. The black wave represents the incoming E field. Left: Exact analytical solutions are provided by Mie theory for spherical particles of arbitrary size, Center: Electrostatic approximation is valid for particles much smaller than the wavelength of light and cross sections can be obtained for spheres and ellipsoidal particles. Right: Numerical methods are required to solve for arbitrary shape and size of the nanostructures.

Electrostatic approximations: Mie-Gans Theory

Consider a homogenous isotropic sphere placed in a uniform static electric field $E = E_0z$. The introduction of the sphere distorts the initial uniform field. The electric field inside and outside the sphere can be derived from the scalar potential as follows,

$$E_1 = -\nabla \Phi_1, E_2 = -\nabla \Phi_2$$  \hspace{1cm} (31)

$$\nabla^2 \Phi_1 = 0 \ (r < a), \ \nabla^2 \Phi_2 = 0 \ (r > a),$$  \hspace{1cm} (32)
The problem possesses azimuthal symmetry and the potentials must satisfy the following boundary conditions: far away from the sphere the field is uniform and at \( r = a \)

\[
\Phi_1 = \Phi_2, \quad \varepsilon_1 \frac{\partial \Phi_1}{\partial r} = \varepsilon_m \frac{\partial \Phi_2}{\partial r} \quad (r = a) \quad (33)
\]

The potentials inside and outside the sphere are given by,

\[
\Phi_1 = -\frac{3\varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} E_0 r \cos \theta \quad (34)
\]

\[
\Phi_2 = -E_0 r \cos \theta + a^2 E_0 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \frac{\cos \theta}{r^2} \quad (35)
\]

The potential due to an ideal dipole is,

\[
\Phi = \frac{p \cdot r}{4\pi \varepsilon_m r^3} = \frac{p \cos \theta}{4\pi \varepsilon_m r^3} \quad (36)
\]

Comparing the above two equations we see that the field outside the sphere is just the superposition of the initial field and the field of an ideal dipole located at the origin with dipole moment,

\[
p = 4\pi \varepsilon_m a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} E_0 \quad (37)
\]

A measure of the induced dipole moment in the sphere due to the field, the polarizability \( \alpha \) is defined as,

\[
p = \varepsilon_m \alpha E_0, \quad \alpha = 4\pi a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \quad (38)
\]

The extinction cross section for a particle in the path of a plane wave is given as,
where the subscripts denote extinction, absorption and scattering respectively. The cross sections for scattering and absorption by a sphere in the electrostatic approximations are given by,

\[ C_{abs} = klm\{\alpha}\ = 4\pi a^3 x \left(\frac{\varepsilon_1-\varepsilon_m}{\varepsilon_1+2\varepsilon_m}\right) \]  

\[ C_{asca} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi^2}{3} \left(\frac{\varepsilon_1-\varepsilon_m}{\varepsilon_1+2\varepsilon_m}\right)^2 \]  

These above equations provide a very good estimate for the optical response of small particles. However, as the particles become larger higher order responses like the quadruple response becomes significant and have to be incorporated into the calculations for the cross sections. The electrostatic approximation can also be employed for ellipsoids. The polarizability of an ellipsoid in a field parallel to its z, x and y axis is given by[72],

\[ \alpha_3 = 4\pi abc \frac{\varepsilon_1-\varepsilon_m}{3\varepsilon_m+3L_3(\varepsilon_1-\varepsilon_m)} \]  

\[ \alpha_1 = 4\pi abc \frac{\varepsilon_1-\varepsilon_m}{3\varepsilon_m+3L_1(\varepsilon_1-\varepsilon_m)} \]  

\[ \alpha_3 = 4\pi abc \frac{\varepsilon_1-\varepsilon_m}{3\varepsilon_m+3L_2(\varepsilon_1-\varepsilon_m)} \]

where a, b, c are the semi axis and
are the geometrical factors. This then is a brief theoretical background where we have investigated and presented important results from classical Mie theory which gives exact solutions to Maxwell’s equations for the case of a spherical nanostructure of arbitrary size. We have also introduced electrostatic approximations and derived expressions for the extinction cross section of spheres and ellipsoids that are much smaller than the wavelength of incident light. For all other situations, theoretical calculations of the optical response must incorporate numerical techniques.

We would now like to introduce the theory behind two phenomena which we will employ later to image the plasmonic response and obtain an estimate for the plasmonic near field enhancement from our synthesized nanostructures. They are:

- Surface enhanced Raman scattering (SERS)
- Nonlinear two photon photoemission (2PPE)
Both these phenomena arise due to the unique response of nanostructures to incoming radiation. Let us first look at the origins of SERS.

1.5 Introduction to surface enhanced Raman scattering

The scattering of light when it is incident on matter results from a complex interaction between the incident EM wave and the molecular and atomic structure of materials. The electron orbits within the metal are perturbed and oscillate at the frequency of incident radiation. This oscillation induces a dipole moment via a separation of charges. We saw earlier that an oscillating dipole radiates. This radiation manifests itself as the scattered EM field. The strength of the induced dipole moment, for a given incident field depends on the polarizability according to the relation

\[ P = \alpha E \]

P- strength of the induced dipole moment, \( \alpha \) is the polarizability and E is the incident field. The polarizability is a property of the material system and hence dependent upon the position of the atoms/molecules (bond structure). In any molecule the atoms are bound to each other via bonds which are confined to specific quantized vibrational modes. The induced dipoles vibrate along these modes at three distinct frequencies \( \nu, \nu + \nu_{\text{vib}}, \nu - \nu_{\text{vib}} \) where \( \nu, \nu_{\text{vib}} \) stands for the frequency of the incident wave and the natural vibrational frequency of the molecule. The induced dipole moments, which vibrate with the frequency of the incident wave, scatter light elastically known as Rayleigh scattering. However, if the dipole radiates with a frequency greater or lesser
than the incident frequency then inelastic scattering occurs and is known as Raman scattering.

In general inelastic scattering is a small fraction of the total scattering from bulk solids, liquids and gases which are dominated by Rayleigh scattering. However, things get very interesting in Raman scattering from molecules adsorbed on nanostructures. A substantial enhancement from Raman signal results and the scattering is now known as surface enhanced Raman scattering. We employ this phenomenon to estimate the near field enhancement from our synthesized nanostructures. This increase in Raman intensity is due to the localized surface plasmon resonance induced field enhancement in the nanostructures. We saw earlier that the polarizability of a sphere with dimensions much smaller than the wavelength of incident light is given by

\[
\alpha = 4\pi a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}
\]

where \(a\) is the radius of the sphere, \(\varepsilon_1\) is the frequency dependent dielectric constant of the metal and \(\varepsilon_m\) is the dielectric constant of the surrounding medium. We approximate the localized electric field to be [76]

\[
E \approx \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} E_0
\]

We then let the denominator in the above equation approach zero (condition for LSPR), such that the quantity in the right hand side of the equation become large and the local field is now much stronger than the incident field. Under such situations, the Raman
probe molecule experiences this enhanced incident field and emits Raman scattered photons which is turn are enhanced once more by the localized electric field. The EM enhancement of Raman scattering is proportional to the product of incident field enhancement and emission enhancement. A comprehensive study of different methods to analytically and experimentally estimate the SERS enhancement factor exists in literature.[77] In our study, we calculate the plasmonic near field enhancement from Ag nanorod arrays and nanorings experimentally employing the following equation:

\[ I = EF I_0 \eta_{max} \frac{\partial \sigma}{\partial \Omega} d\Omega \]

Where \( I \) is the intensity of the Raman scattered photons measured in counts per second, \( I_0 \) is the incident photon flux in photons \( \text{cm}^{-2} \) \( \text{EF} \) is the enhancement factor, \( \eta_{max} \) is the detector efficiency, \( \frac{\partial \sigma}{\partial \Omega} \) is the Raman scattering cross section and \( d\Omega \) is the solid angle. We picked Rhodamine 6G as our SERS molecule because it is well studied and has a scattering cross section reported accurately in literature.[78] The detector efficiency which we chose to be 0.1 depends on the setup used while the incident photon flux was measured periodically using an intensity meter to ensure constant laser intensity. Therefore, with \( \frac{\partial \sigma}{\partial \Omega} \) obtained from literature and all other parameters obtained from the experiment we were able to estimate the plasmonic near field enhancement from our synthesized nanostructures.
1.6 Introduction to two photon photoemission mechanism

In the previous sections we introduced the SERS mechanism and described how it could be exploited to obtain an estimate for the plasmonic near field enhancement. However, to achieve enhanced scattering the surface of the sample is coated with a layer of SERS active molecule which makes it unfit for subsequent characterization. The two photon photoemission mechanism in conjunction with PEEM overcomes this drawback and provides an alternative route to estimate the near field enhancement from nanostructures without the need to contaminate the surface of the sample. In this section, we introduce the detection of photoelectrons emitted from nanostructures via the two photon photoemission mechanism, with PEEM, as a technique to estimate the plasmonic near field enhancement from nanostructures.

