DESIGN AND STUDY OF PLASMONIC
NANOSTRUCTURES FOR APPLICATIONS IN
BIOLOGICAL DETECTION AND PHOTONICS

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TABLE OF CONTENTS

LIST OF FIGURES ....................................................................................................................... VI

LIST OF TABLES ........................................................................................................................ XV

DEDICATION ................................................................................................................................ XVI

ACKNOWLEDGEMENTS ................................................................................................................. XVII

CHAPTER 1 Introduction ............................................................................................................... 19

1.1 Dielectric Function of Metals ............................................................................................... 22

1.2 Plasmons at Metal Nanoparticles ......................................................................................... 25

1.3 Plasmons at Metal-Dielectric Interfaces .............................................................................. 27

1.4 Surface Plasmons in Multi Layers System .......................................................................... 34

1.5 Numerical Simulation Methods ............................................................................................ 38

REFERENCES ................................................................................................................................ 44

CHAPTER 2 Fabrication Methods ............................................................................................... 47

2.1 Nanoantennas by Nanomilling ............................................................................................. 48

2.1.1 Step: 1 ............................................................................................................................... 48

2.1.2 Step: 2 ............................................................................................................................... 48

2.1.3 Step: 3 ............................................................................................................................... 50

2.1.4 Step: 4 ............................................................................................................................... 50

2.2 Electron Beam (e-beam) Nanolithography .......................................................................... 57

REFERENCES ................................................................................................................................ 60
CHAPTER 3 Surface Enhanced Raman Scattering (SERS) for Detecting DNA-Protein Interactions

3.1 Raman Scattering ........................................................................................................ 62
3.2 Surface Enhanced Raman Scattering (SERS) .............................................................. 63
3.3 Electromagnetic Mechanism of SERS ....................................................................... 64
3.4 Chemical Mechanism of SERS .................................................................................. 66
3.5 Protein-DNA Interactions and Detection Methods .................................................... 67
3.6 WT1-Protein ............................................................................................................... 69
3.7 Experimental Section ................................................................................................ 71
  3.7.1 Materials: .............................................................................................................. 71
  3.7.2 Methods and Procedures ...................................................................................... 72
  3.7.3 SERS Measurements and Gel Electrophoresis ..................................................... 74
3.8 Results and Discussion .............................................................................................. 76
3.9 Conclusion and Future Perspectives .......................................................................... 86

REFERENCES .................................................................................................................. 88

CHAPTER 4 Metal-Dielectric-Metal Nanoantennas and Their Cavity Resonance Modes for Single Molecule SERS ........................................................................................................ 91

4.1 Introduction .................................................................................................................. 91
4.2 Nanoantennas Design and Simulation ....................................................................... 92
4.3 Result and Discussion ................................................................................................. 95
4.4 Conclusion ................................................................................................................... 108
LIST OF FIGURES

Figure 1.1. Schematic representation of oscillation of the electron cloud in the metal
nanoparticles upon interaction with electromagnetic wave (taken from the ref [3]) 25
Figure 1.2. Schematic representation of P-polarized light incident at the metal-dielectric
interface (a) and propagation of surface plasmons along the interface (b) ........... 27
Figure 1.3. Schematic plasmon dispersion curve in different frequency regions ........... 32
Figure 1.4. Schematics of metal-dielectric-metal structures: a thin dielectric layer is
sandwiched between two semi-infinite metal layers. ........................................ 34
Figure 1.5. Tangential electric field profiles for the MDM system, (a) symmetric and (b)
anti-symmetric modes (taken from ref. [33]) ................................................. 37
Figure 1.6. Representation of electric and magnetic fields in the unit cells for FDTD
method............................................................................................................. 39
Figure 1.7. Electric voltages e and magnetic fluxes b on the primary grid G and the
dielectric flux d and magnetic grid voltages h on the dual grid \( \tilde{G} \) (taken from ref
[41]) .............................................................................................................. 40
Figure 2.1. Schematics of fabrication of MDM nanoantennas using focused ion beam
(FIB) technique. ................................................................................................. 47
Figure 2.2. Schematics of atomic layer deposition of aluminum oxide (\( \text{Al}_2\text{O}_3 \)) (taken from
ref. [5]) .............................................................................................................. 49
Figure 2.3. Schematics of focused ion beam (FIB) system (taken from ref. [4]) ......... 51
Figure 2.4. SEM images of the Single MDM disk nanoantennas; (a) of diameter 600nm (b) of diameter 450nm (c) of diameter 200nm and (d) damaged. The three distinct layers of the MDM nanoantennas are clearly seen in the SEM images (a-c), where the white part is the silver and the black line in between the white structures is the polymer layer ................................................................. 52

Figure 2.5. SEM images of the MDM nanoantenna arrays; (a-b) horizontal width 300nm; the etching time for Fig. a and b are 5 and 6 min respectively, with the other parameters the same; (c) horizontal width 420nm (d) diameter 380nm. The period for nanoantennas is 600nm. ................................................................. 53

Figure 2.6. Side (a and b) and the top (c and d) view of the cuboid MDM nanoantennas of side widths 100nm (a and c) and 140nm (b and d). ................................................. 54

Figure 2.7. Side (a and b) and the top (c and d) view of the bar shaped MDM nanoantennas of bar widths 84nm (a and c) and 140nm (b and d). ....................... 56

Figure 2.8. Schematics of e-beam lithography to fabricate MDM nanoantennas ........ 58

Figure 2.9. SEM image of the MDM nanoantennas arrays of diameter 110nm and period 200nm with (a) smaller magnification and (b) larger magnification. ................. 59

Figure 3.1 Schematic representation Raman and Raleigh scattering ..................... 62

Figure 3.2. Schematic representation of (a) normal Raman scattering and (b) surface enhanced Raman scattering................................................................. 65
Figure 3.3. Schematic energy level diagram of a molecule adsorbed on a metal surface showing the possible charge transfer between the Fermi level of the metal and the occupied or unoccupied molecular orbits of the adsorbate.  

Figure 3.4. Schematic diagram of the WT1 structure at the DNA, mRNA and protein level (taken from ref. [24]). Lines in the WT1 protein schematic indicate reported regions of WT1 involved in its interactions with selected regulatory molecules. The numbers indicated in the DNA and RNA represent nucleotide sequence and the numbers indicated in the protein are amino-acid residues.  

Figure 3.5. Schematic diagram of hybridization and immobilization of DNA molecules on metal nanoparticles.  

Figure 3.6. Schematic representation of the experimental setup for surface enhanced Raman scattering.  

Figure 3.7. Schematic of Bal 31 exonuclease digestion of DNA with and without WT1 (-KTS) protein binding. (a) Exonuclease digestion of DNA in the absence of binding proteins releases the dye from the Ag nanoparticle. (b) The binding WT1 (-KTS) protein blocks the digestion of the whole DNA sequence and the dye remains on the nanoparticle.  

Figure 3.8. Optical microscopic picture of the nanoparticles immobilized with DNA onto the glass substrate.  

Figure 3.9. SERS and gel electrophoresis analysis of Bal31 exonuclease digestion of TAMRA dye labeled VEGF DNA-nanoparticle complexes. Raman spectrum of the
DNA-nanoparticle complexes (a) before digestion; (b) after digestion without incubation with WT1 (-KTS) protein; and (c) after digestion following incubation with WT1 (-KTS) protein. (d) Gel electrophoresis of the DNA-nanoparticle complexes: (lane 1) after digestion following incubation with the WT1 (-KTS) protein; (lane 2) after incubation with WT1 (-KTS); (lane 3) after digestion following incubation with BSA; (lane 4) after incubation with BSA; and (lane 5) after digestion without incubation with any protein. lane 6 presents the electrophoresis of the 1kbp plus DNA ladder; and the 100 bp smallest fragment of the ladder is larger than the 43 bp uncleaved oligonucleotide as shown in lane 4. 

Figure 3.10. SERS and gel electrophoresis analysis of Bal31 Exonuclease digestion of TAMRA dye labeled VEGF DNA-nanoparticle complexes. (a) Raman spectrum after incubation with WT1 (+KTS) and exonuclease digestion. (b) Gel electrophoresis of the DNA-nanoparticle complexes: (lane 1) after Bal 31 digestion following incubation with the WT1 (+KTS) protein; (lane 2) after incubation with WT1 (+KTS); and (lane 3) before Bal31 digestion. The lane 4 is the 1kbp plus DNA ladder.......

Figure 3.11. SERS and gel electrophoresis analysis of the Bal31 exonuclease digestion of FAM dye labeled VEGF mutant DNA-nanoparticle complexes. (a-c) Raman spectrum of the mutant DNA-nanoparticle complexes (a) before digestion; (b) after digestion following incubation with the WT1 (-KTS) protein; and (c) after digestion without incubation with the WT1 (-KTS) protein. (d) Gel electrophoresis for the
mutant DNA-nanoparticle complexes; (lane 1) after digestion following incubation with the WT1 (-KTS) protein; (lane 2) after digestion without incubation with the WT1 (-KTS) protein and (lane 3) before digestion. Lane 4 is the electrophoresis for the 1kbp plus ladder. .................................................................................................................................................. 84

Figure 4.1. Schematics of nanoantennas with parallel cuboids (a, c), and cylindrical rods (b, d). The pink color represents metal materials (Ag in this paper), and the blue represents dielectric materials (SiO2 in a-b and Al2O3 in c-d)............................ 93

Figure 4.2. Far-field scattering and local field enhancement spectra for the parallel cuboids (a) and cylindrical (b) MDM nanoantennas. The side width or diameter for the nanoantenna is set at 450nm and height is set at 30nm. The thickness of the SiO2 gap layer is set at 10nm for both antennas. For clarity, the spectra above 1.2µm are not shown here. .................................................................................................................................................. 96

Figure 4.3. Snapshots of electrical field distribution in the middle planes of cuboids (a) and cylinder (b) nanoantennas at their four lowest cavity resonant frequencies. The geometrical parameters of these nanoantennas are the same as in Fig 4.2. The numbers denote the cavity mode orders shown in Fig. 4.2; the resonant wavelengths of the first modes, not shown in Fig. 4.2, are at 3.3µm and 2.9µm for the parallel cuboids and cylindrical antennas respectively respectively................................. 97

Figure 4.4. Scattering spectra of (a) parallel cuboids and (b) cylinder nanoantennas of different side widths and diameters. The heights of metals and dielectric parts are kept constant at 30 and 10nm respectively. The numbers labeling the dips in the x
scattering spectra represent the different cavity resonance modes which correspond to the peaks in the local fields.

Figure 4.5. Variation of the cavity resonance wavelength versus the particle side width/diameter for different cavity modes for the parallel cuboids nanoantennas (a) and cylinder nanoantennas (b). The symbols represent simulation results; the solid lines represent theoretical results from Eq. 4.2.

Figure 4.6. Simulated local electric field enhancement and far field scattering spectra for a parallel cuboids (a) and a cylinder (b) nanoantennas. Parameters: (a) Ag 60nm×60nm×60nm; Al₂O₃ 20×20×2.5nm. (b) Ag: 60nm diameter × 80nm height; Al₂O₃ 30nm diameter × 2.5nm height.

Figure 4.7. Snapshots of the local electric fields in the plane through the middle of the dielectric spacer for the parallel cuboids (upper row) and cylinder (lower row) nanoantennas. The red region indicates the local maxima and the blue indicates the local minima. The zero amplitude of the electric field is represented by the green regions.

Figure 4.8. Variation of resonance wavelength as a function of the particle side width or particle diameter for different cavity modes for the parallel cuboids (a) and cylinder (b) nanoantennas. The symbols represent simulation results; the solid lines represent theoretical results from Eq. 4.3.
Figure 4.9. Local field enhancements for the second cavity mode for parallel cuboids (a) and cylinder (b) nanoantennas. Parameters: (a) Ag 60nm×60nm ×60nm and (b) Ag: 60nm diameter × 80nm height. ................................................................. 106

Figure 5.1. (a) Schematic representation of Ag/P3HT/Ag nanoantenna array and (b) fabricated nanoantenna array, for this particular array side width of single nanoantenna is 420nm and the period is 600nm. ................................................................. 112

Figure 5.2. Schematics of experimental setup to measure the optical transmission through nanoantenna array. ................................................................. 114

Figure 5.3. Measured transmission spectra for the 2D arrays of Ag/P3HT/Ag with the side width at 300nm, 340nm, 380nm and 420nm, respectively .................. 116

Figure 5.4. Fitting of measured P3HT dielectric permittivity with second order dispersion relation. The circles and line represent the measured and fitted data respectively. The measured data was taken from the ref. [16]. ................................................................. 117

Figure 5.5. (a) Simulated transmission spectra and (b) local electric field enhancement spectra for the 2D arrays of Ag/P3HT/Ag nanoantennas ..................... 118

Figure 5.6. Local electric field distribution at the middle plane inside the nanocavities corresponding to the dip 1 (a) and dip 2 (b) of the transmission spectra. The electric fields distribution presented here are for the nanoantenna arrays with 380nm side width. .................................................................................................. 119

Figure 5.7. Comparison of dip wavelengths versus nanoantenna side width obtained from the experimental, simulation and analytical resonant condition results. .............. 120
Figure 5.8. Emission spectra of P3HT film ............................................................... 122

Figure 5.9. Simulated transmission spectra of a 2D array of Ag/P3HT/Ag nanoantenna array (a) and the local field enhancement spectra (b). Here the P3HT gap thickness (30nm) is larger than of the nanoantennas as presented in Fig. 5.5. ..................... 123

Figure 6.1. Schematics of the Ag/GaAs composite nanostructure; (a) GaAs nanowire with 1D array of Ag nanoparticles and (b) GaAs sheet with 1D array of nanowires. GaAs and Ag structures are separated by a thin SiO$_2$ layer of same length and width. ... 129

Figure 6.2. Frequency dependence of the GaAs permittivity Red lines are best fits with the Lorentz dispersion model................................................................. 131

Figure 6.3. Nanowire absorption enhancements calculated for different nano-particle periodicities: (a) d=120nm; (b) d=140nm; (c) d=160nm; (b) d=200nm. The particle size L is varied from 60nm 160nm. ................................................................. 133

Figure 6.4. (a) Resonant wavelength of the absorption enhancements as a function of the nanoparticle size at different periodicities. (b) Peak absorption enhancements as a function of the Ag nanoparticle period/wavelength for different particle sizes L=60, 70, 80, and 90nm.................................................. 134

Figure 6.5. Absorption enhancement of infinite GaAs sheet for different nanowire periodicities: (a) d=220nm; (b) d=260nm and (c) d=300nm. The Ag L is varied from 60nm to 280nm. ................................................................. 137
Figure 6.6. Resonant wavelength of the absorption enhancements as a function of the nanowire L at different periodicities; (a) for the first mode and (b) for the second mode................................................................. 138

Figure 6.7 Scaling of resonant wavelength of absorption enhancements; (a) for the first mode and (b) for the second mode................................................................. 139

Figure 6.8. Absorption enhancements as a function of the nanowire L at different periodicities. (a) for the 1st mode and (b) for the 2nd mode................................. 140

Figure 6.9. Local electrical field vectors and phase representation in an incident plane through the middle of the nanowire at the resonant frequency (552THz) of the first mode for L=60nm (a-b); at the resonant frequency (624THz) of the second mode for L=160nm (c-d) and at the de-enhancement resonant frequency (339THz) for L=160nm (e-f). For all three cases a period of 200nm is taken........................................................................................................... 141

Figure 6.10. Local electric field vectors and phase representation in an incident plane through the middle of GaAs sheet at the resonant frequency (475THz) of the first mode for L=60nm (a-b); at the resonant frequency (520THz) of the second mode for L=160nm (c-d). Period is taken as 300nm.............................................................. 143
LIST OF TABLES

Table 3.1. Oligonucleotide sequences designed for studying DNA-WT1 protein interaction ........................................................................................................................................ 76
DEDICATION

I would like to dedicate this dissertation to my parent.
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CHAPTER 1

Introduction

Surface plasmons, light-mediated coherent oscillations of free electrons at metal nanoparticles and metal-dielectric interfaces [1-4], have attracted considerable current interest because of their potential applications in various fields in science and technology [3, 5-9]. Surface plasmons are the electromagnetic modes produced as a result of an interaction of light with oscillating surface electrons of metals. They are localized at metal-dielectric interfaces with the electromagnetic fields exponentially decaying away from the interfaces [4, 10]. By employing metallic nanostructures, it is possible to concentrate and guide light at a length scale much smaller than the wavelength of light in the free space [11, 12]. The concentration of light into a small volume in plasmonic nanostructures leads to large enhancements of local electromagnetic fields, which can boost a number of linear and nonlinear optical phenomena. For example, surface-enhanced Raman spectroscopy (SERS) is a method for enhancing weak Raman signals by placing the molecules in the proximity of metal nanostructures [13, 14]. Using the property of surface plasmons, miniaturized optoelectronic components may bridge the gap of size mismatch between sub-wavelength photonics and electronics [5]. Recent advances in fabrication techniques have made it possible to realize those plasmonic nanostructures with a high accuracy in experiments.
Raman spectroscopy, discovered by C.V. Raman in 1928, has become an important analytical tool [15, 16]. When a sample is irradiated with light, the Raman scattered light from the sample contains specific information about chemical structure of its molecules. The information is in the form of the change in rotational and vibrational energies of chemical bonds. Raman spectroscopy can find wide applications ranging from biology, chemistry, pharmaceutical, food science and semiconductors [15-29]. However, use of the conventional Raman spectroscopy is limited by its extremely low scattering cross section. Because of the extremely low scattering cross section, only a small fraction of the incident photons follow Raman scattering while most of the photons scattered via Raleigh scattering. Meanwhile bio-molecules often also give of a broad fluorescence signal; the fluorescence cross section is ~12-14 orders of magnitude greater than that of the Raman cross section [24]. Thus Raman scattering needs to be enhanced significantly to overcome fluorescence for molecular detection at lower concentrations. Surface enhanced Raman spectroscopy (SERS) is a technique which is able to enhance the weak Raman signal. Initially, it was observed that the enhancement of the order of $10^6$ from the molecules adsorbed on rough metal surfaces [14]. The most commonly used SERS substrates are colloidal metal nanoparticles. People have found that the SERS enhancement up to a factor on the order of $\sim10^{14}$-$10^{16}$ using colloidal metal nanoparticles. The sharp and distinguishable SERS peaks provide complete molecular information and that makes it a better technique for multiplex detection of molecules in comparison to the broad fluorescence [30].
SERS intensity is proportional to the fourth power of the electric field (I~E^4) [14]. Studies have revealed that the maximum electrical field can be obtained at very small gap regions, called hot spots, between metal nanostructures [13, 31]. When the molecules lie at the hot spots, huge local field enhancement generates large enhancement of Raman intensity leading to even single molecule SERS [24, 32].

