Surface enhanced Raman scattering effect and plasmonic properties of metal nanobowls

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**SURFACE ENHANCED RAMAN SCATTERING EFFECT
AND PLASMONIC PROPERTIES OF METAL
NANOBOWLS**

MA YUN

SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES

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MA YUN

School of Physical & Mathematical Sciences

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in fulfillment of the requirement for the degree of
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Summary

Plasmonics is a rapidly emerging subdiscipline of nanophotonics that studies the interaction between the light and metal particles at the nanometer scale, based on the properties of both bounded/localized and radiative/propagating surface plasmon. Its deep penetration into multidisciplinary subjects makes its application widely range from surface enhanced Raman spectroscopy (SERS) for biomolecule and biological agents identification, detection and sensing, near-field optics and tip-enhanced Raman spectroscopy to electromagnetic propagation with metal-based plasmonic waveguides.

In this thesis, we used pulsed laser deposition technique combined with nanosphere lithography method to fabricate the metal nanobowl structure. This method is able to accurately control several key parameters that can tune plasmonic properties of the nanobowl structure. These parameters include material species, bowl size, bowl wall thickness as well as interspacing between nearest nanobowls. This method is also flexible to fabricate multilayered nanobowls by depositing alternate target materials on polystyrene sphere arrays. The flexibility and advances of the fabrication method provide us a chance to systematically study plasmonic properties of nanobowl structure.

Au and Ag metal nanobowl substrates exhibited SERS capability to detect low concentration molecules ($1\mu\text{M/L}$ in molarity), such as rhodamine 6G, crystal violet, 3-mercaptopropionic acid, methylene blue and brilliant cresyl blue. The SERS observation on hybrid structures between Ag nanobowls with Ag tetrahedrons and between Au

nanobowls with Au nanoparticles indicates that it is possible, via tuning surface plasmon resonances, to break Raman selection rules and therefore to excite the original Raman inactive vibrations. This holds the promise for hybrid structures to detect the biomolecules whose molecular vibrations are originally Raman inactive and cannot be measured through normal Raman selection rule.

Inelastic emission intensity images of Au nanobowl showed the electromagnetic enhancement orientation dependence on the incident laser polarization. For the bowl size much bigger than the incident laser wavelength, the strongest electromagnetic enhancement takes place at the bowl rims with the orientation parallel to the incident laser polarization; while for the bowl size smaller than the incident laser wavelength, the strongest electromagnetic enhancement takes place at the bowl rims with the orientation perpendicular to the incident laser polarization. Two different enhancement mechanisms explain the discrepancy on the size effect. However, such observation was not obtained from Ag nanobowl structures. Ag tends to create hot spots at the interspacings of the nanobowl arrays and is independent of the incident laser polarization. Therefore Au nanobowl arrays can be served as the plasmonic waveguides with the controllable waveguiding direction as well as SERS sensor.

The advances in computational electromagnetic design guide us to fabricate the desired nanobowl structures which can be applied in the areas based on both localized and propagating surface plasmons. Numerically, surface plasmon is the exact solution to Maxwell's equations. We used finite element method (FEM) and finite-difference time-domain (FDTD) to simulate plasmonic properties of various metal nanobowls with different bowl sizes and bowl wall thicknesses. The simulation results on the electromagnetic field distributions confirm that positions of strongest EME for Au and Ag

nanobowl arrays are different leading to different polarization dependence behaviors. The simulation results also suggest that adjusting bowl wall thickness can tune the plasmonic resonance frequencies and the variation is regularly changing and therefore is controllable and desirable.

In all, metal nanobowls have shown the potentials in the practical application of both sensing and waveguiding.

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Acronyms

ALD	atomic layer deposition
APD	avalanche photodiode
ATIR	attenuated total internal reflection
BCB	brilliant cresyl blue
CCD	charge coupled device
CE	chemical enhancement
CV	crystal violet
DDA	dipole discrete approximation
EM	electromagnetic
EME	electromagnetic enhancement
FEM	finite element method
FDTD	finite difference time domain
FWHM	full width at half maximum
HOMO	highest occupied molecular orbital
IMI	insulator-metal-insulator
L	longitudinal
LIPSS	laser induced periodic surface structure
LOMO	lowest occupied molecular orbital

Acronyms

xiv

MB	methylene blue
3-MPA	3-mercaptopropionic acid
MIM	metal-insulator-metal
NA	numerical aperture
NSL	nanosphere lithography
PDE	partial differential equation
PH	plasmon hybridization
PL	photoluminescence
PLD	pulsed laser deposition
PS	polystyrene sphere
R6G	rhodamine 6G
RF	radio frequency
RRS	resonance Raman scattering
SDS	sodium dodecyl sulfate
SERS	surface enhanced Raman scattering/spectroscopy
SP	surface plasmon
SPP	surface plasmon polariton
SPR	surface plasmon resonance
T	transverse
TE	transverse electric