Another way to understand the collective electron oscillation in metal nanostructures is in terms of the incident light field coupling to occupied and unoccupied electron states that are separated by the photon energy. The induced polarizations of the different, individual transitions superimpose giving a macroscopic polarization. This manifests itself in the form of collective oscillation of the electronic system in response to incoming light. At particular wavelengths then, the frequency of the collective oscillation of the electrons matches the frequency of the incoming light giving rise to an extremely large polarization field. This results in the extraordinary near field enhancement observed in nanostructures. There are two competing mechanisms that govern the damping of plasmon excitation. The first mechanism is decay caused, due to dipole oscillation through radiation. This
mechanism is exploited by far field optical techniques. The second mechanism which is of more interest to us is internal damping via formation of electron-hole pairs. The fact that single electrons are excited in this process suggests that electron emission techniques like photoemission might be used to probe the plasmonic properties of metal nanostructures. Of particular interest to us is the two photon photoemission mechanism, in which two photon pulses with a time lag of femtosecond between them are incident upon a sample. The first pulse pumps an electron to an intermediate excited state below the vacuum level. The second pulse then pushes the electron past the vacuum level and onto an electron sensitive detector where it is counted. Two factors are of importance to us in achieving an estimate for the plasmonic near field enhancement from nanostructures using the two photon photoemission mechanism. One, the photoelectron yield from the two photon process measured in the PEEM is related to the laser intensity by $y = b^2 I^2$, where $b^2$ is a constant and $I$ is the laser intensity. Since the laser intensity is proportional to the square of the electric field, the photoelectron yield goes as the fourth power of the local electric field. This makes the two photon mechanism very sensitive to changes in the local electric field. Secondly, LSPR modes of the nanostructures couple with light incident at resonant wavelengths and lead to an enhancement of the two photon photoemission from the nanostructure. However, such a mechanism is absent for the bare substrate and the photoemission yield is much reduced. This translates to a change in contrast and allows for nanostructure imaging. The enhancement factor can then be easily calculated using the following ratio:[79]
Thus, the combination of the two photon photoemission and PEEM allows us to image the nonlinear response of the nanostructures to incoming light along with providing techniques to estimate the near field enhancement from the nanostructures. We have described two different methods which exploit the plasmonic excitations of nanostructures to obtain an estimate for the near field enhancement from nanostructures of different geometries.

Figure 6. Schematic of a two photon photoemission. At time $t=0$ a laser pulse pumps an electron to an intermediate excited state below the vacuum level. A second pulse pushes the electron past the vacuum level to an electron sensitive detector. The time between pulses is in femtoseconds to ensure the electron in the intermediate state does not decay back to its ground state.
1.7 Introduction to Ion interaction with matter

In previous sections we introduced ion implantation and FIB lithography as possible routes to synthesize nanostructures. In both cases, an energetic ion beam is allowed to interact with matter. A basic understanding of the processes that occur during such an event is of importance for synthesizing high quality nanostructures with desirable properties. In this section we address this issue. The reactions that occur when an ion beam is incident on a solid are shown below.

Figure 7. Schematics of ion beam interaction with a solid. When the primary ion impacts the surface of a solid it generates a myriad of particles including secondary electrons, backscattered and sputter ions among others. The primary ion itself could be implanted into the solid.
When a low energy ion beam impacts the surface of a target, it sputters the target atoms. This mechanism forms the basis of FIB lithography, where a beam of Ga\(^+\) ions is focused on to the surface of a target, and by selective sputtering of target atoms from pre-determined regions on the substrate, creates patterns of nanostructures. Along with sputtered target atoms, secondary electrons and backscattered ions are generated which are employed for the purpose of imaging. The Ga\(^+\) ions could also be implanted at a certain depth inside the target. Some of the sputtered atoms along with the primary ion are re-deposited on to the surface of the target and an accurate experimental estimate of the sputtering yield which is defined as the number of target atoms sputtered per ion is difficult. Moreover the sputtering yield depends on the material being sputtered, along with the angle of incidence, energy (accelerating voltage) and current of the primary ion beam. Therefore, a theoretical simulation of the relationship between the above parameters will serve as a guide in choosing experimental conditions which will provide us with best possible results. To that end, we ran SRIM simulations to estimate the sputtering yield of Ag with Ga\(^+\) as the primary ion, as a function of ion incidence angle and beam energy. The results are shown below.
Figure 8. The dependence of sputtering yield on (a) ion incidence angle and (b) ion energy and target material. $0^\circ$ is assumed to be normal incidence. The sputtering yield increases for off normal incidence. For a given ion energy at normal incidence Au is sputtered the most while Cu has the least atoms sputtered per ion.

In the plots, $0^\circ$ denotes normal incidence. In Figure 8(a), we see clearly that the sputtering yield increases for off normal angles, peaking at around $80^\circ$ and then falling rapidly down at $89^\circ$ as the primary ion is now almost parallel to the sample and goes to zero at $90^\circ$ incidences. We also note that the sputtering yield increases as the energy of the beam increases. Figure 8(b) shows the relative sputtering yield of Ag, Au and Cu as a function of beam energy. For a given beam energy, Ga$^+$ sputters more Au atoms compared to Ag and Cu while Cu has the least number of atoms sputtered per ion. These data points were collected assuming normal incidence. Along with sputtering target atoms the primary ion could be backscattered, which is employed for ion imaging, or it could be implanted into the substrate.
The second mechanism wherein the primary ion implants itself into metal oxide substrates forms the basis for our nanostructure synthesis via ion implantation. A schematic of the implantation process is shown in Figure 9. Before implantation the host matrix is a pure crystal with perfectly placed lattice atoms. However, upon ion implantation the surface of the crystal is almost amorphized and depending on the energy of the implantation the ions come to rest at a certain depth below the surface. Defects in the form of vacancies and interstitials are created in the implantation region as a result of the ions knocking the host nuclei from their lattice positions. However, due to the greater mobility of the ions and atoms upon annealing, the matrix heals itself while the individual ions coalesce to form nanoparticles. Interestingly, the vacancy centers also aggregate to form vacancy clusters. The ions themselves might occupy a lattice position (substitution) or an interstitial position.
Figure 9. Schematic of the ion implantation process in a crystalline matrix. The crystal develops substantial defects upon implantation and the ions are implanted at a depth determined by the implantation energy. Due to greater mobility, upon annealing, and the ions coalesce to form nanoparticles. Simultaneously, the matrix heals itself. The final result is a nanostructure buried in a crystalline matrix.

An estimate of the peak penetration depth of Ga\(^+\) ions in Ag, Cu and Au is shown in figure 10(a). We note that the peak penetration depth increases linearly with ion energy. Normal ion incidence was chosen, and the range is dictated by the beam energy range available in our FIB ion column. Figure 10(b) shows the dependence of peak penetration depth as a function of implantation energy for Ag\(^+\) ions implanted in MgO. A 7\(^\circ\) incidence was chosen in this case to mimic the actual experimental conditions.
Figure 10. The dependence of penetration depth on beam energy for (a) Ga$^+$ ions at normal incidence in Ag, Au and Cu targets (b) Ag$^+$ ions at 7° incidence in MgO. The data points were obtained from SRIM simulations and the above parameters were chosen to mimic actual experimental conditions. The figures display a linear relationship with peak penetration depth increasing with increase in beam energy.

In this chapter, we have introduced the mathematical framework on nanostructure interaction with light along with the underlying mechanisms governing nanostructure synthesis and characterization. With this knowledge, we are now well equipped to determine experimental parameters and design experiments which will allow us to synthesize and characterize desirable nanostructures for specific applications. A detailed description of the experimental procedures for the synthesis of nanostructures along with a description of the instrumentation employed for nanostructure characterization forms the content of next chapter.
2. EXPERIMENTAL SECTION

In the previous section, we introduced the field of nanotechnology with emphasis on nanostructure synthesis by four diverse techniques each catering to real-life applications. We also developed a theoretical framework which will enable us to understand the plasmonic properties of these nanostructures. In this section, we discuss in more detail, the experimental procedures employed to synthesize and characterize the aforementioned nanostructures. The description from each of the four techniques is subdivided into two subsections:

(a) Sample preparation

(b) Sample characterization

Under sample preparation, we discuss the equipment, substrates and experimental parameters employed to synthesize nanostructures of various shapes and sizes. In the sample characterization section we discuss the various instruments used to study the microstructure, optical response and plasmonic near field enhancements which ultimately led to a better understanding of the structure-property relationships of these nanostructures.
2.1 Ag nanoparticles in MgO by ion implantation followed by subsequent annealing

2.1.1 Sample preparation

Silver ion were implanted both on single and double-sided polished MgO (001) substrates purchased from CrysTec. The substrates were heated to a temperature of 650°C and implanted with 200 keV Ag+ ions. Substrate holder was tilted to 7° off-normal to avoid channeling and ion implantation was carried out with a fluence of $10^{17}$ Ag+ ions/cm$^2$. The beam energy was chosen using SRIM [80] calculations that estimated the peak of Ag-ion concentration maximum at a depth of 60 nm below the surface. The schematic of the implantation process is displayed in Figure 11. After implantation, the double-side polished sample was cut into equivalent pieces that were annealed for 10 and 30 hours in a tube furnace under normal atmospheric conditions. Optical absorption measurements were performed at room temperature on a Cary 5G UV-VIS-NIR spectrophotometer in absorbance mode.
Figure 11. Schematics of nanoparticle synthesis via ion implantation (left). An energetic beam of Ag$^+$ ions is incident upon a host matrix creating a Gaussian concentration profile at a certain depth determined by the energy of implantation. Subsequent annealing allows for greater mobility of the implanted species and it aggregates to form nanoparticles. The nanoparticles size and shape can be controlled by varying the annealing conditions. Finally the top surface of MgO is plasma etched to reveal the partially buried nanoparticles. SRIM simulations (bottom right) estimate the Ag concentration to peak around 60 nm below the surface of MgO.

2.1.2 Sample characterization

Micro-XRD data were collected using a Rigaku D/Max Rapid II instrument with a 2D image plate detector. X-rays, generated with a MicroMax 007HF generator fitted with a rotating Cr anode ($\lambda=2.2897 \, \text{Å}$), were focused on the specimen through a 300 µm diameter collimator. The samples were kept at a 2° incident angle and oscillated within a 50° range in the Phi-axis direction. 2DP, Rigaku 2D Data Processing Software (Ver. 1.0,
Rigaku, 2007) was used to integrate the diffraction rings captured by the 2-D image plate detector. The analysis of diffraction data was carried out using JADE 9.1.5 (Materials Data Inc.) and PDF4+ database from the International Center for diffraction data (ICDD). Ag concentration profiles of the implanted samples were obtained from RBS performed using a 3 MV Tandem accelerator. Random and channeling RBS measurements were performed on both the annealed and as-implanted samples using 2 MeV He+ ions. The backscattering spectra were collected using a silicon surface barrier detector at a scattering angle of 150°. Data analysis was performed using SIMNRA simulation code.[81] Specimens for TEM and APT analysis were prepared using an FEI Helios Nanolab dual-beam focused ion beam (FIB) and scanning electron microscope (SEM) [35] that were subsequently analyzed in a JEOL 2010 TEM operated at 200 kV and an aberration-corrected FEI Titan 80-300 TEM (at 300 kV).