The previous observations on single molecule SERS were from colloidal metal nanoparticles, where the main issue is that hot spots are only found randomly because the gap between particles cannot be controlled; this lack of control makes the reproducibility of SERS extremely low.

A number of efforts have been made to fabricate horizontal nanostructure dimers with controllable gap size but those structures cannot be fabricated using currently available fabrication techniques with a gap of only a few nanometers. However, it is possible to fabricate metal nanostructures with a vertical dielectric gap of a few nanometers. With such structures the electric field in gaps can be enhanced significantly with potential SERS detection at a single-molecule level.

This dissertation mainly focuses on the study of the optical properties of vertical metal-dielectric-metal (MDM) nanoantennas consisting of a thin dielectric layer sandwiched between two metal nanostructures. In these nanoantennas, the dielectric gap thickness can be controlled precisely down to the monolayer level using atomic layer deposition techniques. By controlling the gap thickness, significant enhancement in the
electric field can be achieved in the gap region. Highly enhanced Raman signal can be expected from the molecules adsorbed in the vicinity of the gap region.

The central goal of the work that will be presented in this dissertation is to design and fabricate vertical nanocavities with controllable gap size of a few nanometers for single molecule SERS studies. The dissertation will be organized in the following way: in this chapter, I will present the theoretical basis of surface plasmons and the details of simulations. Chapter Two discusses the techniques used to fabricate the nanoantennas. Chapter Three deals with the application of the surface enhanced Raman scattering (SERS) using conventional colloidal nanoparticles substrates in studies of interaction between DNAs and proteins. Chapter Four explains the designing of new plasmonic metal-dielectric-metal (MDM) nanoantennas and their potential application in SERS by studying their optical properties using numerical simulations. Chapter Five discusses the fabrication of MDM nanoantennas with active material as a dielectric and their optical properties. Chapter Six explains the increase in light absorption efficiency of a semiconductor by placing plasmon nanostructures in proximity. Tuning the amplitude of absorption enhancement and wavelength of resonant absorption are discussed. Chapter Seven is the summary of the dissertation.

1.1 Dielectric Function of Metals

The dielectric permittivity of metallic materials can be described by the classical free electron model, also known as the Drude model because in metals there are highly dense electrons with a very small separation between the energy levels as compared to
the thermal energy ($K_B T$) at room temperature [2]. According to the Drude model, the metal electrons are considered as a moving sea of electrons i.e. an electron plasma, loosely bound to the immobile positive charges. Overall metallic materials remain charge neutral unless an external field is applied. When a time-varying external field is applied, electrons start to oscillate with respect to the nearly immobile positive charges. While oscillating, the electrons collide instantaneously with immobile positive charges, which dampens the electronic oscillations. Other interactions are considered as negligible compared to the effect of these collisions. The equation of the oscillating electrons in a field along a single axis $x$ can be written in the form:

$$m \ddot{x} + m\gamma \dot{x} = -eE$$  \hspace{1cm} (1.1)

where $m$ is the electron mass, $e$ is the elemental electrical charge, $x$ is the displacement of the electron from its equilibrium position, $E$ stands for the external electric field and $\gamma = 1/\tau$ is the collision frequency of electrons. Here, $\tau$ is called the relaxation time of free electrons. Assuming an applied electrical field $E_0 e^{-i\omega t}$, and that the displacement of the electrons can be written as $x = x_0 e^{-i\omega t}$, Eq. (1.1) can be rewritten as:

$$x = \frac{e}{m\omega(\omega + i\gamma)} E$$  \hspace{1cm} (1.2)

The polarization due to the displacement of electrons is given by $P = -nex$

$$P = -\frac{ne^2}{m\omega(\omega + i\omega \gamma)} E$$  \hspace{1cm} (1.3)
The electric displacement vector is defined as \( D = \varepsilon_0 E + P \), or:

\[
D = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \right) E
\]  

(1.4)

Where \( \omega_p^2 = \frac{ne^2}{\varepsilon_0 m} \) is the bulk plasma frequency of the metal. Then the dielectric function of the metal can be written in the form:

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}
\]  

(1.5)

The real and imaginary parts of equation (1.5) are:

\[
\varepsilon'(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + \gamma^2)} \quad \text{and} \quad \varepsilon''(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)}
\]  

(1.6)

The collision frequency is the inverse of relaxation time (\( \tau \)). At high frequencies near to \( \omega_p \), \( \omega >> 1/\tau \) or \( \omega >> \gamma \), the real part of the dielectric function can be approximated as:

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}
\]  

(1.7)

When \( \omega < \omega_p \) the dielectric function becomes negative and the field exponentially decays into the metal, which behaves as a reflector. For \( \omega > \omega_p \) the dielectric function of the metal is positive and the metal becomes transparent and behave as a dielectric. The plasma frequency (\( \omega_p \)) is the characteristic frequency above which metals behaves as dielectrics. Plasma oscillations are longitudinal in nature therefore light cannot couple
with bulk plasmons above the plasma frequency while below the plasma frequency
coupling with plasmons at the surface becomes possible.

1.2 Plasmons at Metal Nanoparticles

Vivid colors exhibited by Au and Ag colloidal nanoparticles have fascinated
people for a long time. The interaction of light with metals causes the collective
oscillation of conduction electrons. The displacement of electrons produces polarization

![Figure 1.1. Schematic representation of oscillation of the electron cloud in the
metal nanoparticles upon interaction with electromagnetic wave (taken from
the ref [3])](image)

charges on particles. A restoring force is set up due to the coulomb attraction between the
polarization charges necessary for resonant electrons oscillations at a particular
frequency. The resonant oscillations of electrons are called plasmons as shown in Fig.
1.1. When the size of particles is much smaller than the wavelength of the incident light
(2R<<\lambda), a uniform dipolar field is produced on the particles and all the electrons move
in a phase with incident electromagnetic wave of wavelength \( \lambda \). The effect is termed as dipolar plasmon resonance, which is responsible for the enhanced absorption, scattering and electric field in the proximity of the particles.

A quasi-static approximation can be used to calculate the polarizibility of particles much smaller than the light wavelength. The polarizibility of the particles imbedded in a dielectric can be written in the form

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

where \( R \) is the radius of particles and \( \varepsilon_m \) and \( \varepsilon_d \) are the dielectric constants of the metal and the surrounding medium respectively. The scattering and the absorption of small spherical particles can be calculated by using Mie scattering theory. The scattering and the absorption cross sections can be expressed in the forms.

\[
C_{\text{scat}} = \frac{k^4}{6\pi} |\alpha|^2
\]

\[
C_{\text{abs}} = k \text{Im}\{\alpha}\]

The polarizibility depends upon the volume of the particles (Eq. 1.8) therefore from Eq. (1.9) and (1.10) it is clear that the extinction is dominated by absorption or by scattering from the particles for \( 2R << \lambda \) and \( 2R > \lambda \), respectively. Scattering and absorption cross sections are maximized when the denominator term in the Eq. 1.8 is close to zero i.e. \( \varepsilon_m \approx -2\varepsilon_d \). The dielectric function of metals varies with frequency. Therefore dipolar
Plasmon resonance occurs at a particular frequency for a particular metal depending upon the dielectric constant of surrounding medium. The resonance frequency also depends upon the size and the shape of the nanoparticles. These factors determine the color that the metal nanoparticles exhibit. For the larger particles, where retardation effects become important, all the electrons no longer oscillate in phase and higher order modes can be observed which can be calculated by considering the higher order Mie scattering coefficients.

1.3 Plasmons at Metal-Dielectric Interfaces

![Diagram](image)

Figure 1.2. Schematic representation of P-polarized light incident at the metal-dielectric interface (a) and propagation of surface plasmons along the interface (b).

Surface plasmons not only exist in metal nanoparticles but also exist at the interfaces between metals and dielectrics. Unlike the localized plasmons at metal nanoparticles, the plasmons at metal-dielectric interfaces can propagate along the
interface. At metal-dielectric interfaces, surface plasmons, i.e. longitudinal surface waves, can be produced due to the coupling of light with an oscillating plasma of electrons. Surface plasmons decay exponentially away from the interface and remain confined at the interface. The dispersion relationship of surface plasmons can be obtained by solving Maxwell equations with appropriate boundary conditions.

Maxwell’s equations for an isotropic, linear, homogeneous medium without free charge or electric current can be expressed as.

\[ \nabla \cdot E = 0 \]  
\[ (1.11) \]

\[ \nabla \cdot B = 0 \]  
\[ (1.12) \]

\[ \nabla \times E = - \frac{\partial B}{\partial t} \]  
\[ (1.13) \]

\[ \nabla \times H = \frac{\partial D}{\partial t} \]  
\[ (1.14) \]

where \( D = \varepsilon \varepsilon_0 E \) and \( B = \mu \mu_0 H \). For waves to be formed that propagate along the interface there must be a component of the electric field normal to the interface. Hence, surface plasmons are transverse magnetic (TM) or P-polarized [i.e. for the light propagating along x-axis \( E = (E_x, 0, E_z) \)] waves propagating along metal-dielectric interfaces and decay exponentially far from the interfaces. S-polarized (TE) [i.e. for the
light propagating along x-axis \( E = (0, E_y, 0) \) incident electromagnetic wave can’t excite the surface plasmons because it doesn’t contain any electric field component perpendicular to the interface. The electric and the magnetic field components of P-polarized field for mediums 1 and 2, as shown in Fig 1.2, can be expressed as:

\[
E_i = (E_{i1}, 0, E_{i2}) \exp [i(k_{i1}x - k_{i2}z - \omega t)]
\]

(1.15)

\[
H_2 = (0, H_{y2}, 0) \exp [i(k_{y2}x + k_{z2}z - \omega t)]
\]

(1.16)

\[
H_1 = (0, H_{z1}, 0) \exp [i(k_{z1}x - k_{y1}z - \omega t)]
\]

(1.17)

\[
E_2 = (E_{x2}, 0, E_{z2}) \exp [i(k_{x2}x + k_{z2}z - \omega t)]
\]

(1.18)

The boundary conditions for electric and magnetic fields at the interface are

\[
E_{i1} = E_{i2}
\]

(1.19)

\[
H_{y1} = H_{y2}
\]

\[
\varepsilon_1 E_{z1} = \varepsilon_2 E_{z2}
\]

From boundary conditions in Eq. 1.19, one can obtain:

\[
k_{z1} = k_{z2} = k_z
\]

(1.20)

Eq. 1.14 for mediums 1 and 2 yields:
The boundary condition (Eq. 1.19) yields:

$$\frac{\epsilon_1}{k_{z1}} = \frac{\epsilon_2}{k_{z2}}$$  \hspace{1cm} (1.22)$$

This equation indicates that surface plasmons only exist at the interfaces of two mediums with dielectric constants opposite in sign. Thus, only the metal-dielectric interface can support propagating surface plasmon waves.

Taking the curl of Eq. 1.13 and then combining with Eq. 1.14:

$$\nabla^2 E = \mu \epsilon_0 \frac{\partial^2 E}{\partial^2 t}$$  \hspace{1cm} (1.23)$$

Combining Eq.1.23 for medium 1 and 2 with the conditions $\mu_0 \epsilon_0 = \frac{1}{c^2}$ and $\mu = 1$ for non-magnetic medium yields:

$$k_1^2 + k_2^2 = \epsilon_1 \left( \frac{\omega}{c} \right)^2$$

$$k_1^2 + k_2^2 = \epsilon_2 \left( \frac{\omega}{c} \right)^2$$  \hspace{1cm} (1.24)$$
Here \( \omega/c \) is the wave vector of light in free space. For bound surface waves, the electrical field should decay in the \( z \) direction. The wave vectors, \( k_{z1} \) and \( k_{z2} \), should be imaginary and opposite in sign. This means that the wave vector \( k_x \) of bounded surface waves is always greater than that of the light wave vectors \( k_1 = (\varepsilon_2)^{1/2} \omega/c \) in the dielectric material.

Combining Eq. 1.24 and 1.22 yields the dispersion relation for the surface plasmon:

\[
k_i^2 = \left( \frac{\omega}{c} \right)^2 \left( \frac{\varepsilon_i \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)
\]

Or

\[
k_x = \frac{\omega}{c} \left( \frac{\varepsilon_i \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}
\]  \hspace{1cm} (1.25)

The condition for \( k_x \) to be a real quantity is \( |\varepsilon_1| > |\varepsilon_2| \), this is the loss-free condition at which plasmon resonance becomes infinitely sharp. But in real metals, there is always some loss which contributes to an imaginary part in dielectric function. The metal dielectric function is in complex form and thus the plasmon wave vector \( k_x \),

\[
k_x + ik_y = \frac{\omega}{c} \left[ \frac{(\varepsilon_i + i\varepsilon')\varepsilon_2}{(\varepsilon_i + i\varepsilon') + \varepsilon_2} \right]^{1/2}
\]  \hspace{1cm} (1.26)

Generally \( |\varepsilon_i'| < \varepsilon_i' \). Using this condition, the real and imaginary part of the wave vector can be expressed in the forms
The dispersion relation of the surface plasmon is shown in Fig.1.3. In the small wave vector limit, i.e. for \(|\varepsilon_1'||>|\varepsilon_2|, the plasmon wave vector is close to the light line \(\omega/c\sqrt{|\varepsilon_2|}\) but still larger than the light wave vector. Due to this wave vector, i.e. momentum mismatch, light in the free space cannot be coupled directly with the surface plasmons, i.e. plasmons are irradiative. For the large wave vector limit, i.e. for \(\varepsilon'\to -\varepsilon_2, k_x \to \infty\), the

\[
k_x = \frac{\omega}{c} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}
\]

\[
k_x = \frac{\omega}{c} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{3/2} \frac{\varepsilon_1'}{2\varepsilon_2^2}
\]

Figure 1.3. Schematic plasmon dispersion curve in different frequency regions
frequency approaches to a characteristic frequency known as surface plasmon frequency \((\omega_{sp})\).

\[
\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_2}}
\]  

(1.28)

In this range the group velocity \(v_g \rightarrow 0\) and surface plasmons are electrostatic in character. When the frequency is in between the bulk plasma and the surface plasmon frequency i.e. \(\omega_p > \omega > \omega_{sp}\) the wave vector \(k_x\) is purely imaginary and no propagation mode can exist in this range as shown in Fig. 1.3. The two important quantities to characterize the surface plasmons are the propagation length and the penetration depth. Because of the imaginary component of the wave vector \(k_x\), the intensity of propagating surface plasmons along metal-dielectric interface decays as \(I \propto e^{-2k_x z}\) and after travelling a certain distance, propagation length (L), intensity decreases as \(1/e\).

\[
L = \frac{1}{2k_x}
\]  

(1.29)

The wave vector is imaginary in the dielectric and metal at both sides of the interface in the z-direction, thus the field amplitude decays exponentially as \(e^{ik_z z}\) along z and after travelling a certain distance, the penetration depth (\(\delta\)), from the interface the field inside mediums decreases as \(1/e\).

\[
\delta = \frac{1}{|k_z|}
\]  

(1.30)
1.4 Surface Plasmons in Multi Layers System

Now consider the case of plasmons in a multilayer system of metal and dielectric. For simplicity consider a three-layer system consisting of a dielectric layer sandwiched between two metal layers i.e. the metal-dielectric-metal (MDM) system. Such a system consists of surface plasmons confined at both metal-dielectric interfaces. When the thickness of the dielectric is greater than the penetration depth, plasmons at two interfaces propagate independently but for thinner dielectric layers, plasmons at both interfaces interact with each other to form coupled surface plasmon modes[2].

The field can be described in the form

\[ E(r,t) = E(z) \exp[i(kx - i\omega t)] \]  

(1.31)
Using Eq. 1.23

\[
\frac{\partial^2 E(z)}{\partial z^2} + \left[ k^2 - (\omega/c)^2 \right] E = 0
\]  

(1.32)

Considering the Maxwell’s Eq. 1.13 and 1.14 along with \( D = \varepsilon_0 E \) and \( B = \mu_0 H \).