Acronyms

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TED	total energy density
TM	transverse magnetic
TERS	tip enhanced Raman scattering/spectroscopy
TIR	total internal reflection

Chapter 1

Introduction

Based on the advances of nanoscience and nanotechnology, the various physical properties of a variety of nanomaterials, such as acoustic [1, 2], optical [3-12], electronic [13-20], magnetic [21-25] as well as thermal properties [26-29], have been greatly explored since the last decade of twentieth century. The single and a combination of two or more properties of nanoscale materials make a wealth of practical, robust and commercializable technological applications possible. Among them, nano-optics/nanophotonics has been the most rapidly developing and growing research field in recent years because of its deep penetration into multidisciplinary subjects and its wide and significant applications ranging from surface enhanced spectroscopy for biomolecule and biological agents identification, detection and sensing [30-42], near-field optics [43-46] and tip-enhanced Raman spectroscopy [47-50] to electromagnetic propagation with metal-based plasmonic waveguides [51-55].

Briefly, nanophotonics studies the behavior of light on nanoscale materials. The fact that the energy of light lies in the range of electronic and vibrational transitions makes great efforts advance the field of optics to the nanometer scale. It addresses the broad spectrum of optics on the nanometer scale both in basic science and in technology. In the basic science side, many explorations have been made in atom-photon interactions in the

optical near-field and their applications for atom trapping and manipulation based on the properties of propagating or localized surface plasmons. In the technology side, nanophotonics offers solutions to decades-old problems such as light can not be focused to dimensions smaller than roughly half a wavelength due to diffraction limit. It is indeed a timely research topic which fills in the blank area where a miniaturized electronic/photonic device can work from gigahertz (GHz) to terahertz (THz) and even to petahertz (PHz) at a nanometer scale size [3-20] as illustrated in Figure 1.1.

Figure 1.1 Illustration of technological development of nanophotonics.

1.1 Background of plasmonics

Plasmonics is a subdiscipline of nanophotonics that studies optical properties of metal-dielectric system at the nanoscale, based on surface plasmon (SP) theory. Surface plasmons are the collective oscillations of electromagnetic (EM) waves that propagate

along the interface between conductors and dielectrics. We first review the history and development of SP.

The physical phenomenon of SP was first observed by Wood R.W. in 1902 [56]. Prof. Wood found the unexplained phenomena in optical reflection measurement on metallic gratings. In 1904, Garnett J.C.M. observed the bright colors in metal doped glasses based on the then newly emerging Drude model of metals [57]. The further understanding of light scattering by spherical particles was developed by Mie G. [58] in 1908, which is still widely used to describe the optical response by spherical particles of any size, also known as Mie scattering theory. In 1956, Pines D. [59] theoretically predicted the characteristic energy losses experienced by fast electrons flowing through metals and called the collective oscillations of free electrons in the metal “plasmons”. In the same year, the term “polaritons” was introduced by Fano R. [60] for the coupled oscillation of bound electrons and light inside transparent media. In 1968, Ritchie R. et al [61] discovered the anomalous behavior of metal gratings as Wood R. W. did nearly seventy years ago. In the same year, Otto A., Kretschmann E. and Raether H. [62] presented methods to experimentally observe the optical excitation of SP on metal films. From then on, the properties of SP were extensively explored and well known, but the connection to the optical properties of metal nanoparticles has not yet been made. In 1970, Kreibig U. and Zacharias P [63] for the first time described the optical properties of Au and Ag nanoparticles in terms of SP. Researchers began to realize the importance of the coupling between the oscillation electrons and EM field, and the term “surface plasmon polaritons” was first introduced to describe such coupling by Cunningham S. L. in 1974 [64]. A breakthrough discovery happened in the same year by Fleischmann M. et al [65], who observed the strong Raman

scattering from pyridine molecules in the vicinity of roughened Ag surface. This observation led to the development of surface enhanced Raman scattering/spectroscopy (SERS), the symbol of transition point for SP from fundamental studies to more application driven research. Since then, plasmonics has been a rapidly growing multidiscipline aiming at exploiting SP for both scientifically and technologically important applications.

The number of scientific literatures is a clear indication to reflect the growth rate and importance of a research field. Figure 1.2 is the citation report of number of publications per year containing the key words “surface plasmon” in the title and their citations from 1990 to present sourced from the Web of Science. The charts show a continuous growing tendency in both publications and citations.

Figure 1.2 Charts for published items and citation in each year from web of science.