The compositional analysis of the nanoparticles was carried out using a LEAP4000XHR local electrode APT system from CAMECA, using a pulsed UV laser with 10 pJ pulse energy at a specimen temperature of 40 K. The 30 hour annealed sample was loaded onto an Oxford Instruments Plasma lab 100 ICP etch and deposition system to etch the MgO surface and expose the buried Ag nanoparticles. Tapping Mode AFM topographic images were collected using a commercially available microscope (NanoScope IIIa, Veeco Metrology). The imaging was performed using a tapping-mode AFM 125 µm silicon cantilever with a resonant frequency of 300 KHz and spring constant 40N/m.
2.2 Electrochemical deposition of Ag, Cu and Au nanorod arrays

2.2.1 Sample preparation

Free standing Ag, Cu and Au nanorod arrays were synthesized via template assisted electrochemical deposition followed by subsequent etching of the template. The process leading to free standing metal nanorod arrays is depicted in Figure 12.

![Figure 12. Schematics of the electrodeposition process for Ag, Cu and Au metal nanorod arrays. (a) bare AAO template with a magnetron sputtered metal layer and a coating of metallic paste, (b) metal nanorods growing in the pores of the AAO template during electrodeposition, (c) vertically aligned metal nanorod arrays upon template removal in 1 M NaOH solution. The metallic paste and the sputtered layer provide a strong electrical contact facilitating fast ultra-long nanorod growth.](image)

Commercial metal foils (Alfa Aesar, 99.9 % purity) were employed as the anode, whereas a through-hole AAO template with a coating of metallic paste on one side was used as the cathode. AAO templates with a diameter of 13 mm, pore sizes of 100 and 200
nm, and a thickness of 60 µm were purchased from Whatman Inc. Ag and Au plating solutions with metal contents of 28.1 g/l and 25 g/l were purchased from Alfa Aesar while the copper plating solution was purchased from RioGrande. A 1 µm layer of Ag, Cu or Au was deposited onto one side of the AAO template using a magnetron sputtering system. A quartz microbalance was used to monitor the layer thickness in situ. 10 µm sized Cu and Au metal powders were purchased from Alfa Aesar and dispersed in an organic mixture (Heraeus V-006A). 90 wt % metallic powder was mixed with a 10 wt % organic mixture and centrifuged at 1440 rpm for 5 min. The resulting paste was used to connect the metal wire to the sputtered contact layer on the AAO template. The paste was dried under ambient conditions, resulting in a strong electrical contact between the template and the cell. Electrodeposition was carried out under galvanostatic conditions using a solartron electrochemical interface operated using Corrview. A schematic of the electrochemical cell is depicted in Figure 13. Constant currents of 5 and 10 mA were maintained while the deposition time was varied depending on the desired length of the nanorod arrays. The cell and foils were washed in acetone and deionized water before and after each deposition process. Following deposition, the AAO template was removed from the cell and rinsed in deionized water to remove the plating solution. Finally, the free standing nanorod arrays were exposed by etching the AAO templates in an aqueous solution of 1M NaOH for 25 min. The nanorod arrays were again rinsed in deionized water, and dried under ambient laboratory conditions.
2.2.2 Sample characterization

Secondary electron SEM imaging was performed using the FEI Helios Nanolab 600 to obtain surface and cross-sectional images. Grazing incidence X-ray diffraction of the Ag, Cu and Au nanorods was carried out on a Phillips X’Pert Multipurpose X-ray diffractometer equipped with a fixed anode operating at 45 kV and 40 mA at a fixed 5-degree incident angle. Analysis of the diffraction data was carried out using JADE 9.4.5 (Materials Data, Inc.). Phase identification was performed using the PDF4+ database (ICSD). Lattice parameters were determined from the

Figure 13. The figure represents the schematics of the electrochemical setup. The high purity Ag foil serves as the anode and an anodized alumina (AAO) template coated on one side with a layer of metallic paste on top of a layer of sputtered metal serves as the cathode. Both electrodes are completely immersed into a plating solution. The electrodes are connected to a solartron electrochemical interface via metal wires. The SEM image on the right is the top view of the AAO template.
angular positions of the peaks in the 20-90° range. Crystallite size was estimated from broadening of the (111) reflections of the metals using JADE’s pseudo-Voigt profile function calibrated with a LaB6 (SRM 660, NIST) internal standard for the grazing-incidence geometry employed. TEM imaging was performed using JEOL 2010 F transmission electron microscope.

To investigate the plasmonic properties of the synthesized nanorod arrays, we collected surface enhanced Raman scattering (SERS) spectra from Ag and Au nanorods. The samples were coated with a 10^{-5} M solution of rhodamine 6G in methanol, followed by vacuum evaporation of the solvent. The SERS setup used is displayed in Figure 14:[82]

Figure 14. Schematic of the SERS measurement setup. The substrate is placed face down on very thin glass slide. The laser is focused on the tip of the rods through the glass slide. The scattered radiation is collected through the same objective and recorded using charge coupled device.
The spectra were recorded under ambient laboratory conditions using an inverted optical microscope (Axiovert 200, Zeiss). The incident 514 nm continuous wave monochromatic light (Innova 300, Coherent) is attenuated using a variable neutral density filter wheel, reflected off a dichroic beam-splitter, and focused using an oil-immersion objective (1.3 NA, 100 X) onto the sample. The electric field was incident normal to the substrate, focused onto the tips of the metal nanorods. The scattered radiation is collected through the same objective, transmitted through the beamsplitter, and filtered using a long pass filter. The resulting light is recorded using a liquid nitrogen cooled charge coupled device coupled (CCD) to a spectrometer (Holespec f/1.8i, Kaiser Optical System). The current effective instrument resolution in the micro-Raman experiments is \( \sim 8 \text{ cm}^{-1} \).

2.3 Ag nanorod arrays by Focused ion beam lithography

2.3.1 Sample preparation

To synthesize Ag nanorod arrays we deposited Ag films of thickness 1\( \mu \text{m} \) on Si substrates. The depositions were performed on the same setup described in the previous section. Post-deposition the films were visually inspected for any irregularities. We then loaded the substrates into the FEI Helios Nanolab system to create patterns using a focused beam of Ga\(^+\) ions from an ion gun. The schematic of the FIB column is displayed in Figure 15.[83] It consists of a Liquid Metal Ion source which produces a steady beam of Ga\(^+\) ions via the electrostatic interaction between the liquid metal on the tip of a needle and the extraction electrode. The ions are focused and collimated into
parallel beams by a condenser lens assembly. The ion beam then passes through a mass separator which eliminates any foreign ion species. Assemblies of stigmatic focusing lens block ions that are not directed vertically. Following this is an objective lens assembly which

Figure 15. Schematic representation of a focused ion beam column. A liquid metal ion source provides a beam of gallium ions while a slew of electrostatic lenses and deflector assemblies help focus the beam onto the required region of the sample.
reduces beam size to obtain better focus. Finally, an electrostatic beam deflector deflects the beam and controls the ion path on to the substrate. The working distance, which is the distance between the column tip and the sample, is set to 4 mm. To ensure normal incidence of Ga\(^+\) ions the substrate is tilted to 52\(^0\). The beam current was varied from 28 pA to 2.8 nA while the accelerating voltage was maintained constant at 30 KeV. Nanostructures are generated via selective sputtering of substrate ions. During this process Ga gets implanted into the host substrate. The depth and concentration of implantation depends on the accelerating voltage, beam current, angle of incidence and substrate material.

Figure 16. SRIM simulations sowing depth of Ga\(^+\) implantation in Ag. Ga implants itself to a depth of 30 nm with peak concentration around 10nm. An accelerating voltage of 30KeV at normal incidence was chosen for the simulations.
SRIM simulations were carried out to estimate the depth of implantation at the above accelerating voltage. The results of Ga\textsuperscript{+} implantation in Ag at normal incidence shown in Figure 16 suggest an implantation depth of 30 nm with peak Ga concentrations at 10nm below the surface.

2.3.2 Sample characterization

To ensure good quality substrates the etching was monitored periodically \textit{in situ} by SEM imaging. Post-etching, the substrate was tilted back to 0\textdegree and top view images of the nanorod arrays were obtained.

To obtain an estimate of the plasmonic near field enhancement, the freshly prepared nanorod arrays were introduced into a UHV PEEM chamber and photoelectron images were obtained. The photoelectron emission microscope consists of a UV light source (Hg discharge lamp) for the generation of photoelectrons via photoemission. The photoelectrons emitted from the substrate surface are imaged, amplified and observed with a CCD camera. The schematic of the PEEM is shown in Figure 17.[84] It consists of an electrostatic tetrode objective lens, a contrast aperture located in the back focal plane, an octopole stigmator/deflector for maximum resolution, a continuously varying aperture located in the first image plane for enhancement of contrast and resolution, and two projective lenses. A high potential of 20 kV is applied between the sample and the objective to accelerate the photoelectrons and reduce chromatic aberrations. Firstly, the nanorod array was centered in the image window with the UV lamp and images were
captured. Subsequently, non-linear photoemission was induced in the nanorod arrays upon exposure to a 150 fs pulsed Ti:Sapphire laser centered at 400 nm at an incident angle of 150° with respect to the sample surface. The laser power was maintained at 1 mW. The polarization vector is controlled by rotation of a λ/2 waveplate. Due to its glancing incidence the laser illuminates an elliptical area on the surface with major (minor) axis length of approximately 100 µm (30 µm). The photoyield integration area and the laser spot size overlap near the center of the image window.