TM waves consist only \( E_x \), \( E_z \) and \( H_y \) components of the electric and magnetic fields and the others are considered as zero.

\[
E_x = \frac{i}{\varepsilon_0 \omega} \frac{\partial H_y}{\partial z}
\]

(1.33)

\[
E_z = -\frac{k}{\varepsilon_0 \omega} H_y
\]

Assuming

\[
H_y = A e^{ik_x x} e^{ik_m z}
\]

(1.34)

For \( z > d \)

\[
H_y = A e^{ik_x x} e^{-km z}
\]

\[
E_x = \frac{iAk_m}{\varepsilon_0 \omega} e^{ik_m z} e^{ik_x x}
\]

(1.35)

\[
E_z = \frac{-Ak}{\varepsilon_0 \omega} e^{ik_m z} e^{ik_x x}
\]

For \( z < -d \)
\[ H_y = Be^{ikx}e^{ikmz} \]
\[ E_x = \frac{-iBk_m}{\varepsilon_m\varepsilon_0\omega} e^{ikx}e^{ikmz} \]
\[ E_z = \frac{-Bk}{\varepsilon_m\varepsilon_0\omega} e^{ikx}e^{ikmz} \]  

(1.36)

For \(-d < z < d\) the surface plasmon modes at two metal-dielectric interfaces couple together and the components of the electric and magnetic field can be written as

\[ H_y = Ce^{ikx}e^{-ik_dz} + De^{ikx}e^{ik_dz} \]
\[ E_x = -\frac{iCk_d}{\varepsilon_d\varepsilon_0\omega} e^{ikx}e^{-ik_dz} + \frac{iDk_d}{\varepsilon_d\varepsilon_0\omega} e^{ikx}e^{ik_dz} \]
\[ E_z = \frac{Ck}{\varepsilon_d\varepsilon_0\omega} e^{ikx}e^{-ik_dz} + \frac{Dk}{\varepsilon_d\varepsilon_0\omega} e^{ikx}e^{ik_dz} \]  

(1.37)

using the continuity conditions for \(H_y\) and \(E_x\) at \(z=d\) and \(z=-d\) and solving the set of four linear equations. For the non-trivial solution the following condition needs to be satisfied [2].

\[ e^{-2kd_d} = \pm \frac{k_d/\varepsilon_d + k_m/\varepsilon_m}{k_d/\varepsilon_d - k_m/\varepsilon_m} \]  

(1.38)

where

\[ k_m = \sqrt{k^2 - (\omega/c)^2} \varepsilon_m \]  

(1.39)

\[ k_d = \sqrt{k^2 - (\omega/c)^2} \varepsilon_d \]

For a very small gap (2d) surface plasmons at two metal-dielectric interfaces couple together and give rise to either low energy symmetric or high energy anti-symmetric
modes. From Eq. 1.38, the dispersion relation for the respective symmetric and anti-symmetric modes can be written in the form

\[
\tanh k_d d = -\frac{k_m \varepsilon_d}{k_d \varepsilon_m}
\]

\[
\tanh k_d d = -\frac{k_m \varepsilon_m}{k_m \varepsilon_d}
\]  

(1.40)

Figure 1.5. Tangential electric field profiles for the MDM system, (a) symmetric and (b) anti-symmetric modes (taken from ref. [33])
The electric field profiles of the symmetric and the anti-symmetric modes in a MDM structure of dielectric thickness d, centered at z=0 and the wave propagation along x-axis is represented in the Fig. 1.5[33].

1.5 Numerical Simulation Methods

For metallic nanostructures more complicated than a planar metal-dielectric interface, the local field distributions and other optical properties such as transmission and scattering spectra become complicated, and cannot be obtained analytically, and numerical simulation methods become indispensible. In general, there are three types of numerical methods to solve the Maxwell equations: (1) finite element method (FEM), (2) finite difference time domain (FDTD) method, and (3) finite integration technique (FIT).

The finite element method (FEM) was developed in 1960s. Initially, it was used in problems such as stress analysis, fluid flow and heat transfer. FEM is used for obtaining approximate solutions of partial differential and integral equations [34-36]. In this method, the simulation region is divided into a number of small units called elements. These elements are connected to each other at specific points called the nodes. Within the elements, the unknown field variables are expressed in terms of the approximate functions, mostly polynomials. To express an approximate solution of the entire system, the equations expressing the elements are gathered. Then the system of equations is solved by employing the boundary conditions to obtain the unknown values at the nodes.
FDTD is a commonly used simulation technique to solve the electromagnetic problems. It is based on the finite difference algorithm and can simulate a wide frequency range in a single run. It solves the time dependent Maxwell’s equations by discretizing them in time and space [35, 37]. In FDTD simulations, the calculation volume is divided by orthogonal grids into a number of cubical unit cells where the electric and magnetic fields are located at the corners and the centers of the faces of the unit cells as shown in Fig. 1.6. The Yee algorithm is used to calculate electric and magnetic fields at a particular position and the fields are calculated at the half time step intervals of one another. For example, in the Maxell’s equation $\nabla \times E = -\mu \frac{\partial H}{\partial t}$, the x-component of the magnetic field at

![Figure 1.6. Representation of electric and magnetic fields in the unit cells for FDTD method](image)
any time \((n+1/2)\Delta t\) can be written as

\[
H_{z}^{n+1/2}(i, j + 1/2, k + 1/2) = H_{z}^{n+1/2}(i, j + 1/2, k + 1/2) + \frac{\Delta t}{\mu} \left[ \frac{E_{z}^{n}(i, j + 1/2, k + 1) - E_{z}^{n}(i, j + 1/2, k)}{\Delta z} - \frac{E_{z}^{n}(i, j + 1/2, k + 1/2) - E_{z}^{n}(i, j, k + 1/2)}{\Delta y} \right]
\]  

(1.41)

where \(\Delta t\) is the time step and \(\Delta x, \Delta y\) and \(\Delta z\) are the side lengths (or space step) of a unit cell in x, y and z directions respectively. The field calculated in one step is used to calculate the field in the next step and the process is repeated for the entire simulation volume. FDTD uses different boundary conditions such as perfect electric conductor (PEC), perfectly matched layer (PML), absorbing and periodic boundary conditions [35].

The Finite integration technique (FIT) is considered as the generalization of FDTD and also used to solve the Maxwell’s equations, but it uses the integral form of Maxwell’s equations rather than the differential ones as used in the FDTD method. For
the numerical simulations presented in this dissertation, we used commercial software CST microwave studio to simulate the nanostructures, which employs the finite integration techniques (FIT) [38-43].

The integral form of the Maxwell equations are

\[
\int \vec{E} \cdot d\vec{s} = -\left[ \frac{\partial \vec{B}}{\partial t} \right] \cdot d\vec{A}, \quad \int \vec{H} \cdot d\vec{s} = -\left[ \frac{\partial \vec{D}}{\partial t} + \vec{J} \right] \cdot d\vec{A} \\
\int \vec{D} \cdot d\vec{A} = \int \rho dV, \quad \int \vec{B} \cdot d\vec{A} = 0
\]  \hspace{1cm} (1.42)

In order to solve the Maxwell equations, the calculation domain is divided into a number of orthogonal dual grids: the primary grid G and the secondary grid \( \tilde{G} \). As indicated in Fig. 1.7 electric and magnetic voltages are allocated at the edges of the primary and secondary grids respectively. For example: the discretized form of the Maxwell first equation in Eq. 1.42 for the face \( A_n \), bounded by the edges \( i, j, k \) and \( l \) (Fig. 1.7) can be written in the form

\[
e_i + e_j - e_k - e_l = -\frac{\partial b_n}{\partial t}
\]  \hspace{1cm} (1.43)

The discretized equation for all the cell surfaces of the grid G can be written as

\[
Ce = -\frac{d}{dt} b
\]  \hspace{1cm} (1.44)

Similarly other Maxwell’s equations in the discrete form can be written as

\[
\tilde{C}h = \frac{\partial}{\partial t} d + j, \quad \tilde{S}d = q \quad \text{and} \quad Sb = 0
\]  \hspace{1cm} (1.45)

The material equations in the discretized form can be expressed as
\[
\begin{align*}
\overline{D} &= \varepsilon \overline{E} \quad \rightarrow \quad d = M_\varepsilon e \\
\overline{B} &= \mu \overline{H} \quad \rightarrow \quad b = M_\mu H \\
\overline{J} &= \sigma \overline{E} + \overline{J}_s \quad \rightarrow \quad j = M_\sigma e + j_s
\end{align*}
\]

In the above discretized equations \(e\) and \(h\) denote the electric and magnetic voltages in the primary and the secondary grid points respectively, \(d, b\) and \(j\) are fluxes over primary grid or secondary grid faces and \(C, \tilde{C}, S\) and \(\hat{S}\) are matrices equivalent to the curl and the divergence operators of primary and secondary grids, respectively. These matrix equations are used to solve the electromagnetic field problems using the discrete grid space in the time domain. Employing the leap-frog scheme to calculate \(e\) and \(h\) values, separated by a half time step, the Maxwell’s grid equations can be written in the form.

\[
e^{n+1/2} = e^{n-1/2} + \Delta t M_\varepsilon^{-1} \left[ \tilde{C} M_\mu^{-1} b^n + j_s^n \right] \]

\[
b^{n+1} = b^n - \Delta t C e^{n+1/2}
\]

As in FDTD method, for the numerical stability the time step between two equidistance grids should be

\[
\Delta t \leq \frac{\sqrt{\varepsilon \mu}}{\sqrt{(1/\Delta x)^2 + (1/\Delta y)^2 + (1/\Delta z)^2}}
\]

FIT not only uses the orthogonal mesh grids but also uses mesh grids of many other shapes, for example tetrahedral grids. In order to account every detail of the structures perfect boundary approximation (PBA) is used to generate meshing. Using PBA, local mesh refinement can be made with respect to one co-ordinate directions; this allows simulating complex structures with curved surfaces [41]. FIT works very well for the
structures just larger than one mesh cell [41], also highly structured mesh cell makes the calculation faster [41].
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CHAPTER 2

Fabrication Methods

Cleanroom techniques have been used to fabricate the plasmonic nanoantennas that we designed.

Figure 2.1. Schematics of fabrication of MDM nanoantennas using focused ion beam (FIB) technique.
2.1 Nanoantennas by Nanomilling

One of the methods we used to fabricate the metal-dielectric-metal (MDM) nanoantennas was focused ion beam (FIB) nanomilling [1-3]. Schematic for the FIB method of nanoantenna fabrication is shown in Fig. 2.1. It consisted of the following steps.

2.1.1 Step: 1

In the first step, a thin metal, e.g. silver (Ag) (in our experiments), film of desired thickness was deposited onto a cleaned glass substrate using a physical vapor deposition (PVD) technique, e-beam evaporation [6]. This process is carried out under vacuum. High energy electrons are emitted by a tungsten filament and strike at a metal target. The electron strikes produce heat and evaporate the metal, which then can deposit on the substrate.

2.1.2 Step: 2

The second step, dielectric film was deposited on the top of the metal film. If we want to deposit a very thin film, atomic layer deposition (ALD) can be used; this technique can deposit material films of thickness down to the monolayer [7, 8]. In ALD, films are deposited through the surface reactions of chemical vapors, i.e. reactants, on the substrates. ALD is a sequential and self-terminating process. Generally two reactants are required for film growth; therefore two surface reactions happen in each cycle.
For example ALD of Aluminum oxide (Al$_2$O$_3$) is shown in Fig. 2.2. As represented in the figure, one cycle completes in four steps: (1) vapor of the first reactant flows into the reaction chamber and reacts with the substrate’s surface (2) reaction byproducts and unreacted gases are pumped out from the chamber (3) vapor of second reactant flows into the chamber and react with the surface (4) reaction byproducts and unreacted gases are pumped out from the chamber. A certain amount of the material is deposited in the form of a layer during the first cycle; the reaction cycle repeats to deposit

![Diagram](image1.png)

**Figure 2.2. Schematics of atomic layer deposition of aluminum oxide (Al$_2$O$_3$)**

(taken from ref. [5])
more material. Thus in ALD thickness of the film can be controlled precisely by the number of reaction cycles.

In our FIB fabrications presented in this dissertation, we did not use ALD for the dielectric deposition. We used comparably thicker polymer films deposited by spin coating of the polymer solution on the top of the metal films because ALD is not available for the deposition of polymer films. The film thickness was controlled by the concentration of polymer in the solution.

2.1.3 Step: 3

In the third step, a metal film was deposited on the top of the dielectric film, again using the PVD technique.

At the end of this step we have flat MDM films deposited on the whole area of the substrate. We need to construct the MDM nanoantennas of desired shape out of the large films.

2.1.4 Step: 4

In the final step, we used the focused ion beam (FIB) technique to carve out those MDM nanoantennas from the large MDM substrate. FIB system works similarly to scanning electron microscopy (SEM), but it uses a beam of focused ions rather than a beam of electrons (schematic diagram Fig 2.3). The ion beam is produced from a liquid metal ion source (LMIS) of gallium ions (Ga⁺) [1, 9]. The FIB system consists of a Ga reservoir in contact with a sharp tungsten tip of radius 5-10nm. Ga flows to the tip and
the application of very high electric field causes ionization of Ga. The emitted Ga\textsuperscript{+} ions are accelerated and focused on the sample by electrostatic lenses. The cross-section of the ion beam follows a Gaussian distribution. The accelerating voltage is generally in the range of 5-50 Kev and the beam current ranges from pico-ampere (pA) to nano-ampere (nA), corresponding to different beam diameters. The schematic representation of an FIB system is shown in Fig. 2.3. Our MDM nanoantennas were fabricated using the FEI Nova Nanolab FIB Workstation at the University of Michigan.

When a focused beam of the Ga\textsuperscript{+} at high energy hits the sample, the material

![Figure 2.3. Schematics of focused ion beam (FIB) system (taken from ref. [4])](image-url)
sputters, leaving the surface either as secondary ions, electrons or neutral atoms. Thus etching can be performed on the surface. The schematic representation of focused ion beam etching is shown in Fig. 2.1

![SEM images of the Single MDM disk nanoantennas](image)

Figure 2.4. SEM images of the Single MDM disk nanoantennas; (a) of diameter 600nm (b) of diameter 450nm (c) of diameter 200nm and (d) damaged. The three distinct layers of the MDM nanoantennas are clearly seen in the SEM images (a-c), where the white part is the silver and the black line in between the white structures is the polymer layer.
We fabricated single MDM nanonantennas and arrays, of different sizes and the shapes. The nanoantennas fabricated using FIB and studied in this dissertation were made up of two silver (Ag) nanostructures stacked vertically and separated by a thin light emitting polymer, P3HT (3-poly hexylthiophene), film. Some of the single circular disc MDM nanoantennas fabricated using the FIB method are shown in Fig. 2.4. For these

![Figure 2.5. SEM images of the MDM nanoantenna arrays; (a-b) horizontal width 300nm; the etching time for Fig. a and b are 5 and 6 min respectively, with the other parameters the same; (c) horizontal width 420nm (d) diameter 380nm. The period for nanoantennas is 600nm.](image)
nanoantennas the bottom Ag layer, P3HT gap and top Ag layer are 45, 20 and 40 nm in thickness respectively. The three distinct layers of the MDM nanoantennas are clearly seen in the SEM images (Fig. 2.4a-c), where the white part is the silver and the black line

![SEM images of cuboid MDM nanoantennas](image)

**Figure 2.6.** Side (a and b) and the top (c and d) view of the cuboid MDM nanoantennas of side widths 100nm (a and c) and 140nm (b and d).

in between the white structures is a polymer layer.
Fabrication of single MDM nanoantennas using FIB is very challenging; it becomes more difficult as the size gets smaller and smaller. To fabricate nanostructures with the optimum size and shape, the proper beam current and etching time should be chosen. High beam current and longer etching time result in over etching and damage the fabrication area. Too small beam currents may not be able to remove the desired material to obtain the structures, and also take very long times to complete the fabrication. Sometimes we made 3-4 attempts to obtain MDM nanoantennas with minimum damage. The possibility of the damage increases as the size decreases. An example of a small damaged MDM nanoantenna is shown in Fig. 2.4d.

Our optical measurements showed that the signals from single MDM nanoantennas were very weak and we could not able to observe any systematic variation in the plasmonic cavity resonance with variation in the size and the gap.

To minimize the damage during the fabrication and obtaining a strong optical signal, we fabricated arrays of MDM nanoantennas of different sizes and shapes. Some examples are shown in Fig.2.5. The Ag thickness in all MDM nanoantennas and PHT thickness in the nanoantennas (Fig 2.5a-c) are the same as that of the single MDM nanoantennas as shown in Fig. 2.4 but the gap thickness of the circular MDM nanoantenna array is ~10nm. These nanoantennas have a constant period of 600nm.

To show the effect of etching time in nanoantennas fabrication, we present SEM images (Fig. 2.5a&b) of cuboid nanoantennas of the same dimensions and the same fabrication parameters (beam current: 5pA, beam energy: 30kv) other than etching time.
It is clear from the figure that etching was not completed in Fig. 2.5a for which etching time (5min) was 1min less than that of the nanoantennas as shown in Fig 2.5b.

From nanoantennas arrays, we got strong optical signals showing the variation of cavity resonances with size. But our aim of putting light emitting polymer inside the cavity was to obtain enhancement in the emission of the polymer by matching cavity and

Figure 2.7. Side (a and b) and the top (c and d) view of the bar shaped MDM nanoantennas of bar widths 84nm (a and c) and 140nm (b and d).
emission wavelengths for lasing applications. The cavity resonances observed (~460-530nm) from these nanoantennas (side width ~300-420nm) are far from the emission wavelength (~700nm) of P3HT (detail in chapter 5). To match these wavelengths together we designed the nanoantennas of different shapes with smaller width (~100nm) and larger gap thickness (~35nm) than those of the nanoantennas in Fig. 2.5. To minimize the damage during fabrication, we used a very small period of 200nm. By decreasing the period, milling can be done with lower current i.e. smaller beam diameter in a short time with minimum damage.

SEM images of the fabricated cuboid and bar shaped nanoantennas are shown in Fig. 2.6 and 2.7. While fabricating cuboids nanoantennas, most of the time we ended up with totally damaged patterns. Some of best the patterns we were able to fabricate are presented in Fig. 2.6 but still their profiles are not look like the cuboids as seen in the side views (Fig. 2.6a-b). Finally we decided to fabricate bar shaped MDM nanoantennas. We were able to fabricate the nanoantenna array with bars width as small as of ~77 nm with minimum damage.

2.2 Electron Beam (e-beam) Nanolithography

MDM nanoantennas can also be fabricated using e-beam lithography [10, 11]. The flow of the fabrication process for MDM nanoantennas is shown in Fig. 2.8. To fabricate nanoantennas; first polymer, polymethylmethacrylate (PMMA), was spin-coated on the substrate and baked at 170°C for about 30 minutes. Then the PMMA layer was exposed to the electron beam which was controlled by a pattern generator. The patterns consisted
of arrays of dots that define the positions at which metal structures will be formed later in the process. Then exposed PMMA was dipped into the developer to remove PMMA material from exposed area. Then bottom, middle and the top metal-dielectric and metal
layers were deposited on PMMA by e-beam evaporation, sputtering [6]. Finally PMMA was removed by dipping the patterned substrate into acetone leaving behind the MDM nanoantennas. The SEM image of the circular MDM disk nanoantennas array is shown in Fig. 2.9. For these nanoantennas 7nm thick SiO$_2$ gap material was used between two 30nm thick Ag disks.

**Figure 2.9.** SEM image of the MDM nanoantennas arrays of diameter 110nm and period 200nm with (a) smaller magnification and (b) larger magnification.
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CHAPTER 3

Surface Enhanced Raman Scattering (SERS) for Detecting DNA-Protein Interactions

Raman scattering has a number of advantages, including: it is label free; sharp and distinct Raman peaks provide fingerprints of molecules; multiple molecules can be detected at the same time without separating them from a mixture. However, conventional Raman scattering suffers from an extremely weak scattering intensity. Therefore it needs to be enhanced significantly for practical applications.

Raman intensity can be enhanced by placing molecules in the proximity of metal nanostructures. This process is called surface enhanced Raman scattering (SERS). Colloidal metal nanoparticles are the most commonly used SERS substrates. In this chapter we will consider an application of such substrates, while in later chapters we will consider well-controlled nanostructures as discussed in the preceding two chapters. In particular, we will discuss an application of SERS in detecting protein-DNA interactions by functionalizing DNA molecules on the colloidal metal nanoparticles, including future prospective for experiments. For clarity, we will begin by discussing the basics of conventional and surface enhanced Raman scattering.
3.1 Raman Scattering

When light interacts with molecules, the molecules become polarized and an induced dipole moment is created. The polarizibility of molecules is responsible for scattering the incident light. Most of the incident light is scattered with the same energy, i.e. same frequency as that of the incident light: this is called elastic or Raleigh scattering. Only a small fraction of the incident light loses or gains energy i.e. scatters with lower or higher frequency than that of the incident light: such processes are called inelastic or Raman scattering.

Figure 3.1 Schematic representation Raman and Raleigh scattering

Raman scattering. If the light scatters with a lower frequency, it corresponds to a Stokes band and if it scatters with a higher frequency, it corresponds to an anti-Stokes band of the Raman scattering. This change in the frequency of scattered light corresponds to the change in polarizibility of the molecules due to the vibration of atoms about their equilibrium position; it provides fingerprints of the molecules. Raman scattering is a non resonance process and can occur for any frequency of incident light.
Schematic for the Raman scattering is represented in Fig. 3.1. When a photon of frequency ‘\(v_0\)’ hits the electrons at lower energy states, the electrons are forced to jump to the higher energy states and then return to the lower energy states by emitting the photons of same (\(v_0\)) or lower (\(v_0-v\)) or higher (\(v_0+v\)) frequency. The emitted photons correspond to Raleigh, Stokes Raman and anti-Stokes Raman scattering respectively. Raman scattering is an extremely weak process because only 1 in \(10^7\) of the incident photons is scattered with different frequency than that of the incident photons, therefore it needs to be enhanced several orders of magnitude for practical applications. How the weak Raman scattering from the molecules can be enhanced by placing them in the proximity of metal nanoparticles will be discussed in the following section.

3.2 Surface Enhanced Raman Scattering (SERS)

In 1974 Fleischmann et al observed an unusual \(\sim 10^6\) fold enhancement in the Raman intensity from the molecules adsorbed on rough silver surfaces [1, 2]. At that time, such an enhancement in the Raman intensity was thought to be a result of the increase in the surface area due to the roughness, and hence the number of molecules adsorbed. Theoretical investigations revealed that enhancement in the intensity was much higher than the contribution from the adsorbed molecules [3]. Later such an extraordinary enhancement in the Raman intensity was attributed to the excitation of surface plasmons at the metal surfaces, called an electromagnetic effect, and the charge transfer between the metal and the adsorbed molecules, called a chemical effect. The discovery of surface enhanced Raman scattering was a turning point in the history of Raman scattering. Since
that discovery, it has been the subject of tremendous research and is increasingly used in different aspects of chemistry, biology and biomedical applications. In 1997 Kniepp and Nie et al. studied SERS from single molecules adsorbed at junctions (hot spots) between metal particles [4, 5]. The enhancement in the Raman intensity was found to be as high as $10^{15}$ from the molecules at the hot spots.

3.3 Electromagnetic Mechanism of SERS

It is well understood that the excitation of surface plasmons at metal nanostructures results in an enhancement of the local electric field. As a result of the interaction of molecules with the enhanced local field of metal nanostructures, the Raman scattered light from the molecules will also be enhanced. The Raman scattered light from the molecules further interacts with proximate nanoparticles. Thus significant enhancement in the intensity takes place.

The electromagnetic enhancement mechanism of SERS is represented in Fig. 3.2. Fig 3.2a represents the normal Raman scattering from molecules, where $N$ is the number of molecules, $I(v_L)$ the laser intensity, $\sigma$ the cross section and $I_{NRS}$ the intensity of normal Raman scattering. When molecules are adsorbed on the metal nanoparticles, the scattering becomes more complex as represented in Fig 3.2b. The Raman scattering intensity is given by [6]

$$I_{SERS}(v_x) = N' I(v_L) |A(v_L)|^2 \cdot |A(v_S)|^2 \sigma_{ads}$$  \hfill (3.1)
where $N'$ is the number of molecules involved in the Raman scattering, $\sigma_{\text{abs}}$ the increase in cross section of the adsorbed molecules, $I(\nu_L)$ the laser intensity, $A(\nu_L)$ the laser field $A(\nu_s)$ the scattering field enhancement factor respectively. The enhancement factor is the ratio of induced or scattered field to the incident field.

**Figure 3.2.** Schematic representation of (a) normal Raman scattering and (b) surface enhanced Raman scattering
example, the enhancement factor for the molecules at a distance d from the metal nanoparticle of radius ‘r’ is in the form of

\[ A(V_L) = \frac{E_M(V_L)}{E_0(V_L)} = \frac{\varepsilon(V_L) - \varepsilon_m}{\varepsilon(V_L) + 2\varepsilon_m} \left( \frac{r}{r + d} \right)^3 \]  \hspace{1cm} (3.2)

The enhancement is at a maximum when the term in the denominator is close to zero i.e.,

\[ \varepsilon(V_L) \approx -2\varepsilon_m \]

The SERS intensity is in the form of

\[ G_{SERS} = |A(V_L)|^2 \cdot |A(V_S)|^2 \]  \hspace{1cm} (3.3)

Inserting the expressions for A(V_L) and A(V_S),

\[ G_{SERS} = \left| \frac{\varepsilon(V_L) - \varepsilon_m}{\varepsilon(V_L) + 2\varepsilon_m} \right|^2 \cdot \left| \frac{\varepsilon(V_S) - \varepsilon_m}{\varepsilon(V_S) + 2\varepsilon_m} \right|^2 \left( \frac{r}{r + d} \right)^{12} \]  \hspace{1cm} (3.4)

The enhancement contribution from the electromagnetic effect was found to be up to the order of \(10^6\)-\(10^7\).

### 3.4 Chemical Mechanism of SERS

In some cases the electromagnetic mechanism alone was unable to explain the Raman scattering enhancement factor. It has been found that for two molecules with identical molecular polarizibilities, there is a large difference between their surface enhanced Raman scattering intensities while their normal Raman scattering intensities are similar. For example, CO and N\(_2\) have similar normal Raman intensities, yet when they
Figure 3.3. Schematic energy level diagram of a molecule adsorbed on a metal surface showing the possible charge transfer between the Fermi level of the metal and the occupied or unoccupied molecular orbits of the adsorbate.

are adsorbed on the metal nanoparticles, under the same experimental conditions, it was found that the Raman intensity of CO is about 2 orders of magnitude larger than that of \( \text{N}_2 \) [7]. Such an effect is termed as chemical effect. It is believed that this effect is due to the charge transfer either from the Fermi level of the metal to the lowest unoccupied molecular orbital (LUMO) of the adsorbed molecule or from the highest occupied molecular orbital (HOMO) of the adsorbed molecule to the Fermi level of the metal as depicted in Fig 3.3.

3.5 Protein-DNA Interactions and Detection Methods

During transcription, information from genes is copied out into mRNAs to encode proteins with the help of RNA polymerase. This process is essential for the formation,
growth and normal function of organs. The process of transcription is regulated by specific DNA binding proteins known as transcription factors. The transcription factors recognize and bind to the specific DNA sequences of the gene, DNA binding domains, and activate or repress the transcription as necessary.

Alteration of gene regulation may result in over or underproduction of proteins, leading to a number of defects, developmental disorders and cancers, such as those caused by abnormal gene expressions [8-11]. Understanding regulation of gene expression is critical for disease diagnosis and drug development [12,13], gene therapy [14], DNA repair [15] and therefore, identification of functional DNA binding sites for specific transcription factors is essential.

The commonly used technique for detecting protein-DNA binding is the electrophoretic mobility shift assay (EMSA) [16]. EMSA determines protein binding based on the mobility difference of free and protein-bound DNAs in electrophoresis. EMSA is laborious, time consuming and uses hazardous radioactive isotopes. To locate the specific protein-binding region of a relatively large DNA fragment, DNA footprinting technique is most frequently used [16]. The DNA footprinting is technically more difficult to perform than EMSA. To circumvent the technical disadvantages of EMSA and footprinting, additional techniques are being developed. For example, based on the fluorescence resonance energy transfer (FRET), the binding activities of proteins can be assessed by measuring the level of energy transfer between two fluorophores in the absence and presence of protein binding during exonuclease digestion [17, 18].
Here, we demonstrate a study of DNA-protein binding by using surface-enhanced Raman scattering (SERS) with a simple assay. We choose the sequence specific protein, Wilm’s tumor (WT1), and a DNA sequence derived from the promoter of the human vascular endothelial growth factor (VEGF) gene which contains a known WT1 (-KTS) binding site. The SERS DNA-Protein binding assay starts with immobilization of dye-modified duplex DNA on Ag nanoparticles, and proceeds with exonuclease digestion of these immobilized DNA molecules in the presence or absence of binding proteins. The presence of binding proteins protects DNA from complete exonuclease digestion and retains the Raman signal. Binding of protein to the DNA was assessed by alterations of the Raman spectrum of the dye in the presence and absence of protein protection.

3.6 WT1- Protein

Transcription factors are classified according to their DNA binding motifs such as helix-turn-helix, beta sheet, leucine zipper, zinc finger etc [19]. WT1 protein, a transcription factor, belongs to a zinc finger family, encoded by WT1 gene. WT1 is expressed during embryonic development to form urogenetial organs, heart and central nerve system [20-23]. Mutation in the WT1 gene causes a kidney tumor in early childhood which affects 1 in 10,000 children [20]. It has been found that the mutation in WT1 has significant role in leukemia, Denys-Drash syndrome and heart diseases [22, 24-26]. The expression of WT1 is necessary for normal function of the kidneys and heart in adults [20, 27]. The WT1 gene is located at the p53 site of the chromosome, consists of
10 exons and encodes 3kb mRNA [24]. Schematic representation of WT1 DNA, mRNA and protein is shown in Fig. 3.4. In mammals an alternating splicing of mRNA occurs at

Figure 3.4. Schematic diagram of the WT1 structure at the DNA, mRNA and protein level (taken from ref. [24]). Lines in the WT1 protein schematic indicate reported regions of WT1 involved in its interactions with selected regulatory molecules. The numbers indicated in the DNA and RNA represent nucleotide sequence and the numbers indicated in the protein are amino-acid residues.
the exon sites 5 and 9, producing four different isoforms of WT1 protein. Seventeen amino acids are inserted or removed between the praline/glutamine rich N-terminal region and the zinc finger region and three amino acids lysine, threonine and serine (KTS) are inserted between zinc fingers 3 and 4 due to the alternative splicing at exon 5 and 9 respectively [24]. The isoforms containing KTS are referred as WT1 (+KTS), while those lacking these are called WT1 (-KTS). The N-terminal domain of WT1 acts as transcription activator or repressor and the Zinc finger region, called the transcription regulatory domain, binds to the specific DNA sequence and regulates the transcription.

Studies have shown that the isoform WT1 (-KTS) has higher affinity to bind with DNA than that of the WT1 (+KTS) therefore the isoform with KTS is supposed to be poor transcription regulator.

3.7 Experimental Section

3.7.1 Materials:

Filtered and deionized water (18.3MΩ-cm: Barnstead International) was used throughout the experiments. HPLC purified single strand oligonucleotides modified with either thiol group or fluorescent dyes (TAMRA or FAM) were obtained from Integrated DNA technology (IDT, IA). Purified full-length WT1 proteins in both the -KTS and the +KTS isoforms were purchased from Protein One, MD. Additional materials used in the experiments include 80 nm colloidal silver nanoparticles (Ted Pella, CA), Bal31
exonuclease (New England Biolab, MA), G25 spin columns (GE Healthcare, UK), glass slides (Corning, NY), and (3-aminopropyl) triethoxysilane (Fluka, MO).

3.7.2 Methods and Procedures

One strand of the oligonucleotides was modified with a thiol group in the 5’ end (Forward), while the complementary strand of the oligonucleotides (Reverse) was

![Diagram of hybridization and immobilization of DNA molecules on metal nanoparticles](image)

Figure 3.5. Schematic diagram of hybridization and immobilization of DNA molecules on metal nanoparticles

attached with a dye molecule in the 3’ end (Table 3.1). When these oligos are immobilized on metal nanoparticles, these end group modifications allow the dye molecules to be in close proximity to the metal nanoparticle surfaces, facilitating strong
surface enhanced Raman scattering. A single Adenine was added to the thiolated DNA strand to accommodate the size of the dye molecules.

To prepare the DNA-nanoparticle complexes, the thiol modified oligonucleotides (Forward) were dispersed in a TE buffer (0.1M Tris, 0.01M EDTA) that contains 0.01M DTT, and the dye modified oligonucleotides (Reverse) were dispersed in the TE buffer. Then solutions of these complementary oligonucleotides were mixed with 1:1 molar ratio. In order to promote the hybridization, 0.1M KCl was added into the mixture to reduce the Debye screening length or the electrostatic repulsion between DNA molecules. For hybridization, the mixture was heated to 90°C for 10 minutes and then cooled slowly down to the room temperature overnight. G25 spin columns were used for buffer exchange to remove the DTT to expose the free thiol groups in the solution. These hybridized double-stranded oligonucleotides were then dispersed in the solutions of 80nm Ag nanoparticles for immobilization. Schematic of DNA molecules on a metal nanoparticle is shown in Fig. 3.5. For optimal SERS measurements and protein binding, three different ratios of DNA and nanoparticle numbers (1600:1, and 8000:1 and 16000:1) were tested. It was found that the optimal DNA to nanoparticle number ratio was around 16000:1. For all experimental results presented in this paper, the DNA-nanoparticle ratio was around 16000:1.

DNA-nanoparticles were diluted in the binding buffer (15 mM Tris-pH 7.5, 90 mM KCl, 100µM ZnCl, 0.2mM DTT, 1mg/ml BSA, and 6.5% glycerol) to a final concentration of 157nM. To this DNA-nanoparticle solution, either WT1 (-KTS) or WT1...
(+KTS) proteins were added with a final concentration of 23.7ng/µl, and then the mixture was incubated at room temperature for 20 minutes for protein binding. Under similar conditions, bovine serum albumin (BSA) was used as a non-specific binding control.

DNA molecules, immobilized on nanoparticles were digested by using Bal31 exonuclease (1.3units/µg of DNA) for 10 min at 30°C in the presence or absence of WT1 protein. Bal31 digests the DNA from its free ends. After digestion, exonuclease was inactivated by incubation at 65°C for 10 minutes, as suggested by the manufacturer. The minimal amount of enzymes needed to digest entire DNA molecules in the absence of WT1 protein and the amount of WT1 protein required to completely block the digestion by Bal31 exonuclease were both determined empirically using electrophoretic analyses (see below).