Figure 17. Schematics of photoemission electron microscope. Photoelectrons that are generated in the sample upon illumination with UV light/Laser are accelerated and focused onto a multichannel plate where they are amplified. A CCD camera is employed to image the photoelectrons upon interaction with a phosphor screen.
2.4 Ag and Au nanostructures by thermal growth technique

2.4.1 Sample preparation: Ag nanostructures

Si (111) substrates with dimensions 10 cm x 10 cm x 1 mm were employed to deposit thin films of Ag. Prior to deposition the substrates were cleaned with acetone and dried in nitrogen. Ag thin films with thickness ranging from 3-50 nm were deposited on the substrates with a magnetron sputter coater. The thickness of the film was monitored with a quartz crystal oscillator. Post-deposition the samples were placed in the center of a tube furnace for annealing. The annealing process is as follows: The furnace temperature was programmed to ramp up to the required annealing temperature of 900°C over a period of 5 hours followed by annealing at 900°C for 5 hours. Post annealing the sample was allowed to cool down to room temperature. A constant flow of Ar at 125sccm was maintained to provide an inert atmosphere throughout the annealing process.

2.4.2 Sample characterization: Ag nanostructures

Secondary electron SEM imaging was performed on the FEI Helios Nanolab 600 to image the surface of the substrates. To investigate the plasmonic properties of the above synthesized Ag nanorings, we collected surface enhanced Raman scattering (SERS). A 10⁻⁵ M methanol solution of Rhodamine 6G was drop cast until an even coating of the molecule on the substrates was obtained. The methanol was subsequently vacuum evaporated. The SERS measurement setup used is described in detail elsewhere. An inverted optical microscope (Axiovert 200, Zeiss) operating under ambient laboratory
conditions was employed to record the spectra. A continuous wave monochromatic laser operating at 514nm (Innova 300, Coherent), attenuated using a variable neutral density filter wheel, reflected off a dichroic beam-splitter, was focused on the substrates using an oil-immersion objective (1.3 NA, 100 X). The electric field was incident normal to the substrate. The radiation scattered from the sample is collected through the same objective, transmitted through a beam splitter and filtered using a long pass filter. A liquid nitrogen cooled charge coupled device coupled to a spectrometer (Holespec f/1.8i, Kaiser Optical System) was used to record the resulting light. The current effective instrument resolution in the micro-Raman experiments is ~8 cm$^{-1}$.

2.4.3 Sample preparation: Au nanocages

Arrays of gold particles with diameters from 100 nm to 2000 nm were produced by electron beam lithography using the following algorithm: a 50 nm layer of PMMA electron beam resist was spin-coated onto a [111] silicon substrate (Sumitomo Sitix Silicon) with an extant native oxide layer. Pre-designed patterns were written on the sample by electron beam lithography (EBL, Raith eLiNE operating in writing mode); the resist-covered substrate was then developed in MIBK:IPA (1:3) for 45 s; next, 20 nm of gold was deposited by e-beam evaporation (Åmod 600, Angstrom Engineering Inc.); after lifting off the unwanted PMMA, the desired gold patterned film remained. The gold films were inserted into a quartz tube in a horizontal tube furnace (Thermolyne #F21135 furnace, Barnstead International) for a time-sensitive reformation step under a stream of dry, ultra-pure nitrogen (100 sccm) for 10 hr at 940 ± 5 ºC. The gold film thickness,
annealing time, annealing temperature, and nitrogen flow rate were set the same for all of the experiments.

2.4.4 Sample characterization: Au nanocages

Post-annealing SEM was employed to image the surface of the samples. Gold particles with a clear opening feature, observed using the Raith eLiNE SEM, were randomly selected as candidates for cross-section cutting by focused ion beam milling. A FEI FIB 200 XP focused ion beam system, using a gallium ion beam that operates at 30 kV (50 k magnification, 1 pA current, and 10 nm resolution), was used to cross-section the hollow particle. The Gold particles were cut from the edge to the center using the cleaning cross-section tool with proper spatial parameters. Then, the FIB-cut, hollow particles samples were analyzed at a tilt angle of 45° with a Hitachi S4200 SEM examine the topology and morphology of the cross-sectioned region.

To investigate the plasmonic near field enhancement, PEEM was employed to image the photoexcited electrons from the solid and hollow gold particles. After synthesis, the samples were transferred to the UHV PEEM chamber and exposed to a 150 fs pulsed laser centered at 400 nm at an incident angle of 15° with respect to the sample surface. A more detailed explanation of the PEEM setup employed in this experiment is presented in detail in the following section.

This concludes our section on the description of experimental procedures and instrumentation used to characterize the nanostructures. In the next section, various
results will be presented along with a discussion of the nanoparticles microstructure and structure-property relationships. An estimate for the near field enhancement from the Ag nanorod arrays and Ag nanorings will also be presented and discussed.
3. RESULTS AND DISCUSSION

In the previous section, we described in detail the procedure and equipment used to synthesize nanostructures. We then provided background information on the instruments used to characterize the synthesized substrates. In this section, we present the results and discussion of our investigations into the microstructure, plasmonic properties and structure-property relationships of these samples. We will again subdivide this section into four, each subsection catering to nanostructure synthesized by each of the four methods enumerated earlier.

3.1 Ag nanoparticles in MgO by ion implantation followed by subsequent annealing

Random and channeling RBS spectra of the as-implanted, 10, and 30 hour annealed samples are shown in Figure 18. Figure 19 displays detailed RBS data fitted using the SIMNRA simulation package. RBS analysis indicates the Ag concentration peaks at around 30 nm below the MgO surface. This is in contrast to SRIM simulation that estimates the concentration of 200 keV Ag ions to peak at a depth of 60 nm. The discrepancy between SRIM simulation and the measured Ag distribution is attributed to the elevated temperature of the sample throughout the implantation procedure. As the implantation distributions are computed with SRIM assuming a temperature of 0K, diffusion processes taking place under our experimental conditions are not accounted for. Another possible source of error in the simulated distributions is associated with the
stopping power estimates employed. The experimental Ag profiles are broader compared to SRIM profiles, which does not account for the diffusion process. The minimum yield is the ratio between the backscattering yields of channeling over the random spectra. A low minimum yield (between 3 to 5%) indicates a highly crystalline sample while a high minimum yield (>50%) indicates a poor crystalline quality of a sample. The Ag minimum yield for the as-implanted sample is 90% in the energy range of 1660 to 1700 keV indicating no shadowing of Ag atoms. The minimum yield for Mg is approximately 85% between 800 to 900 keV. This high yield can be attributed to the presence of a substantial number of structural defects in the implanted region. These structural MgO defects manifest themselves in the optical absorption spectra, as peaks at 225 and 250 nm corresponding to absorption by F and F⁺ centers.

Figure 18. Random (blue) and channeling (red) RBS data for Ag⁺ ions implanted at 6500°C with 200 keV with an ion dose of 1017 Ag⁺ ions/cm² in MgO a) as-implanted sample; b) 10 hour annealed sample; and c) 30 hour annealed sample.
Figure 19. RBS Experimental spectra (red circles) for the as-implanted sample showing the Ag peak and Mg edge fitted (blue line) using SIMNRA simulation package. The inset shows the decrease in the concentration of Ag with increasing annealing. The Ag concentration was estimated using the SIMNRA peak fitting of RBS data.

Figure 20 displays the optical UV-visible absorption spectra for the ion-implanted sample as a function of annealing time. A broad surface plasmon resonance peak, centered at 475 nm, is evident. Previous studies of Ag implanted in MgO[26] which were carried out at room temperature, do not exhibit an LSPR peak. We therefore conclude Ag nanoparticles with size distributions that can influence LSPR are formed because of the elevated temperature during implantation. The non-uniform nanoparticle size distribution formed during implantation is indicated by the broad Ag LSPR peak and by the micro-XRD pattern, for the as-implanted sample, which also shows broad peaks corresponding to Ag (111) and Ag (311) reflections (see Figure 21). The size distribution of the as-implanted nanoparticles was estimated to be between 1 and 4 nm from broadening of the Ag (111)
reflection using JADE’s pseudo-Voigt profile function calibrated with a LaB6 (SRM 660, NIST) internal standard for grazing-incidence geometry.

Figure 20. UV-visible absorption spectra for MgO (100) implanted with 1x10¹⁷ Ag⁺ ions at 200 keV. The dashed (brown), dash-dot (red) and solid (blue) lines show data for the as-implanted, 10 hour and 30 hour annealed samples, respectively. The LSPR band peaked near 500 nm progressively red shifts and narrows with anneal time. A reduction in F, and F⁺ center absorption and an increase in the 375 nm shoulder intensity are also observed with increasing annealing times.

The random and channeling spectra from the 10 hour annealed sample are also shown in Figure 18(b). The minimum yield for Mg in the region between energies 800 to 900 keV is approximately 43% for the 10 hour annealed sample as compared to 85% for the as-implanted sample, indicating an improvement in the crystalline quality of the sample upon annealing. There is significant shadowing of Ag atoms in the 10 hour annealed
sample, which gives a minimum yield of 52% between 1660 and 1700 keV, in contrast to the as-implanted sample. This improvement in the MgO crystalline quality is also evident in the optical absorption spectra, which show a decrease in intensity of the peaks attributed to F and F$^+$ defect centers (Figure 20).