3.7.3 SERS Measurements and Gel Electrophoresis

The DNA-functionalized Ag nanoparticles were immobilized on glass substrates and SERS spectra were typically taken from aggregates of these Ag nanoparticles. To facilitate the adhesion of nanoparticles on glass substrates, the glass substrates were treated with silane [(3-aminopropyl) triethoxysilane] to make their surfaces positively charged. Normally, 10µl of the digested or non-digested DNA-nanoparticle solution was dropped onto a glass slide and left to dry for 2-3 hours. After being flushed several times with deionized water and dried with nitrogen gas, the glass substrates were mounted on the stage of an inverted optical microscope (Leica DM-IRB) that was coupled with an imaging spectrometer for inspection and SERS spectral measurements. The Raman
spectra were excited by a 532nm (125mW) solid state laser; and the scattered light was collected using a 40× (0.6NA) objective. The experimental setup for the SERS measurement is shown in Fig. 3.6.

As a method for validating the protein binding and subsequent protection of labeled oligonucleotides from exonuclease digestion, gel electrophoresis was used to analyze DNA-nanoparticle complexes with or without exonuclease digestion. Gel electrophoresis of double stranded DNA was performed using 4% low melt agarose (SEAKEM, ) in TAE buffer (Tris-Acetate-EDTA) containing Ethidium Bromide and DNA was visualized by a
gel doc system (BioRad, CA). The gel loading buffer contained both Bromophenol Blue and Xylene Cyanol dyes (Sambrook 1994), and the latter migrated with the 200 bp ladder marker in the 4% low melt agarose gels. The size marker used in the electrophoresis was the 1kb plus DNA ladder (Invitrogen, Carlsbad CA) containing the 100 bp fragment that was larger than the 43 bp uncleaved oligonucleotides.

3.8 Results and Discussion

In the SERS protein-binding assay, the fluorophore-labeled double-stranded DNAs were firstly covalently bound to 80 nm Ag nanoparticles via the thiol group at the 5’ end of one DNA strand, while the dye molecules (TAMRA/FAM) were tagged at the 3’

<table>
<thead>
<tr>
<th>Oligonucleotide Type</th>
<th>Sequence</th>
</tr>
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<tbody>
<tr>
<td>VEGF Forward</td>
<td>5’/5ThioMC6D/AGGACAGAGTTTCCGGGCGGATGGTAAATTATCGGTACAAA-3’</td>
</tr>
<tr>
<td>VEGF Reverse</td>
<td>3’/TAMSp36/CCTGTCTAAAGGGCCCCGCCTACCCATTAATAGCCATGGTTT-5’</td>
</tr>
<tr>
<td>Mutant VEGF-Forward</td>
<td>5’/5ThioMC6D/AGGACAGAGTTTCCGGAGCTGATGGGAATTAATAGCGATGGTTTACAAA-3’</td>
</tr>
<tr>
<td>Mutant VEGF-Reverse</td>
<td>3’/FAM36/CCTGTCTAAAGGACCTGACTACCCATTAATAGCCATGGTTT-5’</td>
</tr>
</tbody>
</table>

Table 3.1. Oligonucleotide sequences designed for studying DNA-WT1 protein interaction
end of the complementary strands. Since the local enhancements of electromagnetic fields due to the excitation of surface plasmons of the Ag nanoparticles decays exponentially from the particle surface, the close proximity of the dye molecules to the

Figure 3.7. Schematic of Bal 31 exonuclease digestion of DNA with and without WT1 (-KTS) protein binding. (a) Exonuclease digestion of DNA in the absence of binding proteins releases the dye from the Ag nanoparticle. (b) The binding WT1 (-KTS) protein blocks the digestion of the whole DNA sequence and the dye remains on the nanoparticle
particle surfaces leads to fluorescence quenching and producing strong SERS. The binding of proteins to specific sites of the DNA molecules can be assessed by measuring the SERS signals from the dye molecules before and after *Bal31* exonuclease digestion. The *Bal31* enzyme can degrade double-stranded DNA from both the 3′- and 5′- ends when single-stranded DNA is not present. When the proteins bind to the double-stranded DNA molecules to protect them from exonuclease digestion, then *Bal31* exonuclease digestion is blocked at the protein binding sites, leading to preservation of SERS signals from the dye molecules. Conversely, when proteins are not bound to double-stranded DNA molecules, *Bal31* digests the entire DNA and the dye molecules are detached from the nanoparticle surfaces, leading to disappearance of SERS signals from the dye molecules.

To demonstrate the utility of this protein-DNA binding assay, we designed two sequences of 43 base pair (bp) double stranded DNA. One sequence was derived from the promoter of the human vascular endothelial growth factor (VEGF) gene and contains a known WT1 (-KTS) binding site, as demonstrated by previous studies based on EMSA and Chromatin immunoprecipitation binding assays [29]. The other sequence was modified by substitution of guanine with thymine or adenine within the WT1 (-KTS) binding region (Table 3.1). Two different fluorescence dye tags, TAMRA and FAM were used as Raman reporters for the wild-type and mutant sequences respectively. The optical microscopic image of the DNA-nanoparticle complexes is shown in Fig. 3.8. Raman scattering was measured mainly from the aggregates where many of the DNA molecules
were supposed to be bound. The majority of Raman peaks of the TAMRA and FAM dye
molecules are in the range of 1200-1650 cm\(^{-1}\) due to the aromatic ring stretching of the molecules, as described previously [30-33]. In order to validate the SERS assay, we also performed gel electrophoresis to analyze DNA fragments before and after digestion. Binding of WT1 (-KTS) to the VEGF DNA was demonstrated by protection from Bal31.

Figure 3.8. Optical microscopic picture of the nanoparticles immobilized with DNA onto the glass substrate.
Figure 3.9. SERS and gel electrophoresis analysis of Bal31 exonuclease digestion of TAMRA dye labeled VEGF DNA-nanoparticle complexes. Raman spectrum of the DNA-nanoparticle complexes (a) before digestion; (b) after digestion without incubation with WT1 (-KTS) protein; and (c) after digestion following incubation with WT1 (-KTS) protein. (d) Gel electrophoresis of the DNA-nanoparticle complexes: (lane 1) after digestion following incubation with the WT1 (-KTS) protein; (lane 2) after incubation with WT1 (-KTS); (lane 3) after digestion following incubation with BSA; (lane 4) after incubation with BSA; and (lane 5) after digestion without incubation with any protein. Lane 6 presents the electrophoresis of the 1kbp plus DNA ladder; and the 100 bp smallest fragment of the ladder is larger than the 43 bp uncleaved oligonucleotide as shown in lane 4.

digestion as shown in Fig. 3.7. Before Bal31 digestion of DNA, clear Raman peaks for
TAMRA can be observed (Fig. 3.9a). These key Raman peaks of TAMRA at 1646 cm$^{-1}$, 1564 cm$^{-1}$, 1535 cm$^{-1}$, 1504 cm$^{-1}$, 1407 cm$^{-1}$, 1351 cm$^{-1}$, and 1208 cm$^{-1}$ are in close agreement with previous measurements [30, 33]. The effect of digestion with Bal31 exonuclease on the double stranded DNA is demonstrated in Fig. 3.9b. The characteristic Raman peaks for the TAMRA were not detected in the Raman spectra from Ag nanoparticles, suggesting degradation of the double stranded DNA. Note that two broad peaks around 560 cm$^{-1}$ and 1102 cm$^{-1}$ in the Raman spectra are from the glass substrates and can only be seen with long measurement times in the absence of the strong Raman signals from the dyes. In contrast, when the Bal31 digestion was performed after incubating the DNA-nanoparticle complexes with WT1 (-KTS) proteins, the characteristic Raman peaks for TAMRA were preserved (Fig. 3.9c).

It is expected that certain a fluorescence background exists in these spectra. Previous studies have demonstrated that the fluorescence emission can be significantly quenched by placing a dye in the vicinity of a metal nanoparticle [34, 35]. Importantly, it was shown that the quenching efficiency decreases not only with increasing distance of the dye to the metal surface but also with increasing nanoparticle size [34, 36, 37]. As a result, the fluorescence emission from a dye can be almost 100% quenched by silver or gold nanoparticles of 1-2 nm diameters, while fluorescence can only be partially quenched by metal nanoparticles with larger diameters like those used in our experiments[36].
In addition, it is notable that the relative Raman peak intensities decrease after the enzyme digestion, a phenomenon that can be attributed to the suppression of particle aggregation. As can be seen by dark-field optical microscopy, Ag nanoparticles easily form aggregates after immobilization on glass substrates before the enzyme digestion, while they rarely form aggregates on glass substrates after the digestion. The exact physical mechanism preventing aggregation is complicated, but we believe that it is

Figure 3.10. SERS and gel electrophoresis analysis of Bal31 Exonuclease digestion of TAMRA dye labeled VEGF DNA-nanoparticle complexes. (a) Raman spectrum after incubation with WT1 (+KTS) and exonuclease digestion. (b) Gel electrophoresis of the DNA-nanoparticle complexes: (lane1) after Bal 31 digestion following incubation with the WT1 (+KTS) protein; (lane 2) after incubation with WT1 (+KTS); and (lane 3) before Bal31 digestion. The lane 4 is the 1kbp plus DNA ladder.
related to alteration of nanoparticle interactions by the reaction buffers added during the protein binding and the enzyme digestion. As it is well known that plasmon coupling between nanoparticles or nanoparticle aggregates is critical to achieving large SERS enhancements, it is understandable that the Raman peak intensities dwindle after the enzyme digestion in our experiments.

We want to emphasize that the fluorescence background and the variation in the Raman peak intensity after the enzyme digestion are not intrinsic issues to the SERS protein-DNA binding assay proposed here. For example, fluorescence can be minimized by using a laser of longer wavelength for SERS excitation; and the dependences of Raman signals on nanoparticle aggregation can be avoided by using arrays of metal nanoparticles fabricated on substrates using nanolithography methods.

These experiments demonstrated that WT1 (-KTS) bound to the VEGF DNA molecules and protected them from complete digestion by the Bal31 exonuclease. As a control for non-specific binding, the effects of BSA treatment were also measured. With the incubation of BSA with DNA-nanoparticle complexes, Raman signals of TAMRA disappeared after Bal31 digestion, indicating no non-specific binding of BSA with the DNA molecules. Additional analyses by gel electrophoresis of these DNA-nanoparticles before and after enzyme digestion showed clear agreements with the results from Raman spectroscopy (Fig. 3.9d). In agreement with previous investigation, the WT1 (-KTS) proteins bound and protected the VEGF DNA while the BSA specificity control failed to protect.
The Raman spectroscopy assay was also used to test the binding of WT1 (+KTS) to DNA-nanoparticle complexes. Figure 3.11 shows SERS and gel electrophoresis analysis of the Bal31 exonuclease digestion of FAM dye labeled VEGF mutant DNA-nanoparticle complexes. (a-c) Raman spectrum of the mutant DNA-nanoparticle complexes: (a) before digestion; (b) after digestion following incubation with the WT1 (-KTS) protein; and (c) after digestion without incubation with the WT1 (-KTS) protein. (d) Gel electrophoresis for the mutant DNA-nanoparticle complexes; (lane 1) after digestion following incubation with the WT1 (-KTS) protein; (lane 2) after digestion without incubation with the WT1 (-KTS) protein and (lane 3) before digestion. Lane 4 is the electrophoresis for the 1kbp plus ladder.

The Raman spectroscopy assay was also used to test the binding of WT1 (+KTS)
isoforms with the VEGF DNA. To facilitate the comparison with WT1 (-KTS) binding, the same concentration of WT1 (+KTS) protein was mixed and incubated with DNA-nanoparticle complexes. The digestion of the VEGF DNA by Bal31 in the presence of WT1 (+KTS) protein was shown by the disappearance of the Raman signals from TAMRA (Fig. 3.10a). These experiments showed clearly that, unlike WT1 (-KTS), the WT1 (+KTS) protein did not bind the VEGF DNA; in agreement with previous studies using different methods [29]. Again, this was confirmed by gel electrophoresis of DNA-nanoparticles before and after enzyme digestion (Fig. 3.10b).

To test the sequence specificity of WT1 (-KTS) protein, the binding site was altered by substitution of three guanines essential for zinc finger interactions. Before WT1(-KTS) and exonuclease digestion, the measured spectra exhibit several Raman peaks at 1628cm\(^{-1}\), 1550cm\(^{-1}\), 1534cm\(^{-1}\), 1471cm\(^{-1}\), 1411cm\(^{-1}\), 1321cm\(^{-1}\), 1175cm\(^{-1}\), 759cm\(^{-1}\) and 632cm\(^{-1}\) (Fig. 3.11a), which are close to the characteristic Raman peaks obtained in previous measurements for the FAM dye [31]. Binding and exonuclease digestion experiments with this mutated VEGF DNA showed that these key Raman peaks from the FAM dye disappeared after digestion with Bal31 enzyme (Fig. 3.11b). This indicated that the WT1 (-KTS) protein did not bind and protect the VEGF mutant DNA from exonuclease digestion. This was verified by the gel electrophoresis experiments (Fig. 3.11d). The lack of protection by the WT1 (-KTS) protein of the VEGF DNA containing the mutated binding site was identical to that observed in the absence of WT1.
(-KTS) protein. As discussed above, the fluorescence background in (Fig. 3.11a) was related to only partial fluorescence quenching by Ag nanoparticles of relative large size.

There are several potential advantages for the SERS based protein-DNA binding assay as demonstrated here. Firstly, SERS can be an ultrasensitive technique as recent experiments showed that single molecule sensitivity can be achieved with SERS in certain aggregates of metal nanoparticles [4, 5]. With recent progress in plasmonic nanoantenna designs and nanofabrication techniques, controllable and repeatable SERS active substrates are achievable [38, 39]. Secondly, since the sharp Raman peaks can be used as fingerprints for direct molecular identification, the SERS technique can be multiplexed, as demonstrated previously in DNA and protein detecting systems [31, 40, 41]. We expect that the SERS assay demonstrated here can be further improved for multiplexed ultrasensitive protein-DNA binding detection by using more repeatable SERS active substrates such as those made with top-down nanofabrication techniques [38, 39, 42, 43].

3.9 Conclusion and Future Perspectives

In conclusion, we have developed a simple label free method of detecting sequence specific transcription factor-DNA binding by using surface enhanced Raman scattering (SERS). Double strand DNA molecules with potential protein binding sites labeled with dye molecules are immobilized on metal nanoparticles; the binding of proteins protects these DNA molecules from complete digestion by exonuclease enzyme, and can be detected by the SERS signals before and after the exonuclease digestion. As a
proof of concept, we demonstrated this SERS based protein-DNA interaction assay by studying the binding of WT1, a zinc finger transcription factor with DNA sequences derived from the promoter of the human vascular endothelial growth factor (VEGF).

It is well known that the local electric field is significantly enhanced in the gap between two metal nanoparticles. Sufficient enhancement in the electric field can be achieved when the gap between the nanoparticles is of few nanometers. But in colloidal nanoparticles systems the gap cannot be controlled therefore high field enhancement regions or hot spots are rarely found. The probability of getting highly enhanced signal which completely overcomes the strong fluorescence signal is still low even from a relatively large number of molecules and is extremely low using SERS for single molecule detections. Thus robust SERS substrates are highly desirable where inter-particle spacing can be controlled to provide sufficient local electric field enhancement for SERS in general and for SERS at single molecule detections in particular. Efforts have been made to fabricate Raman-active substrates for single molecule studies employing the currently available advance nanofabrication techniques.

In the next chapters we will discuss the design and the fabrication of the nanostructures which can be fabricated with controlled gap size between them and provide the significant field enhancement in the gap applicable for single molecule and single nanoparticle SERS.
REFERENCES


CHAPTER 4

Metal-Dielectric-Metal Nanoantennas and Their Cavity Resonance Modes for Single Molecule SERS

4.1 Introduction

As discussed in Chapter 2, previous observations of single molecules SERS were primarily from molecules conjugated with colloidal nanoparticle systems. In such systems, hotspots were only rarely found from aggregates to provide single molecule SERS signals, which make the experiments unpredictable and not precisely controllable. Theoretical insights into the plasmon resonances of nanoparticle dimers have shown that the maxima of the local fields are located at the nanogap between two particles, and the nanogap needs to be less than 5nm to achieve sufficiently large local field enhancement for single molecule SERS [1-6]. With state-of-the-art fabrication techniques it has been possible to realize these particle dimers with nanogaps in experiments [7-9]. It remains a challenge to fabricate these dimers, nanoantennas with gaps below 5nm, in a reproducible fashion at large scale. To address this demanding issue, we propose a design of nanoantennas with a vertical intra-particle nanogap between two metal cuboids/ cylinders [10]. In comparison to other existing nanoantennas and nanocavities, the new design has two advantages: (1) nanoantennas and nanocavities [8, 9, 11-13] are integrated on a single platform and (2) the nanogaps can be controlled precisely by advanced deposition methods such as atomic layer deposition; and (3) the cavity resonance wavelengths can
be fine-tuned by the diameter of the dielectric disc while keeping the cavity thickness small for optimized local field enhancements. Similar plasmonic nanostructures such as MDM nanodisks have been proposed and studied by a few groups [14-16]; however, the resonant cavity modes in these structures are not understood in details and thus not optimized for achieving high local field enhancements. Miyazaki et al. has shown in experiments that the visible light waves can be squeezed into rectangular MDM nanocavities of 3nm thickness [17].

In this chapter, we present numerical studies of the near field and far field optical properties of the MDM nanoantennas. Two geometrical shapes considered are the parallel cuboids and cylinders. Extraordinary local field enhancements and interesting resonance features are observed by fine tuning the antenna and cavity resonant frequencies. Narrow band resonant peaks can be clearly seen in local field enhancements; at the same positions of these local field peaks, dips can be observed in the far-field spectra. It can be understood that these local field peaks and far-field dips are due to resonant cavity modes inside the dielectric gaps formed by interfering gap plasmons. The tunability of the gap size with high accuracy renders this kind of nanoantenna design a good candidate for single molecule SERS studies.