Figure 21. MicroXRD patterns for MgO (100) implanted with Ag (a) as-implanted; (b) annealed in air for 10 hours; and (c) annealed in air for 30 hours showing the progressive sharpening of Ag peaks that indicate particle size is increasing with annealing time. Data collected using Cr radiation ($\lambda=2.2897$ Å).
These results suggest that there may be some ordering of Ag particles as particle sizes increase during annealing. Furthermore, upon annealing, the Ag surface plasmon peak displays increased intensity, narrows and red-shifts indicating that the average particle size increased and the size distribution has possibly narrowed. A weak shoulder, near 375 nm on the Ag surface plasmon resonance peak, which is attributed to the formation of F and F$^+$ vacancy clusters[21], is evident in the 10 and 30 hour annealed samples. The observation that the nanoparticle size increases is also supported by the sharpening of the Ag diffraction peaks in micro-XRD patterns (Figure 21). The average size of the nanoparticle was estimated to be 12 nm from micro-XRD. To obtain a deeper understanding of the size and spatial distribution of the Ag nanoparticles and defect clusters formed after 10 hours of annealing, TEM was performed on a FIB-prepared cross-sectional sample. The cross-sectional bright-field TEM image clearly shows spherical Ag nanoparticles and vacancy clusters (Figure 22). Interestingly, many of the vacancy clusters were located adjacent to Ag nanoparticles.

The random and channeling spectra for the 30 hour annealed sample are shown in Figure 18(c). The minimum yield for Mg in the region between energies 800 and 900 keV is approximately 50% for the 30 hour annealed sample as compared to 86% for the as-implanted sample. However this value is higher than the 10 hour annealed sample which might be because of the influence of larger size nanoparticles and vacancy clusters in the 30 hour annealed sample. These results are consistent with the absorption spectra, for annealed samples, which show decreasing absorption intensity for the F and F$^+$ centers.
The shoulder attributed to vacancy clusters is best defined in the 30 hour annealed sample. This observation, along with the decreased intensity of the F and F\(^+\) centers, suggest that individual F and F\(^+\) centers coalesce into vacancy clusters upon annealing. The Ag plasmon resonance peak for the 30 hour annealed sample is more intense, narrower and red-shifted when compared with both the as-implanted and 10 hour annealed sample, also indicating an increase in nanoparticle size (Figure 20).

![Cross-sectional TEM image of 10 hour annealed sample (top) and 30 hour annealed sample (bottom) indicating the increased size of the particles along with the transformation from strain accommodated coherent spherical morphology to a semi-coherent faceted morphology upon annealing from 10 hours to 30 hours at 1000\(^0\)C.](image)

Figure 22. Cross-sectional TEM image of 10 hour annealed sample (top) and 30 hour annealed sample (bottom) indicating the increased size of the particles along with the transformation from strain accommodated coherent spherical morphology to a semi-coherent faceted morphology upon annealing from 10 hours to 30 hours at 1000\(^0\)C.
The Ag (111) reflection peak became sharper in the microXRD patterns, as anneal time increased. Based upon the micro-XRD result, an average particle size of 14 nm was estimated for the 30 hour annealed sample (Figure 21). Figure 22 displays bright-field cross-sectional TEM images of 10 and 30 hour annealed samples showing the Ag nanoparticles developed a faceted morphology, after 30 hours annealing, in comparison to the spherical morphology observed after 10 hour annealing.

Our RBS results suggest a reduction in the amount of Ag as a function of annealing as estimated by SIMNRA, which gives an Ag concentration of $1.27 \times 10^{17}$ atoms/cm$^2$ for the as-implanted sample and $1.21 \times 10^{17}$ atoms/cm$^2$ and $9.7 \times 10^{16}$ atoms/cm$^2$ for the 10 hour annealed and 30 hour annealed samples respectively (Figure 19). This translates to a 5% and 24% loss of Ag in the 10 and 30 hour samples when compared to the as-implanted sample. We believe the Ag loss is due to diffusion to the surface followed by evaporation as discussed in previous works [13, 31].

The spherical (coherent) to faceted (semi-coherent) transition of Ag nanoparticles appears to occur between 10 and 30 hours of annealing. As evident in Figure 22, the typical shape of the nanoparticles changes from spherical to faceted. TEM images and electron diffraction indicate that the Ag particles are predominantly well registered with the MgO matrix. The 30-hour annealing time yielded the largest Ag particles, for which HAADF-STEM images from the [100] and [110] directions suggest a nominally octahedral shape, truncated at the (001) surfaces (see Figure 23). Interestingly, a greater degree of truncation is observed along those (001) planes parallel to the substrate surface.
Figure 23. Aberration-corrected HAADF-STEM image of Ag nanoparticles in MgO in 30 hour annealed sample taken along the a) [110] b) [100] directions, respectively, showing the octahedral shape truncated along (001) planes parallel to substrate surface.

Implantation and annealing parameters were targeted toward testing the viability of these samples for plasmonic applications. Subsequently we partially exposed the Ag nanoparticles in the 30 hour annealed sample using fluoride plasma etch. The surface features of the etched sample were imaged using SEM. A relatively low electron accelerating voltage of 2 kV was chosen so that the detected signal would be biased towards electrons emitted from collisions nearer the sample surface. The SEM image displayed in Figure 24 clearly shows a random distribution of Ag nanoparticles partially buried in the MgO matrix. Subsequently, we obtained a height distribution for the Ag nanoparticles protruding from the surface of the plasma etched sample using AFM to confirm the SEM result.
Figure 24. 2 kV SEM image of the 30 hour annealed sample recorded with a sample tilt towards the detector showing Ag nanoparticles partially buried in MgO following a fluoride plasma etch in a mixture of SF$_6$ + Ar in a ratio 2:1. Inset: AFM image of the surface of the plasma etched sample clearly showing the protruding Ag nanoparticles.

For a comprehensive understanding of the Ag nanoparticles formed after 30 hours of annealing, a study of both the structure and the composition is essential. Laser-assisted APT can provide a three-dimensional map of the Ag/MgO samples with high spatial and mass resolution as has recently been demonstrated for Au nanoparticles embedded in MgO matrix.[85] Figure 25 shows the complete APT data set collected, with blue dots
representing oxygen atoms, magenta for Mg atoms, and red for Ag atoms. The Ag nanoparticles can be better visualized by forming a 50 at% Ag isoconcentration surface delineated from the MgO surface as shown in Figure 25(b). An isoconcentration surface corresponds to a specific concentration threshold (50 at% Ag). The size distribution of Ag nanoparticles obtained from the isoconcentration surface is consistent with the TEM results (Figure 22(b)), showing a mixture of larger, ~50 nm sized particles coexisting with smaller (<10 nm) Ag particles in the matrix.

The composition change across the interface between the largest Ag nanoparticle and MgO matrix was estimated by using a proximity histogram which provides a measure of the proximity of each point in space with reference to a chosen interface.[86, 87] We exploited this analysis to confirm that the nanoparticles are nearly pure elemental Ag by plotting the nearness of Ag, Mg and O atoms (Figure 25(c)) around a large 50 % isoconcentration Ag nanoparticle interface with the surrounding MgO matrix. The results show clearly that within the nanoparticle (positive distances on the X-axis) we have 100 % Ag concentration. Presence of other Ag nanoparticles within a 10 nm distance from the 50 at% isocomposition surface of larger nanoparticle results in the nonzero Ag concentration outside the Ag nanoparticle (negative distances on the X-axis). Broad compositional width of the interface may be attributed to local magnification artifacts which are not accounted for by the reconstruction. To better visualize the Ag distribution across the nanoparticle and MgO matrix, a 2D Ag concentration contour plot was obtained (inset in Figure 25(c)). This was plotted by quantifying the concentration across
a 1 x 50 x 50 nm slice volume passing through the Ag nanoparticle and surrounding MgO matrix. The red regions in the contour plot correspond to 100 at% Ag and the blue corresponds to 0% Ag (MgO matrix). The high purity of Ag nanoparticles embedded in the MgO matrix makes them promising candidates for a variety of plasmonic applications.

Figure 25. (a) Atom map of 30 hours annealed sample (blue: O, Magenta: Mg, red: Ag) obtained by atom probe tomography; (b) 50 at% isocomposition surface delineating the Ag particle regions from MgO matrix; (c) Proximity histogram showing the compositional partitioning between the largest Ag nanoparticle and MgO matrix. Inset shows 2D Ag concentration contour plot consisting of pure Ag nanoparticles (shown by red regions) in MgO matrix (blue region).
For a quicker assimilation of the results obtained from the above analysis, we have constructed a table below showing the effect of annealing on the size, shape and optical response of Ag nanoparticles in MgO annealed at 1000 °C in air for 10, 20 and 30 hours.

Table 1. The effect of annealing on the size, shape and optical response of Ag nanoparticles in MgO annealed at 1000 °C in air for 10, 20 and 30 hours.

<table>
<thead>
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<th>As-Implanted</th>
<th>10 hour annealed</th>
<th>30 hour annealed</th>
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<tbody>
<tr>
<td><strong>Ag concentration</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RBS)</td>
<td>1.27 x 10^{17} atoms/cm^2</td>
<td>1.21 x 10^{17} atoms/cm^2</td>
<td>9.7 x 10^{16} atoms/cm^2</td>
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<tr>
<td><strong>Nanoparticle Morphology (TEM)</strong></td>
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<td>Faceted</td>
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<td><strong>Ag LSPR Peak</strong></td>
<td>475 nm</td>
<td>492 nm</td>
<td>502 nm</td>
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<td><strong>Compositional analysis (APT)</strong></td>
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<td>-</td>
<td>Ag nanoparticle purity is confirmed</td>
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3.2 Electrochemical deposition of Ag, Cu and Au nanorod arrays

AAO template-assisted electrochemical synthesis of metallic nanorod arrays can be broadly differentiated into two categories, namely DC electrodeposition and AC pulsed electrodeposition.[88] Currently, AC pulsed electrodeposition is the method of choice where the template is porous on one side and still retains an aluminum layer on the other side. This technique results in the formation of a thin oxide layer (or barrier layer) towards the bottom of the well (pores), and owing to its high resistivity, does not allow
direct current to pass through it.[89] One way to overcome the barrier layer limitation and improve electrical contact is to employ a through-hole template and deposit a metal layer on one side of the template. However, this renders the template brittle and difficult to handle. To overcome this limitation, a metal paste is applied on top of the sputtered layer. The paste dries out and leaves a thick layer of metal on one side of the sample which adheres well to the sputter coated layer, thereby rendering the sample more robust. Another advantage of incorporating this layer into the template is an increased electrical contact throughout the deposition. This enabled us to employ DC electrodeposition, a relatively simple process which allowed for the growth of very high aspect ratio nanorods. Top view and cross-sectional SEM images for the Ag, Cu and Au nanorod arrays are shown in Figures 26 and 27. A rather uniform length distribution and even coverage for Ag nanorod arrays is apparent. Note that the SEM images are representative of the entire nanorod array, (see Figure 27). The lengths of the nanorods were obtained from cross-sectional SEM images. Nanorod length can be varied, by choice of deposition time, from a few hundred nanometers to few tens of µm. It must be noted here that, in the cross-sectional images the nanorods on the surface are fractured during sample preparation for imaging.
Figure 26. A higher magnification top view image of the Ag, Cu and Au nanorod arrays.