4.2 Nanoantennas Design and Simulation

The proposed metal-dielectric-metal nanoantennas are composed of two metallic parts stacked vertically, and a thin layer of dielectric material sandwiched between them. Two geometrical shapes are considered for the metal parts: parallel cuboids and
cylinders. Two different cases are considered for the dielectric layer: one with its cross section of the same size as the metallic parts (Fig. 4.1a and b), and the other with its cross section of smaller size than that of the metallic parts (Fig. 4.1c and d). The free volume inside the nanogaps in the second case (Fig. 4.1c and d) allows not only for

Figure 4.1. Schematics of nanoantennas with parallel cuboids (a, c), and cylindrical rods (b, d). The pink color represents metal materials (Ag in this paper), and the blue represents dielectric materials (SiO2 in a-b and Al2O3 in c-d).
accommodating SERS molecules in hotspots but also for tuning the cavity resonant wavelength through variation of the dielectric disk side width or diameter. While circular MDM nanodisks (Fig. 4.1b) have been proposed and studied by a few groups, detailed studies of their plasmonic cavity modes are presented here for the first time.

The optical properties of these nanoantennas were studied by numerical simulations using the commercially available software package, *CST Microwave Studio* [18]. The *CST* software is based on the finite integration technique (FIT), and can be regarded as a generalization of the finite-difference time domain method, which has been already discussed in Chapter 1. The dispersive media are implemented in the simulations by combining the FIT method with a state-space formulation; the algorithms used in the software are applicable to arbitrary material dispersions.

As for material properties, the Drude model $\varepsilon_{Ag} = \varepsilon_{\infty} - \omega_p^2 / \omega(\omega - i\gamma)$ was used to describe the frequency dependent dielectric constant of silver. The parameters, $\varepsilon_{\infty}=3.57$, $\omega_p=1.388 \times 10^{16}$ rad/s, and $\gamma = 1.064 \times 10^{14}$ Hz were obtained by fitting the Drude model to the experimentally measured permittivity for bulk Ag [19]. Bulk permittivity for SiO$_2$ and Al$_2$O$_3$ were taken as 2.13 and 3.09 respectively.

Open boundary conditions are used in the simulations with vacuum as the surrounding medium. These nanoantennas of two different cases are excited at different configurations: for the first case, the incident wave shines from the top (along: -z) with a polarization parallel to the y axis as shown in Fig. 4.1(a-b); for the second case, the incident wave shines from the side (along: -y) with a polarization parallel to z axis as
shown in Fig. 4.1(c-d). The hexahedral meshing scheme was used with the mesh size set much smaller than the wavelength of the surface plasmons. Depending on the geometrical sizes of individual nanoantennas, the mesh size ranges from 0.6 nm to 5.7 nm (limited by computer memory). Local field enhancements were calculated by placing near-field probes at the points represented by the black spots as shown in Fig. 4.1. In our simulations, far field spectra were calculated at 100µm away from the nanoantennas along z (Fig. 4.1a-b) and y-axis (Fig. 4.1c-d). To understand the resonant cavity modes, electric field distributions were calculated at the planes through the middle of the nanocavities.

4.3 Result and Discussion

Firstly, we present numerical results on the parallel cuboids and cylinder nanoantennas where the dielectric layer has the same diameter or width as the metal layer (Fig. 4.1a-b). Examples of both far and near field scattering spectra are shown in Fig. 4.2 for parallel cuboids and cylinder nanoantennas. Clear dips can be observed in the far field scattering spectra, while at the corresponding wavelengths for these dips, peaks can be observed in the local electric field spectra. These dips in the far field spectra and corresponding peaks in the near field spectra clearly indicate the cavity resonances.

To understand these resonant cavity modes, the electric field distributions at these resonant wavelengths were calculated. Representative snapshots of the electric field distributions at the middle planes of the nanocavities are presented in Fig. 4.3 for the first 4 modes (that is, the 4 lowest resonant frequencies). Here for a particular particle size, the
cavity mode with the longest resonant wavelength is denoted as its 1st mode, while the corresponding higher order modes occurring at smaller resonant wavelengths are denoted as its 2nd, 3rd, 4th and 5th modes in descending order of wavelength. It can be seen that these resonant modes for the parallel cuboids and cylinder nanoantennas are similar. All the modes are transverse magnetic (TM). The time sequences of the transient electric

Figure 4.2. Far-field scattering and local field enhancement spectra for the parallel cuboids (a) and cylindrical (b) MDM nanoantennas. The side width or diameter for the nanoantenna is set at 450nm and height is set at 30nm. The thickness of the SiO2 gap layer is set at 10nm for both antennas. For clarity, the spectra above 1.2µm are not shown here.
field distributions show that electric fields form standing waves inside the nanocavities, similar to those in a Fabry-Perot resonator. It is also clear that the electric fields inside

![Figure 4.3](image)

Figure 4.3. Snapshots of electrical field distribution in the middle planes of cuboids (a) and cylinder (b) nanoantennas at their four lowest cavity resonant frequencies. The geometrical parameters of these nanoantennas are the same as in Fig 4.2. The numbers denote the cavity mode orders shown in Fig. 4.2; the resonant wavelengths of the first modes, not shown in Fig. 4.2, are at 3.3µm and 2.9µm for the parallel cuboids and cylindrical antennas respectively.

these cavities are largely enhanced at these resonant modes. The concrete enhancement factors vary with the geometrical parameters of the nanoantennas, especially the gap thickness of the nanocavities [17, 20].

It can be found that these TM modes are strikingly similar to those of patch antennas. A patch antenna is formed by a metallic patch of circular or square shapes on a
planar metallic wall,: the dielectric gap between them forms a cavity [21]. The TM cavity modes of the patch antennas can be described by three integer indices (m, n, p), or represented as $TM_{mnp}$. For square patch antennas, m, n and p indicate the number of nodes in the x, y and z direction respectively. While for circular patch antennas, m indicates the number of antinodes in azimuthal direction within an angle of $\pi$, and n and p indicate the number of antinodes in radial and z directions respectively. For small dielectric gap like

![Figure 4.4](image_url)

**Figure 4.4.** Scattering spectra of (a) parallel cuboids and (b) cylinder nanoantennas of different side widths and diameters. The heights of metals and dielectric parts are kept constant at 30 and 10nm respectively. The numbers labeling the dips in the scattering spectra represent the different cavity resonance modes which correspond to the peaks in the local fields.

in our system, the mode index p should be zero. For the case of parallel cuboids nanoantennas, the first, second, third and forth modes correspond to the $TM_{010}$, $TM_{030}$,
For the cylinder nanoantennas, the first, second, third and forth modes correspond to the $TM_{110}$, $TM_{120}$, $TM_{130}$, $TM_{140}$ modes of a circular patch antenna respectively [22].

It is interesting to note that the cavity modes excited in these nanoantennas do not show all the sets of the cavity modes predicted in the patch antennas. For example, only angular cavity modes with $m=1$ can be observed in the cylindrical nanoantennas although the resonant frequencies of other lower or higher angular modes such as $TM_{010}$ and $TM_{210}$ should be in the frequency ranges of calculations. This is because of the incidence direction and the linear polarization of the excitation light which together set the anisotropy of the induced dipole moment of the whole nanoantennas; simulations with light illumination from the side show that more modes can be excited.

The confinement of the electromagnetic fields inside the nanocavities and these cavity resonances can be understood in terms of gap plasmon modes. The dispersion relation of the surface plasmon mode at an interface between semi-infinite metal and dielectric materials is well known: $k_{sp} = \omega/c\sqrt{\varepsilon_m\varepsilon_d/(\varepsilon_m + \varepsilon_d)}$ where $\varepsilon_m$ and $\varepsilon_d$ are the permittivity of the metal and dielectric materials respectively, $\omega$ and $c$ are the radial frequency and speed of the electromagnetic waves in vacuum. When two metal/dielectric interfaces are brought into close proximity like in our MDM structures, the surface plasmons at two metal/dielectric interfaces couple with each other, leading to splitting of one plasmon mode into two, or so-called symmetric and anti-symmetric gap plasmon...
modes [23]. The symmetric mode has higher energy than the anti-symmetric mode, and is beyond the wavelength range of interest in our nanoantenna structures.

The excited surface plasmon wave propagates inside the dielectric gap of the MDM nanoantenna and is reflected at the edge of the MDM waveguide, forming a Fabry-Perot

\[ \tanh(2k_m t/\epsilon_d) = -\epsilon_d k_m / \epsilon_m k_d \]  \hspace{1cm} (4.1)

where \( t \) is the dielectric gap thickness, and \( k_m = \sqrt{k_{gsp}^2 - \epsilon_m \omega^2 / c^2} \), \( k_d = \sqrt{k_{gsp}^2 - \epsilon_d \omega^2 / c^2} \).

As the effective refractive index of the dielectric layer is larger than that of the vacuum, no phase change occurs on reflection of the surface plasmon waves at the edge.

**Figure 4.5.** Variation of the cavity resonance wavelength versus the particle side width/diameter for different cavity modes for the parallel cuboids nanoantennas (a) and cylinder nanoantennas (b). The symbols represent simulation results; the solid lines represent theoretical results from Eq. 4.2.
As a result, the incident and the reflected waves interfere constructively at the edge of the gap. In consequence, the resonant condition for the formation of standing waves can be written as

\[ k_{gsp} \cdot L = (2n + 1)\pi, \quad n = 0, 1, 2, 3, \ldots \quad (4.2) \]

where \( k_{gsp} \) is the wave vector for the anti-symmetric surface plasmons, and \( L \) is the length.

Figure 4.6. Simulated local electric field enhancement and far field scattering spectra for a parallel cuboids (a) and a cylinder (b) nanoantennas. Parameters: (a) Ag 60nm×60nm×60nm; Al\(_2\)O\(_3\) 20×20×2.5nm. (b) Ag: 60nm diameter × 80nm height; Al\(_2\)O\(_3\) 30nm diameter × 2.5nm height.
(or diameter) of the nanocavity. The first cavity mode corresponds to n=0, the second cavity mode corresponds to n=1 and so on.

Based on this resonant condition, it can be expected that as the side width or diameter of the nanocavity increases, new dips appear in the far field spectrum owing to more allowed cavity resonant modes. Also, the cavity modes of the same order shift

Figure 4.7. Snapshots of the local electric fields in the plane through the middle of the dielectric spacer for the parallel cuboids (upper row) and cylinder (lower row) nanoantennas. The red region indicates the local maxima and the blue indicates the local minima. The zero amplitude of the electric field is represented by the green regions.
towards the longer wavelengths (or lower frequency). This is exactly observed in the far-field scattering spectra for different nanoantenna side widths/diameters (Fig. 4.4.). For example, only the first two modes are observed for the 150nm side-width/diameter nanoantenna, while four additional modes are observed for 450nm-wide nanoantennas. The first mode resonances occur at 876 and 778nm respectively for 100nm cuboids and cylinder particles, while beyond 1.2 microns for larger nanoantennas (>150nm). Fig. 4.5. presents the resonant wavelength as functions of the width/diameter of the parallel cuboids/cylindrical nanoantennas for different cavity modes. The resonant wavelengths calculated from the resonant condition Eq. 4.2 agree very well with the simulation results.

With the side width or the diameter of the dielectric the same as that of the metallic parts, the field enhancement hardly goes beyond 100 even when the thickness of the dielectric is made 5 nm. To address this issue we modified the design of the optical nanoantennas where the side width or diameter of the dielectric is made smaller than the metallic parts as shown in Fig. 4.1c-d. This modification is based on two considerations: (1) smaller side width or diameter of the dielectric layer leaves room to accommodate SERS molecules inside the nanocavity (or hotspot); (2) it allows for fine tuning the cavity resonance frequencies by the variation of the dielectric layer side width or diameter while keeping the gap small for high local field enhancements. The SiO$_2$ core was replaced with Al$_2$O$_3$ to have better tunability.

For this case, we excited the nanoantennas from side as shown in Fig. 4.1(c-d). Representative local electric field enhancements and far field scattering spectra are
shown in Fig. 4.6a-b for both parallel cuboids and cylindrical nanoantennas. Again peaks in local field enhancement spectra and dips in far-field scattering spectra can be observed at the same wavelengths. Clearly these resonant nanocavity modes are similar to those shown above. It is worth pointing out that the scattering spectra show a broad peak (separated by the second mode dip), which, similar to previous observations in dimer particle nanoantennas, corresponds to the plasmon resonance of the whole antenna as a dipole.

One interesting phenomenon to notice in Figure 4.6 is the sharpness of the dip in the far field due to the second mode and the shallowness of the dips for the first and third modes. A close look into the distribution of the electric field profile in the nanocavity explains this finding. In Fig. 4.7 we show the electric field distribution through the middle plane of the Al₂O₃ layer at the frequencies corresponding to the first three cavity modes of Fig. 4.6. From the sequences of transient electric field distribution snapshots, we find that the first mode and third modes are actually hybrid modes, where a propagating wave is superimposed on these standing interference patterns like those shown in Fig. 4.3. On the other hand, for the second mode the electric field distribution of the surface plasmon wave forms a perfect standing wave pattern, therefore maximum confinement of energy within the cavity takes place for this mode. For the second mode, a resonance condition similar to Eq. 4.2 can be written as:

\[ k_{gsp} d + k_{gsp}^* (D - d) = 2\pi \]  

(4.3)
where D and d are the diameters of the metal cylinder and dielectric disk respectively, \( k_{\text{ep}} \) and \( k'_{\text{ep}} \) are the gap surface plasmon wave vectors in Al\(_2\)O\(_3\) and air gaps respectively. A

**Figure 4.8.** Variation of resonance wavelength as a function of the particle side width or particle diameter for different cavity modes for the parallel cuboids (a) and cylinder (b) nanoantennas. The symbols represent simulation results; the solid lines represent theoretical results from Eq. 4.3.

comparison with simulation results shows reasonable agreement (Fig. 4.8). However, similar resonant conditions for the first and third modes show poor agreement with the simulation results, indicating differences of these hybrid cavity modes.

It is noted that much richer cavity modes can be excited with side illumination in this situation. For parallel cuboids antennas, the first and third cavity modes shown in Fig. 4.7 are equivalent to the \( TM_{010} \) and \( TM_{220} \) modes in the square patch antennas; the second mode does not have equivalence in the square patch antennas but have some similarity
with the $TM_{020}$ mode in cylindrical patch antennas. The first three cavity modes in the cylindrical nanoantenna shown in Fig. 4.7 are equivalent to the $TM_{110}$, $TM_{020}$, and $TM_{120}$ modes in the circular patch antennas. It is also found that the modes that can be excited in the plasmonic cavities strongly depend on the size of the dielectric layer. For example, when the dielectric layer side width is increased from 20nm to 40nm, the third mode will be different from the one in Fig. 4.7.

High local field enhancements are essential to single molecule SERS applications. To optimize field enhancements, we simulated nanoantennas with different aspect ratios of the dielectric layer and different heights of the metal parts (Fig. 4.9). As the thickness of the cavity is gradually reduced, the electric field enhancement increases monotonically due to the increasing confinement of gap plasmons. For gaps below 5nm the optimal

Figure 4.9. Local field enhancements for the second cavity mode for parallel cuboids (a) and cylinder (b) nanoantennas. Parameters: (a) Ag 60nm×60nm ×60nm and (b) Ag: 60nm diameter × 80nm height.
enhancement is achieved when the diameter or side width of the dielectric gap is about half of that of the Ag cuboids or cylinders. The exact physical reason for this is not clear yet, while we believe it is related to the reflection of gap plasmons at the interface of the dielectric disc edge and air.

Another finding is that both the antenna resonances and cavity resonances play critical role in achieving high local field enhancements. When the nanocavity thickness is further reduced (e.g., 1nm), the second cavity mode resonance shifts to long wavelength while the antenna resonance changes only a little. Simulations can show that the third cavity mode, whose resonant wavelength coincides with that of the antenna, provides highest local field enhancements. A general observation in simulations is that the highest local field enhancements are achieved with the cavity mode having its resonant wavelength coincident with the antenna resonant wavelength, as can be seen in Fig. 4.6.

While the cavity resonant wavelengths can be accurately tuned by varying the thickness and side width or diameter of the dielectric, the antenna resonances are sensitive to the variations in the length of the metallic parts. By fine tuning the dielectric side width and thickness of the dielectric disc and the length of the metal cuboids, we can achieve about 300 local field enhancements with 1nm gap and 60nm×60nm×80nm Ag parallel cuboids. With such local field enhancements, the SERS enhancement factor from the electromagnetic enhancement alone is expected to be $10^{10}$, which should provide single molecule sensitivity.
4.4 Conclusion

In conclusion, we have numerically studied plasmonic nanoantennas which are composed of a dielectric layer sandwiched between two metal cuboids/cylinders. It is shown that for the nanocavities with dielectric gap of the same side width/diameter as the metallic parts, cavity resonance modes can be excited by illuminating the structures from the top. The cavity resonance modes produce dips in far fields and peaks in the local electric fields. The number of cavity resonance modes and their wavelengths vary systematically with the dielectric size and are in close agreement with the calculated results.

By making the dielectric layer of smaller side width/diameter than the metallic parts and illuminating from the side, lower order resonant modes with axial symmetry can also be generated inside the cavity with greater field enhancements, while the resonance modes are more complex in nature. The local field enhancements can be optimized to 300 by fine tuning and matching the antenna and cavity resonant frequencies. This large local field enhancement and the potential control of the nanocavity thickness using atomic layer deposition making this new nanoantenna design very promising candidate for single molecule SERS applications.