Figure 27. Secondary electron SEM images of the surface (left, scale bar: 5 µm) and cross-section (right, scale bar: 10 µm) of uniform Cu, Ag and Au nanorods grown via the DC electrodeposition technique.
Figure 28 shows the (111), (200), (220), and (311) GIXRD reflection peaks for all three nanorod arrays, suggesting that the individual nanorods are polycrystalline. The crystallite size was estimated to be 29, 27, and 32 nm for Ag, Cu, and Au, respectively. The size estimate was obtained from broadening of the (111) reflection peaks via the Scherrer equation using JADE’s pseudo-Voigt profile function, calibrated with a LaB6 (SRM 660, NIST) internal standard for the grazing-incidence geometry employed.[90] The lattice parameters for the crystallites obtained from the location of the reflection peaks were 4.09, 3.62, and 4.08 Å for Ag, Cu and Au, respectively, which are identical to literature values of 4.09, 3.61 and 4.08 Å for bulk Ag, Cu and Au. [91-93] No significant residual contamination of the templates due to immersion in the plating solution was observed. The Ag and Au nanorod arrays do not exhibit reflection peaks for oxides, indicating that oxidation of the noble metal nanorod arrays is negligible in the fresh samples (although the Cu nanorod array displays a very minor Cu$_2$O reflection peak around 36°). However, it must be noted that XRD, a bulk technique, does not give information about surface oxides.

Further detailed characterizations of the nanorods were performed using TEM. The nanorod samples were ultrasonicated in DI water to disperse them in solution. The colloid was drop casted on TEM grids to image the nanorods. The bright field TEM images of the top portion of Ag, Cu, and Au nanorods are given in Figure 29 (top). The selected area diffraction patterns from the same are given in Figure 29 (bottom). These selected area diffraction patterns were taken from some thin regions of the nanowires and the
lattice parameters estimated from the selected area diffraction (SAD) match well with the lattice parameters calculated from XRD. The extra spots visible in Cu SAD pattern corresponded to copper oxide.

Figure 28. GIXRD spectra showing the reflection peaks for a) Au b) Ag C) Cu. The Cu pattern shows an additional peak at low angles, which is attributed to Cu2O.
Figure 29. TEM images (top) and electron diffraction patterns (bottom) of Ag, Cu and Au nanorods obtained by ultra-sonicating the nanorod arrays in DI water and subsequently drop cast onto TEM grids. The lattice parameters obtained from the patterns were similar to bulk Ag, Cu and Au crystals.

SERS spectra were collected from randomly selected spots on the nanorod substrates. Typical ensemble averaged SERS spectra of rhodamine 6G coated onto the Ag and Au nanorod arrays are shown in Figure 30. These spectra were obtained by averaging ~1000 spectra individually integrated over 10 seconds at 10 different sites on each substrate. The 614 cm\(^{-1}\) vibrational mode of rhodamine 6G - measured from both samples - was fitted to a Lorentzian function. The derived widths of the vibrational state in both cases were instrument limited (8 cm\(^{-1}\)), and the areas under the two bands were 63 and 180 counts s\(^{-1}\)
for Au and Ag, respectively. We use the intensities derived from the fitted spectra to estimate a lower limit for the SERS enhancement factor (EF) according to:

\[
I = EF I_0 \eta_{\text{max}} \frac{\partial \sigma}{\partial \Omega} d\Omega
\]

Based on an incident intensity of \(I_0 = 1.72 \times 10^{22}\) photons cm\(^{-2}\) s\(^{-1}\) (~67 \(\mu\)W \(\mu\)m\(^{-2}\)), an upper limit for detection efficiency \(\eta_{\text{max}} = 0.1\), a Raman scattering cross-section \(\frac{\partial \sigma}{\partial \Omega}\) of \(\sim 10^{-24}\) cm\(^2\) sr\(^{-1}\) for the 614 cm\(^{-1}\) vibrational mode at 514 nm,[78] and a solid angle \(d\Omega = \pi\), we derive enhancement factors of \(1.1 \times 10^4\) and \(3.3 \times 10^4\) for the Ag and Au samples, respectively. The total enhancement in SERS arises from two cooperative mechanisms. The first is chemical in nature, associated with (i) the change in molecular polarizability as a result of chemical/physical adsorption onto a metal, (ii) whether or not the incident photon is resonant with an electronic excited state of the molecular system. The second is due to the coupling of the incident field with the plasmons of the reported nanorod arrays. The molecular differential scattering cross section[78] used to evaluate EF takes into account the resonance enhancement of the SERS reporter. This is by far the most dominant contribution to chemical enhancement. Thus the derived enhancement factor - \(\left(\frac{E}{E_{\text{laser}}}\right)^4\) - mainly gauges the physical enhancement mechanism or the plasmonic response of the samples. For rhodamine 6G at 514nm excitation, it has been reported that an enhancement factor of \(10^5\) renders the detection of a single molecule possible.[77] We note that the different (randomly selected) spots across the sample yielded enhancement
factors that agree within an order of magnitude, indicating that the substrates are rather uniform. This also suggests that molecular scattering is dominated by the averaged response of the ensemble, as opposed to that of a single or a few molecules at the nanogaps between the individual nanorods.

Figure 30. Left panel: SERS spectra of a 10-5 M rhodamine 6G solution evaporated on the Ag and Au nanorod arrays. The 614 cm⁻¹ mode of the molecule is highlighted and expanded in the right panel. The areas under the two bands are shown next to the spectra.

3.3 Ag nanorod arrays by focused ion beam lithography

The Ag nanorod arrays patterned by FIB lithography is shown in Figure 31. The patterns were created on an Ag film sputter coated on a Si wafer. The Ga⁺ ions which were incident normal to the surface selectively etch Ag in pre-determined regions. The etching proceeds as a result of Ga⁺ ions sputtering the surface Ag atoms. The quality of the
patterns depends upon a variety of factors such as beam current, accelerating voltage, angle of incidence, focus, stigmation, sputtering rate and re-deposition. The beam current is a measure of the number of ions incident on the surface of the target, the accelerating voltage is the energy with which the ions are incident on the surface. The focus and stigmation should be optimal to achieve the required nanostructure shape with sharp features. The rate at which the material is removed from the target depends upon the angle of incidence and beam energy. An estimate of the sputter rate is important for the process of ion beam patterning. SRIM is a widely used theoretical simulation package that calculates the sputter yield (number of atoms sputtered per ion), ion energy loss, ion implantation among other parameters. The results obtained from SRIM simulations are displayed in Figure 7 & 9 and are discussed.

Figure 31. FIB lithography patterned Ag nanorod arrays. The nanorod arrays were patterned using a Ga⁺ beam accelerated at 30KeV with a beam of 0.46nA. The ion beam was incident normal to the surface.
in the introduction section. An accurate control over the etching depth is important as can be seen in Figure 32 displayed below. All parameters were maintained constant except for the patterning duration which was progressively decreased until the Si layer was not visible. In the leftmost, and in the center image to a lesser extent, Ga$^+$ has etched through the Ag film and into the Si wafer. The etching of Si causes re-deposition of Si onto the nanorod patterns thereby contaminating the sample. The rightmost image does not have any such contamination since the Ag layer is still intact. Therefore precise control of pattern duration is of paramount importance.

Figure 32. The effect of pattern duration on the Ag nanorod arrays. From left to right: The arrays were patterned for progressively less duration. In the leftmost figure the Ga$^+$ ions have patterned through the Ag layer and on to the Si layer. The rightmost figure shows the Ag layer still intact in between the nanorods.

Figure 33 displays the effect of focus and stigmation on the nanorod patterns. In the image on the left the patterns were created without optimum focus resulting in non-rod like shape whereas the nanorod arrays from the image on the right and in previous images were patterned with optimum focus resulting in nanorods with desired shape and sharp features.
Figure 33. The effect of focus and stigmation on the nanorod patterns. The image on the left has patterns created with non-optimal focus and stigmation whereas the image on the right was created with optimum focus and stigmation.

To obtain an estimate for their plasmonic near field enhancement, the photoelectrons emitted by the above patterned Ag nanorod arrays was addressed and imaged with a photoemission electron microscope. In a typical experiment, the nanorod arrays are first illuminated with an unpolarized UV source ($h\nu \sim 5$ eV). The UV light source provides a steady stream of photons and the majority of photoemission occurs via single photon process (since the upper limit for the work function of Ag at 4.7 is still less than the incident photon energy). Hence, similar photoemission yields from both the nanorod arrays and the surrounding Ag film were observed. This situation changes drastically when we switch the UV source with a laser. The localized surface plasmon resonance for Ag nanostructures occur around 400 nm. Upon illumination with a 400 nm, 150 fs laser, the nanorod arrays yielded substantially larger photoemission via the two photon photoemission mechanism. To determine the effect of laser polarization on the plasmonic
near field enhancement, the arrays were illuminated by both s and p polarized laser (see Figure 17 for polarization assignments) and images were compared (see Figure 34).

Figure 34. 2PPE PEEM images of Ag nanorod array (right) and Ag film (left) illuminated with a 400 nm 150 fs laser. The Ag nanorod arrays exhibit substantially enhanced photoemission when compared with the Ag film. The enhancement results from the coupling between the incident laser and the LSPR modes of the Ag nanorod arrays. No such mechanism exists for the Ag film. The images were obtained upon illumination with a p- polarized light of same intensity. (Field of view = 30 µm)

The enhancement factors which we defined earlier as the ratio between photoemission yield from the nanostructure and the film were then obtained by dividing the above two images using IGOR an image processing and data analysis software tool. The above images which correspond to a p polarized light (Figure 34) were then compared to images obtained with an s polarized light (Figure 35). Care was taken to ensure that all other experimental parameters are same between the two measurements. The photoyield images obtained with an s polarized light is shown below.
Figure 35. 2PPE PEEM images of Ag nanorod array (right) and Ag film (left) illuminated with a 400 nm 150 fs laser. Even though the photoemission from the Ag nanorod arrays are still far greater than the film it is overall much lesser than the photoemission yield from the p polarized light.

The reason behind this discrepancy in the photoemission yields from the nanorod arrays is due to the fact that p polarized light is polarized perpendicular to the surface and hence aids photoemission from the nanorod tips and into the detector whereas s polarized wave is polarized parallel to the surface. Enhancement factors of 67 and 6 were obtained for p and s polarized laser respectively. It must be noted here that the variations in photoyield within the nanorod array which is manifest in the images as a variation in brightness is a result of structural variations and defects between different nanorods in an array. This coupled with the fact that 10 – 20 nm resolution can be achieved in the PEEM makes it a powerful tool for studying the structure –property relationships of plasmonic metal nanostructures.
3.4 Ag and Au nanostructures by thermal growth technique

3.4.1 Hollow and solid Au nanostructures

The Si substrates with 2000 nm circular patterns of Au were imaged post-annealing in an SEM. The images are shown in the Figure 36.

Figure 36. SEM images of Au nanoparticles a) circular patterns of Au films, 2000 nm in diameter patterned via e-beam lithography b) the circular films curl up upon annealing yielding both solid and hollow Au nanoparticles c) a high magnification image of Au nanoparticle. The hollow nature is clearly discernible from the contrast difference. d) high magnification image of a solid nanoparticle.
The image clearly displays the formation of multiple solid and hollow nanoparticles per patterned site. Even though the hollow nature of the nanoparticles are clearly discernible from their image contrast, confirmation was obtained by FIB milling a randomly selected nanoparticle with subsequent cross sectional SEM imaging of the milled surface. The cross sectional SEM image tilted at 45° is displayed as Figure 37 below.

Figure 37. SEM image of the hollow Au nanostructure after FIB milling. The inner void and a shell of finite thickness are clearly visible. The sample was tilted to 45° for imaging.

To compare the plasmonic near field enhancement between the solid and hollow gold particles two samples were chosen for analysis: 1) single solid gold particles 2) multiple gold particles containing both smaller solid gold particles and larger hollow particles. The results, upon excitation with an UV light source (mercury arc lamp) and a 400 nm, 150 fs pulsed laser are shown in Figure 38. The mercury arc lamp is predominantly used for
imaging the sample surface and provides a linear photoemission response (single-photon process) from both the flat surface and the particles. However, once we illuminate the sample using the laser, the regions containing both the solid and hollow particles are significantly brighter than the surrounding flat surface.

![Figure 38](image.png)

Figure 38. PEEM images of Au nanoparticles taken with a UV lamp (left) and a 400 nm laser, 150 fs laser (right). The brighter spots correspond to hollow Au nanoparticles indicating they have a higher near field enhancement compared to the Au gold nanoparticles.

This is again due to the fact that the resonant localized surface plasmon (LSP) modes of the gold particles couple with the incoming electric field (due to laser of particular wavelength) leading to an enhancement of the field intensity in the vicinity of the particles. This leads to non-linear (two-photon) photoemission from the particles. However, such a mechanism is not available for the flat surface as it couples very weakly with the incident electric field. Interestingly, the larger gold particles have a greater
plasmonic field enhancement when compared with the smaller particles. This behavior is attributed to the fact that the larger particles are hollow whereas the smaller particles are solid.[94] This greater enhancement observed from the hollow gold particles makes them attractive candidates for sensing applications.

3.4.2 Spherical nanoparticles and nanorings

In the previous subsection we annealed Au films and obtained both solid and hollow Au nanoparticles whereas the Si substrate itself was not affected by the annealing process. However, this was not the case when we annealed thin films of Ag on Si. Figure 39 displays the SEM images obtained following annealing of Ag films of various thickness on Si.

Figure 39. SEM images of the surface of Si following annealing in a tube furnace at 900°C for 5 hours. Clockwise from left: top surface of Si coated with 3, 5, 10, 20, 30, and 50 nm. The images show the formation of two distinct shapes. A brighter spherical nanostructure and a nanoring structure is clearly discernible.
5 nm seems to be the minimum thickness of Ag film on Si required for the nanorings to form as evidenced by the absence of nanorings (see Figure 39 and 40) in the 3 nm sample. This suggests that a minimum concentration of Ag is required for the formation of nanorings. The nanorings size increases with increasing film thickness. We collected SEM images from 3-50 nm Ag films on Si. A higher magnification image of the nanorings is shown in Figure 40.

Figure 40. A higher magnification image showing the structural changes in the nanorings as a function of film thickness. An increase in film thickness leading to an increase in nanorings diameter seems to be the trend.

Interestingly two different nanorings morphologies, with different ratios between inner and outer diameter, are evident in the 10-50 nm samples. This might be attributed to local changes in the thickness of Ag films. The images are displayed in Figure 41.
Figure 41. Two different nanorings morphologies are evident in the 10-50 nm samples. Both these images were obtained from the same 10 nm sample.

Figure 42 below displays the Ag-Si phase diagram over a range of temperatures. The Ag-Si eutectic occurs at 835°C with 89% Ag concentration. Temperatures of at least 1330°C are required for forming Si rich alloy nanostructures suggesting the nanorings and spherical nanoparticles are Ag rich. This is promising for photoemission studies since the presence of an oxide has been shown to reduce the work function of metals like Ag.

Figure 42. Ag-Si phase diagram showing the eutectic point occurs at a temperature of 835°C with an Ag concentration of 89%.
To obtain compositional information from both the nanorings and the spherical nanoparticles we collected EDX spectra at specific spots. The results which are displayed below (See Figure 43) indicate that the spherical nanoparticles are predominantly Ag whereas the nanorings are predominantly SiO$_2$. However, a more careful analysis with a specific technique which can provide the concentration of Ag, Si and O is required to obtain reliable compositional information from the above synthesized nanostructures. One route to obtain the elemental concentration from these nanostructures is to perform a FIB lift-out from specific locations followed by subsequent analysis of the prepared sample using atom probe tomography.

Figure 43. EDX spectra collected from both the spherical nanoparticles and nanorings. The spectra clearly show a higher concentration of Ag in the spherical particles when compared to the nanorings. The inset shows the points from which the spectra were collected.
In all the images shown earlier the nanostructures are randomly distributed over the whole substrate with no control over where they grow. This limitation can be overcome to a certain extent by patterning selected regions on the substrates thereby forcing the nanostructures to grow in those regions. We first selected and exposed a rectangular region on the 10 nm sample to the Ga\(^+\) beam. We subsequently employed FIB lithography on the same sample to pattern circular islands of Ag. The sample was imaged in an SEM after annealing (See Figure 44) Comparison of images captured in the unexposed regions (left) and exposed region (right) clearly shows selective growth of nanorings on the right after exposing the sample to Ga\(^+\) beam. The beam etched away most of the Ag leaving no opportunity for the Ag rich spherical nanoparticles to form.

![Figure 44. SEM images of the 10 nm sample. The image on the left is annealed without exposure to the Ga\(^+\) beam while the image on the right is annealed after exposing a rectangular region to Ga\(^+\). The Ga\(^+\) removed most of the Ag thereby allowing only the nanorings to form.](image_url)
However, re-deposition must have introduced sufficient quantities of Ag for the nanorings to form. The images obtained after annealing the patterned circular Ag islands is shown below (see Figure 45). Again the images show selective growth of Ag rich spherical nanoparticles and Ag poor nanorings. Interestingly, the Ag rich nanoparticles seem to form around a region that consists exclusively of nanorings.

The underlying Si substrate behaves very differently depending on whether we deposit a layer of Ag or Au. The exposed Si/SiO$_2$ surface on the Au nanocages sample which was patterned with e-beam lithography does not change its morphology upon annealing whereas the Si surface associated with Ag film forms nanorings. This could be due to the following: (i) e-beam lithography removes all traces of Au from the Si/SiO$_2$ substrate thereby not allowing the formation of nanorings via Au/SiO$_2$ intermixing. The Ag film on the other hand was patterned using FIB lithography which always re-deposits some Ag back onto the patterned area and this Ag is sufficient for Ag/SiO$_2$ intermixing to form nanorings. However, like we mentioned before a more detailed analysis is required before we can nail down the growth mechanism of the spherical nanoparticles and nanorings.

To explore the plasmonic near field enhancement from the above synthesized nanostructures we collected SERS spectra from the 10 nm film after annealing. The procedure we used for data collection and analysis follows the one we employed for our nanorod arrays. A detailed explanation of that procedure was given in the nanorod arrays via electrodeposition section under results and discussion and hence will not be repeated here. The samples were coated with rhodamine 6G and spectra were collected from
randomly selected spots on the substrates. This was done to obtain the averaged SERS signal from the various regions on the sample. The collected spectra are displayed in Figure 46. An enhancement factor of $3.3 \times 10^5$ was obtained after averaging the spectra from seven different spots on the substrate.