In the next chapters, we will discuss the fabrication and experimental observations of cavity resonance modes of metal-dielectric-metal nanoantennas.
REFERENCES


CHAPTER 5

Fabrication and Characterization of Coupled Metal-Dielectric-Metal (MDM) Nanoantennas with Active Medium

5.1 Introduction

As discussed in the last chapter, in vertical MDM nanoantennas changing the gap thickness and size of dielectric and the metal structures can lead to tremendous enhancement in the local electromagnetic field and the antenna and the plasmonic nanocavity resonance can be precisely tuned. In such structures, dielectric gap thickness can be controlled precisely by advanced deposition methods such as atomic layer deposition and shows promise for large scale manufacturing. Miyazaki et al have shown in experiments that light can be squeezed into rectangular metal-dielectric-metal nanocavities of 3nm thickness [13], and Qin et al [14] demonstrated that MDM nanoantennas can be synthesized by using the on-wire lithography technique, a technique in which nanowire materials are electrochemically deposited into the porous alumina template of desired pore diameter and the nanowires are detached from the template by dissolving it in suitable solvent. These nanoantennas can then be employed as hotspots for surface enhanced Raman scattering (SERS) applications.

This chapter takes a different direction. Rather than fabricating MDM nanoantennas of very small gap thickness for the SERS applications, by using advanced
deposition techniques, we present the fabrication and the characterization of 2D arrays of MDM nanoantennas composed of a relatively thick layer of light-emitting polymer sandwiched between two metal nanoparticles. By introducing light emitting material in an optically hot region, we can observe the effect of plasmon coupling on the emission
and the life time of the material for possible applications in lasing. We study the cavity resonance of these nanostructures by measuring the optical transmission through the antenna arrays. We performed numerical simulations by using a finite integration (FIT) method, and were able to reproduce those transmission dips in the calculated transmission spectra.

We incorporated active material in the cavity for the following purposes, (1) studying the SERS from the material and (2) having the active materials inside the nanocavities of very small mode volume and fine tuning the cavity resonance to match with the active material’s optical emission peak, the nanocavities can be potentially used in lasing application.

5.2 Nanoantenna Fabrication

A schematic representation of the MDM nanoantennas is shown in Fig. 5.1a. The 2D arrays of the MDM nanoantennas are composed of a thin layer of light emitting conjugated polymer 3-polyhexothiophene (P3HT) sandwiched between two silver (Ag) cuboids. To fabricate these nanoantennas, the first layer of Ag film was deposited on a quartz substrate using e-beam evaporation, and then a thin layer of P3HT was coated on this Ag film by spin-coating P3HT dissolved in chloroform at a spin speed of 3000 rpm followed by baking on a hotplate at 95°C for five minutes. After that, a second layer of Ag film was deposited through e-beam evaporation. 2D arrays of cuboids MDM nanoantennas were fabricated using a focused ion beam (FIB) milling (FEI Nova Nanolab). For the better control over the nanoantenna dimension and to reduce the
fabrication time, two steps were followed in the focused ion beam milling process. In the first step, a 30kv Ga\textsuperscript{+} beam with 50 pA beam current was used to make a large trench around the area where nanoantenna arrays were to be fabricated. The un-milled area in the middle of the trench was milled by the ion beam with a smaller beam current (10pA) to form the nanoantenna arrays.

To control the thickness of P3HT films, its dependence on various physical parameters were studied and calibrated. Chloroform solutions of P3HT at different concentrations were spin-coated on clean silicon substrates at different spin speeds; and their film thicknesses were measured by atomic force microscope (AFM). It was

Figure 5.2. Schematics of experimental setup to measure the optical transmission through nanoantenna array.
observed that the film thickness depends primarily on the concentration and has little variation with the spin speed. For a concentration of 1.38 mg/ml, the P3HT film is about 10nm thick; while for a concentration of 2.9 mg/ml, the P3HT film is 20nm thick.

For the data presented in this chapter, the thickness of the P3HT layer used is 20nm; the thicknesses of the bottom and top Ag cuboids are 40 and 50 nm respectively. The side width of nanoantennas is varied from 300 to 420nm; and the array period was fixed at 600nm. As an example, an SEM image of a 2D array of the fabricated nanoantennas is shown in Fig. 5.1b.

5.3 Results

We measured the optical transmission through the fabricated 2D arrays of Ag/P3HT/Ag nanoantennas. For the measurements, the nanoantenna arrays were illuminated perpendicularly with a collimated white light beam from the top, with a polarization parallel to the side widths of the nanoantennas. The transmitted light was collected by using a 40× objective with 0.6NA. The experimental set up for the transmission measurement is shown in Fig. 5.2. The measured transmission spectra are presented in Fig. 5.3. Two dips can be observed from the transmission spectra. Both dips show a distinctive red shift in the dip wavelength when the side width of the nanoantennas is increased. One interesting observation is that with the same amount of increase in side width, the left dip (dip 1) shifts about twice as much in the wavelength as the right dip (dip 2).
To understand the origin of these resonant dips, we performed numerical simulations employing the Finite Integration Technique (FIT) by the means of a commercial software package (CST Microwave Studio). The Drude dispersion model was used to describe the Ag permittivity, where the parameters are obtained by fitting the model with previous experimental data [15] as described in section 4.2 (chapter 4). To describe the permittivity of P3HT general second order dispersion model:

\[
\epsilon(\omega) = \epsilon_\infty + \frac{\beta_0 + i\omega\beta_1}{\alpha_0 + i\omega\alpha_1 - \omega^2}
\]

was used, where the parameters \(\epsilon_\infty=2.5\), \(\alpha_0=4.26\times10^{32}\) (rad/s)^2, \(\alpha_1=4.14\times10^{15}\) rad/s, \(\beta_0=1.87\times10^{32}\) (rad/s)^2, and \(\beta_1=3.71\times10^{15}\) rad/s, were

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Figure 5.3. Measured transmission spectra for the 2D arrays of Ag/P3HT/Ag with the side width at 300nm, 340nm, 380nm and 420nm, respectively.
obtained by fitting the model with previously measured refractive index of P3HT [16]. A glass substrate with a thickness of 550nm and a permittivity of 2.13 was also used in the simulations. A plane polarized light wave was used to illuminate the nanoantennas from the top with its electric field parallel to one side of the nanoantennas as shown in Fig. 5.1a. The hexahedral meshing scheme was used with the mesh size set much smaller than the wavelength of the surface plasmons (~λ/35). Transmission spectra were calculated by integrating the Pointing vectors at the plane that is 500nm below the nanoantennas and

Figure 5.4. Fitting of measured P3HT dielectric permittivity with second order dispersion relation. The circles and line represent the measured and fitted data respectively. The measured data was taken from the ref. [16]
inside the glass substrate. The optical transmission through the substrate with nanoantennas was normalized by the transmission through the bare substrate.

The simulated transmission spectra (Fig. 5.5a) which show two distinctive dips are in close agreement with the experimental results, as can also be seen from the comparison of dip wavelengths in Fig. 5.7. We also calculated the spectra for the local electrical field at the middle point in the cavity edge as indicated by the black spot of the nanoantenna (inset Fig. 5.1a). Clear local field enhancement peaks are observed at the wavelengths of the left dips, indicating that the left dip (dip 1) corresponds to resonant excitation of a cavity mode inside the nanocavities. In contrast, the near field spectra do not show any peaks at the positions of the right dips (dip 2), indicating the dips do not originate from cavity resonances. Considering the absorption and emission of the P3HT
polymers at around 600nm, the right dip (dip 2) can be attributed to the permittivity variations of the polymer.

The electric field distributions in the middle plane of the nanocavities at corresponding wavelength of these dips were calculated. Representative snapshots of the

Figure 5.6. Local electric field distribution at the middle plane inside the nanocavities corresponding to the dip-1 (a) and dip-2 (b) of the transmission spectra. The electric fields distribution presented here are for the nanoantenna arrays with 380nm side width.

electric field distributions are shown in Fig. 5.6a-b. The red and blue colors represent the respective maxima and minima of the electric field. At the cavity resonance (dip 1), it can be observed that the electric fields form standing waves along the polarization direction (i.e., vertical direction) (Fig. 5.6a), and that the electrical fields form varying or propagating waves in horizontal directions. For the local field distribution corresponding
to the right dip, the interference patterns are varying in time in both vertical and horizontal directions, indicating no standing waves formation (Fig. 5.6b).

Based on previous studies, plasmonic cavity resonances are formed by the interfering gap plasmons confined between two metal surfaces. The dispersion relation of the surface plasmon mode at a semi-infinite metal-dielectric interface is given by:

$$k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$, where $\varepsilon_m$ and $\varepsilon_d$ are the permittivity of the metal and dielectric materials respectively, $\omega$ and $c$ are the radial frequency and speed of the electromagnetic waves in vacuum. In a MDM type of structures, the surface plasmons coupling between two close metal/dielectric interfaces causes the splitting of single

![Graph showing comparison of dip wavelengths versus nanoantenna side width](image)

**Figure 5.7.** Comparison of dip wavelengths versus nanoantenna side width obtained from the experimental, simulation and analytical resonant condition results.
surface plasmon mode into two (symmetric and anti-symmetric) \cite{11, 17}. The symmetric mode has higher energy than the anti-symmetric mode, and is ignored here. The dispersion relation for the anti-symmetric mode is given by Eq. 5.1, where wave vectors in the metal and dielectric are related with gap plasmon wave vector \( k_{\text{gap}} \) by the expressions

\[
 k_m = \sqrt{k_{\text{gap}}^2 - \varepsilon_m \omega^2 / c^2} \quad \text{and} \quad k_d = \sqrt{k_{\text{gap}}^2 - \varepsilon_d \omega^2 / c^2} .
\]

As a result of constructive interference between incident and reflected gap plasmon waves the antinode is always formed at the edge. The resonance condition for isolated plasmonic nanocavities can be expressed as in Chapter 3:

\[
k_{\text{gap}} L = (2n+1)\pi, \quad n = 0, 1, 2, 3, \ldots ,
\]

where \( k_{\text{gap}} \) is the gap plasmon wave vector\cite{17} of the anti-symmetric mode and can be calculated using Eq. 5.1, and \( L \) is side width of the nanocavity. The integer \( 2n+1 \) represents the number of antinodes formed by the interfering surface plasmon waves. The local field distributions show that \( n=2 \) for the left resonance dip (dip 1). A comparison of the resonance wavelength obtained from experiments and simulations and calculated from Eq. 5.1 is showed in Fig. 5.7. Good agreement between calculated and experimental and numerical results is achieved.
5.4 Matching the Cavity Resonance with the P3HT Emission

It is necessary for lasing applications of plasmonic nanocavities with active materials that the cavity resonance wavelength should be closer to the emission peak for enhanced photon emission. The cavity resonance can be tuned by varying the gap thickness and size of the metal nanostructures. As discussed above in this chapter and the

![Emission spectra of P3HT film](image)

**Figure 5.8. Emission spectra of P3HT film**

last, the cavity resonance shows a red shift with decreasing gap thickness and increasing size of the metal nanostructures. As shown in Fig. 5.8, upon excitation of 532nm laser, a major emission peak of a P3HT film was observed around 700nm but the experimental and the simulation results (Fig. 5.3 and 5.5) of Ag/P3HT/Ag nanoantennas of above mentioned side widths and gap thickness didn’t provide any cavity resonance close to the
emission peak wavelength of P3HT. In order to match the emission and the cavity resonance wavelengths together, we simulated 2D array Ag/P3HT/Ag nanoantennas of smaller side widths and larger gap thickness in comparison to the above discussed nanoantennas. The thickness of Ag and the glass substrate and the period were the same as used for the nanoantennas discussed before. We found that for the P3HT thickness of 30nm and ~100nm for the side widths of metal nanostructures, the cavity resonance was observed at the wavelengths ~700nm, providing enhancement in the local electric field

![Image of transmission spectra](image)

**Figure 5.9.** Simulated transmission spectra of a 2D array of Ag/P3HT/Ag nanoantenna array (a) and the local field enhancement spectra (b). Here the P3HT gap thickness (30nm) is larger than of the nanoantennas as presented in Fig. 5.5.

(field inside the cavity i.e. in the P3HT region) corresponding to the dips in the simulated transmission spectra (Fig. 5.9). This cavity resonance mode shows a red shift with
increase in side width of nanoantennas. In spite of the cavity resonance mode around 700nm, other resonance modes were observed which also shift with change in side width of nanoantennas (Fig. 5.9). It may possible to observe emission enhancement from P3HT by fabricating the nanoantennas with similar parameters as used in the simulations.

5.5 Summary and Future Work

In conclusion, we have fabricated 2D arrays of plasmonic nanoantennas, which are composed of a thin layer of conjugated polymer sandwiched between two metal cuboids. We experimentally and numerically studied the optical transmission of nanoantennas arrays, and numerically calculated their local field spectra. It is shown that for the nanoantennas with conjugated polymer gap, cavity resonance modes can be excited. The cavity resonance modes produce dips in the transmission spectra and peaks in the local electric fields. The cavity resonance modes and their wavelengths vary systematically with the size of the nanoantennas at a constant gap size. We have found the nanoantenna parameters to match the cavity resonance and emission wavelengths of P3HT. Matching the emission and the cavity resonance together these nanocavities with emitter inside can find the potential application in lasing.

However the main goal of the ongoing nanoantenna project is to fabricate metal-dielectric-metal nanoantennas for single molecule SERS studies. In the next step we will fabricate the MDM nanoantennas with a gap thickness as predicted by the numerical simulations shown in chapter 4 for the SERS studies at single molecule level and the
nanoantennas with light emitter inside for the lasing applications as discussed above in this chapter.
REFERENCES


CHAPTER 6

Plasmon Coupling between One Dimensional Ag Nanoparticles and GaAs Nanowires

6.1 Introduction

Plasmonics or surface plasmon based photonics has attracted continued research interest with the potential of integrating photonics and electronics into a single platform on nanometer scales. The small wavelengths of surface plasmons make it possible to scale down significantly the dimensions of photonic devices to match that of electronic circuits. The local field enhancements brought by the surface plasmon excitation lead to the enhanced emission or absorption of light in light emitting, photodetection and photovoltaic devices [1-7].

Recent studies show interesting behaviors of plasmon coupling in various kinds of nanostructures [8-13]. For example, plasmon coupling between two metal nanoparticles in close proximity leads to a shift in the resonance wavelength with nanoparticle gap [8-10, 14]. Coupling of nanoparticle plasmons with excitons in semiconductor nanowires can lead to a stronger and blue-shifted emission [12, 15, 16]. Optical absorption of nanowires with metal nanoparticles can be resonantly increased at wavelengths that are widely tunable.
In this chapter, we present a new type of composite nanomaterials composed of GaAs nanowires and sheets containing periodical Ag nanoparticle and nanowire arrays, and study their optical absorption properties by using numerical simulations. We demonstrate that such composite nanostructures exhibit greatly enhanced optical absorption due to the resonant excitation of surface plasmons in the Ag nanostructures.

Figure 6.1. Schematics of the Ag/GaAs composite nanostructure; (a) GaAs nanowire with 1D array of Ag nanoparticles and (b) GaAs sheet with 1D array of nanowires. GaAs and Ag structures are separated by a thin SiO$_2$ layer of same length and width.

and study their optical absorption properties by using numerical simulations. We demonstrate that such composite nanostructures exhibit greatly enhanced optical absorption due to the resonant excitation of surface plasmons in the Ag nanostructures.
First we present the optical absorption of GaAs nanowires containing Ag nanoparticles arrays. Interestingly, for the nanoparticles of size larger than a certain value, de-enhancements in the absorption can be observed. The resonant wavelength of absorption enhancements increases linearly with nanoparticle size and with little dependence on nanoparticle separation. The enhancements in nanowire absorption increase with nanoparticles separation, while decrease with nanoparticles sizes.

The absorption enhancement peaks of GaAs nanowires with Ag nanoparticles can be tuned only over a short wavelength range. To acquire a wide tunable range, we simulated infinite sheets of GaAs with a 1D array of Ag nanowires. Increasing the dimensionality of both the GaAs and the Ag led to absorption enhancement peaks that can be tuned over a wide wavelength range. The resonant wavelength changes with L of Ag (L is as represented in Fig 6.1). The absorption enhancement first increases with L but after a certain L, it decreases and finally disappears for L greater than a certain value. The response of the two types of structures will be compared in detail below.

6.2 Design and simulation

A schematic diagram of the nanoparticle/nanowire composite structure is shown in Fig. 6.1a. The design and geometrical parameters are based on the structure and feature sizes that are achievable with top-down nanofabrication techniques. A one dimensional array of Ag nanoparticles is placed on top of the GaAs nanowire; and a thin silicon dioxide layer is placed between them for electrical isolation. The width and thickness of GaAs are set to 50nm and 60nm respectively. Ag nanoparticles have the same width as
that of the nanowire and their thickness is fixed at 30nm. The length (L) and periodicity (d) are varied to explore their effects on the nanowire absorption. SiO₂ layer has the same dimension as the Ag nanoparticle except that its thickness is fixed at 10nm.

In simulations, the Lorentz dispersion model \( \varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_0^2}{(\omega_0^2 - i\omega\delta - \omega^2)} \) is utilized to describe the complex permittivity of GaAs, where the parameters, \( \varepsilon_\infty=7.8 \), \( \varepsilon_s=12.26 \), \( \omega_0=4.725\times10^{15}\text{rad/s} \) and \( \delta=4.74\times10^{12} \text{Hz} \) were obtained by fitting the previously measured complex permittivity in the frequency range between 325THz and 700THz (Fig. 6.2) [17]. In Fig. 6.2, symbols corresponds to the measured values of the dielectric permittivity at different frequencies and the lines are obtained by fitting the

![Figure 6.2. Frequency dependence of the GaAs permittivity Red lines are best fits with the Lorentz dispersion model.](image)

previously measured complex permittivity in the frequency range between 325THz and 700THz (Fig. 6.2) [17]. In Fig. 6.2, symbols corresponds to the measured values of the dielectric permittivity at different frequencies and the lines are obtained by fitting
measured data to the Lorentz model. The Drude model was utilized to describe the permittivity of silver, with parameters as described in chapters 3 and 4.

To excite the surface plasmons at the metal-dielectric interface, the GaAs nanowire is illuminated by linearly polarized light perpendicularly from the top (Fig. 6.1a), with the polarization parallel to the nanowire. The optical absorption is calculated by integrating the Poynting vectors around the nanowire surface, and the absorption enhancements are obtained by normalizing the absorption spectra of nanoparticle-loaded nanowires by that of a bare GaAs nanowire of the same size.

6.3 Result and Discussion

Representative calculated absorption enhancements at different nanoparticle periods and sizes are shown in Fig. 6.3a-d. One observation is that when the length of the nanoparticles is less than 100nm, the absorption spectra exhibit a resonant peak with its peak wavelength increasing with the increase of the nanoparticle length (L). Meanwhile, the resonant peak height in the absorption spectra decreases with gradual increase of the particle length (L). Interestingly, when the nanoparticle length L is larger than 100nm, the enhancement peaks disappear and the peaks of de-enhancements or dips emerge. Fig. 6.4a shows the peak wavelengths of the absorption enhancements as a function of the nanoparticle length. An approximate linear increase of the resonant wavelengths with the increase of nanoparticle length L can be observed. A close analysis of these absorption spectra reveals that the resonant wavelengths of these absorption peaks also have slight dependence on nanoparticle periods. Specifically, for small L/d ratios (<0.4), the resonant
wavelength exhibits negligible dependence on the particle period; while for large L/d

Figure 6.3. Nanowire absorption enhancements calculated for different nanoparticle periodicities: (a) d=120nm; (b) d=140nm; (c) d=160nm; (b) d=200nm.

The particle size L is varied from 60nm 160nm.

ratios (>0.4), the resonant wavelength shifts towards red when the period decreases.

The linear dependence of the plasmon resonance wavelength on the nanoparticle size has been observed previously in other systems, and can be attributed to a phase retardation effect for particle size above 5nm. Previous studies have shown that near field
between nanoparticles can lead to shift in a plasmon resonance wavelengths. For a 1D or a finite 1D array of nanoparticles, this resonant wavelength shift decays monotonically with interparticle gap when nanoparticles are relatively small\[10, 19\], but decays non-monotonically for relative large particles\[10, 19\]. The period-dependence of the resonant wavelengths shown above indicates the effect of near field coupling between Ag nanoparticles; and it can be seen from Fig. 6.4a that the resonant wavelength is a non-monotonic function of the particle separation in our system.

As depicted in Fig. 6.3 the enhancement of optical absorption varies among the particles with the same period but different lengths (L) and for a particular particle length it also varies with period (d). It has been shown that for small particles only lower order

**Figure 6.4.** (a) Resonant wavelength of the absorption enhancements as a function of the nanoparticle size at different periodicities. (b) Peak absorption enhancements as a function of the Ag nanoparticle period/wavelength for different particle sizes L=60, 70, 80, and 90nm.
surface plasmon modes occur. As the size of the particles increase, the lower order modes shift towards longer wavelengths and the higher order modes come into existence at the shorter wavelengths of the spectra. In our case, when $L/w<2$ (small particles) at a constant $d$, only single surface plasmon resonance modes ($1^\text{st}$ order) occur; they shift towards longer wavelengths as the particle length increases (i.e. $L/w$ increases), and the peak enhancement goes down. The enhancement peak disappears for the particles $L \geq 100$nm (i.e. $L/w \geq 2$) and dips appear in the absorption spectra instead of peaks. The change in the extinction intensity of surface plasmon modes with size of particles has been observed in different systems [20, 21]. We found that the decrease in absorption enhancement may be due to the optical properties of GaAs. It has also been shown that there is a drastic decrease in absorption of GaAs for the wavelengths above 500nm and that there is no absorption above $\lambda \approx 900$nm [22]. The enhancement due to plasmon resonance may not be enough to compensate for the decreasing absorptivity of GaAs in the higher wavelength region. It is also noted that for the longer particles second order (2$^{\text{nd}}$ mode) plasmon resonance modes appear at the shorter wavelengths and shift towards the longer wavelengths with further increase in $L/d$, for example: a second order mode appears at $\sim 480$nm for a particle of length 160nm ($L/w=3.2$) and a period of 200nm is as shown in Fig. 6.3d. It is clear from Fig. 6.4b that for the same particle size but different periods the enhancement becomes maximum when the period is close to the resonance wavelength (grating effect) i.e. $d = \frac{\lambda}{n_{\text{GaAs}}} = \frac{\lambda_{\text{GaAs}}}{d_{\text{GaAs}}}$ where $d$ the period, $\lambda$ the wavelength of light in the free space, $n_{\text{GaAs}}$ the refractive index of GaAs at the resonance
frequency and $\lambda_{\text{GaAs}}$, the wavelength of light in GaAs corresponding to resonance wavelength ($\lambda$) in the free space.

### 6.4 Tuning the absorption enhancement

As discussed above, GaAs nanowires with 1D array of nanoparticles have a narrow range of tunable optical absorption enhancement wavelength. At a constant particle width of 50nm, enhancement of optical absorption cannot be observed for the particles $L \geq 100$nm and the wavelength beyond 650nm. We found that the absorption enhancement peaks can be observed for the particles $L \geq 100$nm, if width ($w$) of the particles is increased. To obtain a wide range of tunable absorption peak wavelengths, we simulated 1D array of infinitely long Ag nanowires placed on the top of an infinite sheet of GaAs, separated by a SiO$_2$ spacer. The schematic representation of simulated structure is as shown in Fig 6.1b. Thickness of each component is same as used in GaAs nanowire/Ag nanoparticles simulations. To make comparing the results easier, the same notations are used for the structures presented in Fig. 6.1a and b. Thus in Fig 6.1b, L does not mean the long dimension. As discussed above, for Fig 6.1a, we studied the absorption enhancement by changing L and keeping d constant. In Fig. 6.1b, Ls are comparable to those as used in Fig.6.1a and we also studied the same effect by changing L but the main difference from Fig. 6.1a is that the d was made infinitely large. We calculated the absorption enhancement of GaAs sheet by varying L of the Ag nanowires at different constant periods (d). The periods are chosen larger than that used in the 1D array of nanoparticles so that structures with a wider variation in Ag L can be simulated. In order
to calculate the absorption enhancement, plane polarized electromagnetic wave was used to excite structures from the top with an electric field direction as shown in Fig 6.1b. The same material parameters and procedure to calculate the absorption enhancement were employed as described in section 6.2.

6.4.1 Results

![Figure 6.5](image1.png)

**Figure 6.5.** Absorption enhancement of infinite GaAs sheet for different nanowire periodicities: (a) d=220nm; (b) d=260nm and (c) d=300nm. The Ag L is varied from 60nm to 280nm.

The absorption enhancement of a GaAs sheet when varying L for Ag nanowires at three different periods (d) 220,260 and 300nm is shown in Fig. 6.5. The absorption spectra reveal that the occurrence of two resonant peaks i.e. two modes at longer and shorter wavelengths (1\textsuperscript{st} and 2\textsuperscript{nd} modes respectively). The results show the red shift of the absorption enhancement peak wavelength for increasing in L of the Ag nanowires. In the case of 1D array of Ag nanoparticles, the resonance enhancement peak of the 1\textsuperscript{st} mode disappears for L≥100 nm. Using a 1D array of Ag nanowires, the tunability of absorption
enhanced peak wavelengths significantly increased and enhancement in optical absorption of the 1st mode can be achieved for Ag nanowires beyond L=100nm. It is interesting to note that when L ≤ 120 the mode at shorter wavelength (2nd mode) doesn’t move with increase in L and no or very small absorption enhancement was observed while for the nanowires L >120nm, the resonance wavelengths show significant red shift with increasing absorption enhancement as L increases.

![Graph showing resonance wavelength vs L for first and second mode](image)

**Figure 6.6.** Resonant wavelength of the absorption enhancements as a function of the nanowire L at different periodicities; (a) for the first mode and (b) for the second mode.

The variation of resonance wavelength with Ag nanowire L is shown in Fig. 6.6. The resonance wavelength showed an almost linear increment with L for the first mode (Fig. 6.6a). It did not show any periodic dependence for the nanowires L≤120nm but for L≥120nm the resonance wavelength shifts towards longer wavelength with decreasing period i.e. the decrease in the nanowire separation, and the shift goes on increasing as L
increases (decreasing the nanowire separation). This may be due to inter-wire plasmon coupling between two nanowires as a result of the decrease in the distance between them. Interestingly, for nanowires with $L \leq 120 \text{nm}$, the resonance wavelength for the second mode almost remains constant but for $L > 120 \text{nm}$, it shifts towards longer wavelength with increasing $L$ (Fig. 6.6b). To scale the behavior of resonance wavelength shift with $L$, we plotted the shift in resonance wavelength relative to the initial resonance wavelength ($\Delta \lambda / \lambda_o$) with the gap between nanowires divided by square of $L$ [Gap/(L$^2$)]. Interestingly, resonance modes for the nanowires of different periods follow the same scaling law as represented in Fig. 6.7.

The variation of absorption enhancement for the 1$^{\text{st}}$ and 2$^{\text{nd}}$ modes with $L$ of the Ag nanowires is shown in Fig. 6.8. As represented in the figure, the amplitude of the

Figure 6.7 Scaling of resonant wavelength of absorption enhancements; (a) for the first mode and (b) for the second mode.
absorption enhancement for the 1\textsuperscript{st} mode increases with increase in L and becomes maximum for L=120nm; for L>120 the enhancement goes on decreasing and finally disappears after a certain L. On the other hand absorption of the 2\textsuperscript{nd} mode remains almost constant up to L= 120 then it starts to increase as L increases and becomes maximum for the nanowires with the largest L used in our simulations. Thus, we found that L=120 as the critical length, for L<120 absorption due to the 1\textsuperscript{st} mode is prominent and for L>120nm absorption enhancement due to the 1\textsuperscript{st} mode decreases, while absorption due to the 2\textsuperscript{nd} increases as L increases.

Figure 6.8. Absorption enhancements as a function of the nanowire L at different periodicities. (a) for the 1\textsuperscript{st} mode and (b) for the 2\textsuperscript{nd} mode.
The variation of resonance wavelength and the absorption enhancement depend

Figure 6.9. Local electrical field electric field vectors and phase representation in an incident plane through the middle of the nanowire at the resonant frequency (552THz) of the first mode for L=60nm (a-b); at the resonant frequency (624THz) of the second mode for L=160nm (c-d) and at the de-enhancement resonant frequency (339THz) for L=160nm (e-f). For all three cases a period of 200nm is taken.
upon L of the nanowires and the material property of GaAs. For small L only lower order surface plasmon modes are observed. As L increases, they broaden and shift towards longer wavelength. For large L, higher order surface plasmon mode (2\textsuperscript{nd} mode) appears at the shorter wavelength and shifts towards longer wavelength with further increase in L. The decrease in absorption enhancement at the longer wavelengths may be due to drastic decreases in the absorption of GaAs at long wavelength range [22] and the plasmon contribution may not be enough for the absorption enhancement.

6.5 Local field distribution

To gain a better understanding of plasmon coupling in such Ag/GaAs composite systems, we also calculated the local electrical field distribution in the plane through the middle of the nanowires and sheets. In the case of the GaAs nanowires, vector and phase representations of the electric field are shown in Fig 6.9. The colors correspond to the magnitude of the instantaneous electric field where red and blue colors represent the maximum and minimum of the electric field respectively. For the 1\textsuperscript{st} modes one minimum and one maximum (Fig. 6.9b) and for the second modes two minima and two maxima are observed (Fig. 6.9 d) in the SiO\textsubscript{2} gap region. For the first resonant excitation (1\textsuperscript{st} mode), the electrical field around the nanoparticle is significantly enhanced (~17 times of the incident electric field, Fig. 6.9b), due to coupling of the electromagnetic energy with that of the surface plasmons. The vector representation of the near field shows the electric field profile with little inter-particle coupling effect. The plasmon enhanced electric field leading to the high localization of the incident energy has an
evanescent wave in the perpendicular direction propagating away from the surface. The decay length of the field in the dielectric is of the order of half the wavelength of the incident light and that in the metal is determined by its skin depth. As evident from Fig. 6.9 for the 1st resonant excitation (1st mode Fig. 6.9a), the local field intensity in the dielectric is significantly greater than in the case when the excitation wavelength is in the

Figure 6.10. Local electric field vectors and phase representation in an incident plane through the middle of GaAs sheet at the resonant frequency (475THz) of the first mode for L=60nm (a-b); at the resonant frequency (520THz) of the second mode for L=160nm (c-d). Period is taken as 300nm.

de-enhancement for nanowire absorption (for L=160nm at 339THz≈ λ=880nm) (Fig. 6.9f) while profile of near field distribution is the same as that of the resonant enhancement at the 1st mode. For the 2nd resonant excitation (2nd mode) near electric field enhancement (Fig. 6.9d) is just 1.31 times larger than that of electric field at the de-
enhancement resonance frequency (Fig. 6.9f) but a small absorption enhancement peak can be observed at the lower wavelength. It shows that de-enhancement at the higher wavelength may also be related to the material properties of the semiconductor which causes the quenching of the 1st order plasmon resonance in that region. In the case of the GaAs sheet with Ag nanowires, similar electric field distribution profiles are seen for the 1st and the 2nd modes as shown in Fig. 6.10.

6.6 Conclusion

In summary, we have shown by FIT simulations that the plasmon resonance coupling between metal and semiconductor structures makes the spectral response widely tunable, and several applications can be envisioned including chemical and biological sensing and photovoltaics. Surface texturing semiconductor nanowires with metal nanoparticles and varying the size and the period of the metal nanostructures allows the optical response and local charge concentration to be modulated at different parts of the nanowire, which could lead to greater detection limits in nanowire sensors. The Ag nanostructure pitch and dimension should be optimized such that the diffraction wavelengths in the semiconductor lie in close proximity to that of the plasmon resonance wavelength of the individual metal nanostructures for maximum light absorption efficiency. It is possible to design arrayed GaAs photodetectors which could provide not only information about the intensity of the illuminating light but can be used for a wide range of optical signal processing.
REFERENCES


CHAPTER 7

Conclusion

We have developed a simple method of detecting sequence specific transcription factor-DNA binding by using surface enhanced Raman scattering (SERS). DNA molecules with potential protein binding sites labeled with dye molecules were immobilized on colloidal metal nanoparticles; the binding of proteins protects these DNA molecules from complete digestion by exonuclease enzyme, and can be detected by the SERS signals before and after the exonuclease digestion. We demonstrated the binding of WT1, a zinc finger transcription factor with DNA sequences derived from the promoter of the human vascular endothelial growth factor (VEGF).

Sufficient enhancement in the electric field can be achieved when the gap between the nanoparticles is of few nanometers. But in colloidal nanoparticles systems the gap cannot be controlled therefore high field enhancement regions or hot spots are rarely found which makes SERS reproducibility extremely low using them as a single molecule SERS substrates. We discussed the design and the fabrication of the plasmonic MDM nanoantennas which can be fabricated with a controlled gap size. By proper designing these nanoantennas, the local field can be enhanced significantly. The large local field enhancement and the potential control of the gap thickness using atomic layer deposition making this new nanoantenna design very promising candidate for single
molecule SERS applications. We fabricated some of MDM nanoantennas and used as a substrate for the SERS. The SERS enhancement factor of $10^7$ (not included in the dissertation) was obtained, however we still need to fabricate the nanoantennas of optimized dimension as suggested by the numerical simulations for single molecule SERS applications.

We have also fabricated 2D arrays of plasmonic nanoantennas, which are composed of a thin layer of P3HT (a conjugated polymer) sandwiched between two metal cuboids. It is shown that for the nanoantennas with conjugated polymer gap, cavity resonance modes can be excited. We have found the nanoantenna parameters to match the cavity resonance and emission wavelengths of P3HT. Matching the emission and the cavity resonance together these nanocavities with emitter inside can find the potential application in lasing.

We have shown by FIT simulations that the plasmon resonance coupling between metal and semiconductor structures makes the spectral response widely tunable, and several applications can be envisioned including chemical and biological sensing and photovoltaics.
LIST OF PUBLICATION

1. Bhuwan Joshi and Qi-Huo Wei, “Cavity resonances of metal-dielectric-metal nanoantennas” Optics Express, 16, 14, 10315-10322 (2008) [Chapter 4]


6. Xiuli Zhou, Qiangmin Wei, Lumin Wang, Bhuwan Joshi, Qi-Huo Wei and Kai Sun “Enhanced photoluminescence from gallium arsenide semiconductor coated with

7. Bhuwan Joshi and Qi-Huo Wei, “Plasmon Coupling between One Dimensional Ag Nanoparticles and GaAs Nanowires” (to be published) [Chapter 6]