Figure 45. SEM images of the patterned region after annealing. Top and bottom figures have patterns with Ag islands having different diameters. The images on the right are a higher magnification image of the boxed region in the left image.
Figure 46. SERS spectra of $10^{-5}$ M methanol solution of rhodamine 6G evaporated on the surface of the Ag nanorings synthesized from a 10nm layer of Ag on Si. The 614 cm$^{-1}$ molecular mode (highlighted and expanded in right panel) was used to calculate the near field enhancement factors.

Interestingly, the enhancement factors from these nanostructures are higher by a factor of 10 when compared to the SERS spectra obtained from the electrodeposited nanorod arrays. Such a comparison is reasonable since all the experimental parameters along with the data collection and analysis procedures are similar in both the cases. This result indicates that these interesting nanostructures are plasmonically active and will exhibit nonlinear response when irradiated with light of particular wavelengths. However, it must be noted that SERS collects spectra from an ensemble average of nanostructures and hence is unable to reveal the relative contribution from the spherical nanoparticles and the nanorings to the total enhancement. To obtain that information, a more in depth study of the structure-property relationship is warranted by coupling structural and
compositional characterization techniques like TEM and APT with plasmonic near field enhancement imaging instruments like PEEM. Such a study on these promising nanostructures will open up new avenues for research and device applications.
4. CONCLUSIONS

The confluence of the fields of nanotechnology and plasmonics has led to new and interesting phenomena. The industrial need for fast, efficient and miniature devices which constantly push the boundaries on device performance tap into the happy marriage between these diverse fields. Designing devices for real life application that give superior performance when compared with existing ones are enabled by a better understanding of their structure-property relationships. Among all the design constraints, without doubt, the shape, size of the nanostructure and the dielectric medium surrounding it has the maximum influence on the response and thereby the performance of the device. Hence a careful study of the above mentioned parameters is of utmost importance in designing efficient devices.

In this dissertation, we synthesized and studied the optical properties of nanostructures of different shapes and size. In particular, the plasmonic near field enhancement was estimated via SERS and 2P-PEEM. The nanostructures were synthesized using four different techniques. One synthesis technique, the thermal growth method was employed to grow interesting Ag and Au nanostructures on Si. The absence of toxic chemicals during nanostructure synthesis via the thermal growth technique opens up myriad possibilities for applications in the fields of biomedical science, bioengineering, drug delivery among others along with the huge advantage of being environment friendly. The other three synthesis techniques (ion implantation, Electrodeposition and FIB lithography) were chosen with the specific goal of designing novel plasmonic metal,
metal hybrid nanostructures as photocathode materials in next generation light sources. The synthesis techniques for these novel nanostructures were dictated by the requirement of high quantum efficiency, robustness under constant irradiation and coherent unidirectional electron emission. Two designs, (i) partially exposed metal nanostructures in an oxide matrix (ii) metal nanorod arrays, couple with incoming light at particular wavelengths which leads to plasmonic near field enhancement from the nanostructures. This plasmonic response is expected to lead to enhanced photoemission and thereby enhanced quantum efficiency. Moreover, the plasmonic enhancement and the shape of the nanostructure enable coherent unidirectional electron emission.

To realize the first design, we fabricated Ag nanoparticles embedded in an MgO matrix by ion implantation followed by high temperature annealing. Particle sizes ranging from a few nanometers to roughly 50 nm were created by a judicious choice of implantation and annealing parameters. The optical absorption spectra of the samples are dominated by the Ag surface plasmon resonance, with contributions from vacancy centers and vacancy clusters. The strain accommodated coherent spherical morphology of Ag nanoparticles was shown to transform to a semi-coherent faceted morphology upon annealing from 10 to 30 hours at 1000°C. Successful Atom Probe Tomography analysis was performed on the 30 hour annealed sample, and the Ag nanoparticles were shown to be nearly pure Ag. The detailed optical and microstructural characterization carried out in this work enabled us to clearly understand the distribution and microstructure evolution of Ag nanoparticles inside a crystalline MgO matrix. Small Ag particles begin to form
within the as-implanted sample that grows larger and more crystalline when annealed. The MgO matrix also evolves during annealing reducing the number of isolated F and F+ centers and forming larger F\textsubscript{n} vacancy clusters. Our ability to vary ion dose, implantation energy, substrate temperature and anneal time provides a high degree of control over nanoparticle formation with respect to selecting the ultimate particle size, depth, morphology and crystallinity. Subsequent controlled fluoride plasma etching of the final annealed microstructure enabled us to partially expose the pure Ag nanoparticles embedded in MgO matrix. The photoemission from these nanostructures is enhanced by two different mechanisms. The surrounding MgO dielectric matrix serves to lower the work function of Ag thereby enhancing the photoemission. The partially exposed nanostructures will display enhanced photoemission upon illumination at particular wavelengths, and hence, act as localized electron emitters. These characteristics make this structure a promising design for high yield photocathode materials. Moreover, the ability to relate both the size and the shape evolution of the nanostructures with the shape and position of the LSPR peaks provides us a fundamental understanding of the structure-property relationship of these nanostructures. This understanding will equip us with the knowledge to choose the correct experimental parameters to realize the best design possible for our intended application.

We approached the challenge of synthesizing metal nanorod arrays by adopting two different routes. In the first route we created nanorod patterns using FIB lithography. This technique provides excellent control over the shape, size and inter-rod distance, making
them ideally suited for fundamental studies of the structure-property relationships. The experimentally measured plasmonic near field enhancement factors with the PEEM gave a value of 70 for the nanorod array when compared with the bare substrate. However, it takes a long time to pattern and the area coverage is small. In other words, even though lithographic techniques are ideally suited for a fundamental study they are not commercially viable. To overcome this constraint, metal nanorod array geometry was realized by growing vertically aligned Ag, Cu and Au nanorods, with good reproducibility, using template assisted electrodeposition. The length of the nanorods varies from one to tens of µm and was controlled by varying the deposition time. Due to good electrical contact between the template and electrochemical cell via the application of metallic paste to one side of the through-hole template, we were able to use DC electrodeposition to grow nanorods of a uniform size distribution over a large area. The nanorod arrays were polycrystalline, with crystallite sizes averaging at about 30 nm. To test the viability of these structures for photocathode applications the plasmonic response of the electrodeposited nanorod arrays was examined using surface-enhanced Raman spectroscopy. SERS enhancement factors of $\sim 10^4$ were obtained for the 614 cm$^{-1}$ vibrational mode of Rhodamine 6G coated on the Au and Ag substrates. A tenfold higher enhancement factor is feasible by integrating over all the observable bands in the probed region of the spectrum. These result shows beyond doubt that these structures are plasmonically active, and hence, could lead to enhanced quantum yield. Since, all the rods are more or less vertically aligned and have similar lengths and diameters; they
resonate at the same energies, thereby ensuring coherent unidirectional electron emission making them attractive candidates for photocathode materials.

We successfully adopted a technique that is non-chemical, non-lithographic to synthesize Au and Ag nanostructures on Si. The nanostructures are formed via Ag/SiO₂ intermixing at elevated temperatures. For the case of Au on Si both hollow and solid nanostructures were synthesized and their plasmonic near field enhancement was estimated using the PEEM. The hollow nanostructures were found to display a higher near field enhancement when compared with the solid Au nanostructures. For the case of Ag on Si two types of nanostructures, a spherical Ag rich nanoparticles and a Ag poor nanorings were synthesized. Both these structures collectively display an plasmonic field enhancement factor of $10^5$ making them promising candidates for plasmonic applications. Moreover the non-chemical nature of synthesis makes these nanostructures free of toxic chemicals and hence will find applications in the field of biomedicine, drug delivery among other applications.

4.1 Future work

The future looks very promising indeed for research in the interdisciplinary field of plasmonics-nanotechnology. Interesting phenomena has been recorded with increasing frequency, pushing the boundary of our understanding of nanostructure properties and facilitating the design of superior devices. In this dissertation, we have taken the first and important step of synthesizing and characterizing nanostructures via different techniques
dictated by specific end goals. However, a lot of interesting work remains. In the case of ion implanted Ag nanostructures in MgO matrix a thorough understanding of the plasmonic near field enhancement must be obtained by subjecting the samples to PEEM analysis. Even though, we have an understanding of the overall response of an ensemble of nanostructures within a matrix, which is sufficient for our purposes, a more detailed study of the dependence of size and shape of individual nanostructures will be significant for other applications. Such a study can be performed by identifying individual particles in the SEM with the help of a FIB mark and subsequently studying the plasmonic response of the same particles in a PEEM. Finally, the enhanced quantum yield can be measured by irradiating the samples in an UPS chamber at resonant wavelengths.

With regards to electrochemically grown nanorod arrays, in the near future, photoemission from nanorod arrays of various lengths will be investigated. This will allow us to determine the aspect ratio which provides optimum photoemission. The exact growth mechanism of the nanorods is also not completely understood. They are believed to grow via Ostwald ripening, oriented attachment or a mixture of both mechanisms. Comparing the experimental growth rate curves with the theoretical fits governing the mechanisms will shed light on this issue enabling us to grow better quality nanorods. In real world photocathodes, constant irradiation with light causes heating effects and might result in destruction of the sample structure. Thus an investigation of the robustness of the nanorod arrays upon heating will be investigated.
FIB lithography is ideally suited to study the dependence of optical properties of nanostructures on the shape, aspect ratio and inter rod distances. Nanorod patterns of various shapes like square, triangles among others and different aspect ratios and inter-rod distances will be created, and their enhanced photoemission will be compared by characterizing the samples in a PEEM.

For the case of the nanostructures grown by thermal growth technique, experimental parameters that allow for a higher concentration of spherical nanoparticles or nanorings would be investigated. A thorough study of the relative concentrations of Ag and Si in the various nanostructures would be determined. Following this a careful study of the effect of relative concentration changes on the optical properties of the nanostructures will be investigated. Further, the size-shape effect on the plasmonic response of the individual nanostructure will be investigated by employing procedures described earlier for the ion implanted samples thereby opening up the possibility of using these structures for a variety of plasmonic applications.
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