The reasons for the fast growth of plasmonics can be attributed to three advances. The first aspect is the advance of nanoscience and nanotechnology which enables the fabrication of plasmonic nanostructures with a variety of shapes, such as spheres, shells, triangles, prisms, rods, cubes and wires with controllable sizes. Both the physical methods,

such as electron beam lithography, focused ion beam milling and self-assembly, and wet chemical synthesis methods have provided routes to engineer complex metal nanostructures. The shape and the size are the important factors to determine plasmonic properties of metal nanostructures. For spherical nanostructures, it is easy to determine the plasmon resonance frequency by Drude model. A plasmonic resonance occurs when the negative real part of a metal particle's dielectric function is twice the value of the dielectric constant of the surrounding medium, i.e. $\epsilon_m = -2\epsilon_d$, because this resonance condition results in a strong extinction of light at the plasmon resonance frequency. But for non-spherical particles, i.e. the arbitrarily shaped nanoparticles, the plasmon resonance conditions become complicated as the electron oscillation becomes anisotropic and leads to shape dependent depolarization. The second aspect is the advance in computational EM design. For a given geometry of a nanoparticle or nanostructure, the degree of EME induced by resonant plasmons can be predicted by solving Maxwell's equations analytically and numerically. The third advance is the wide applications of plasmonics based on bound/localized and radiative/propagating surface plasmons, scientifically and technologically. In Section 1.2 we will review the literature and present a few outstanding application-driven research topics on plasmonics.

1.2 Literature review

The two main research areas can be distinguished based on SP modes: bound/localized and radiative/propagating SP. Based on localized SP theory, plasmonic nanostructures can be applied to anywhere that utilizes the amplified EM field, such as SERS detector in

bioscience and biotechnology, tip-enhanced Raman scattering (TERS) which can make Raman imaging with nanometer resolution possible, excitation of optical EM waves and enhancement of the absorption and photoluminescence in semiconducting films. Propagating SP can manipulate or guide light below the conventional diffraction limits using plasmonic waveguides, which is necessary for nanophotonic device applications.

1.2.1 Localized Surface Plasmons

Since the first experimental observation of SERS effect from pyridine molecules in the vicinity of roughened Ag surface in 1974, a variety of nanostructures that support localized SP mode have shown the capability as the biomolecular sensors. Lu Y. et al [32] reported that the Au nanocrescent moon structure with sharp edge can enhance local EM field and the electromagnetic enhancement (EME) factor of single nanocrescent moon is estimated larger than 10^{10} suggesting the promising application in ultrasensitive biomolecular detection using SERS. Xia Y.N. et al [35] used wet chemical synthesis method to fabricate Ag nanocube, nanobar and nanorice structures. These nanostructures all show the SERS activity. In addition, they present strong SERS signal dependence on their orientation relative to laser polarization. Levi G. et al [37] used thermal evaporation method combined with electron-beam lithography to fabricate Au nanoparticle arrays with narrow particle size distribution. They showed the optimization of SERS effect on the Au nanoparticle arrays by tuning the maximum of the SPR. One-dimensional nanostructure, the nanowire has also been reported to have SERS capability. Yang P.D. et al [41] used Langmuir-Blodgett technique to assemble aligned Ag nanowires with 50 nm in diameter and 2-3 μm in length. The pentagonal cross-sections and pyramidal tips of the nanowires result in EME factor to 10^9 and exhibit the potential to be used in ultrasensitive, molecule-

specified sensing using vibrational signatures. The more complicated geometry, the nanostar which is highly anisotropic, was fabricated by seed-mediated, surfactant-directed wet chemical synthesis method [66]. The nanostar shows the effect of polarization dependence on incident laser polarization.

The hybrid structure, the combined nanostructures with different size or different geometries have shown better sensitivity of SERS detection compared with the single nanostructure. More than that, the hybrid structure also shows the ability to tune the plasmon resonance frequencies and therefore to tailor the plasmonic properties. For example, Xu H.X et al [39] used hole-particle hybrid structure for SERS detection. They compared the SERS signals detected from single hole, single particle and hole-particle hybrid structure and found the hole-particle hybrid structure has the better SERS sensitivity than both single structures. Xu H.X. et al also used another hybrid structure, nanoparticle-nanowire system, to demonstrate the strong EME and SERS enhancement induced from the strong coupling between the nanowire and nanoparticle system. An important discovery is polarization dependence of SERS in such hybrid structure and the enhancement is remarkably insensitive to the detailed geometrical structures of the nanoparticles. Another example for hybrid structures is the core-shell structure, i.e. nanoshell, nanorice and nanocup, which have been introduced by Halas N.J. et al [42-43, 67, 68]. They describe the plasmon response of the hybrid structure as the interaction or hybridization of elementary geometries. And the large EM field enhancement can be used to perform SERS detection.

In addition to SERS sensing, the strongly localized SP can be used to concentrate light as demonstrated by high-harmonic generation using resonant plasmon field enhancement

[69]. This has been achieved by the local field enhancement induced by resonant plasmons within bow-tie-shaped Au nanostructures. The bow-tie arrays serve as numerous nanoantennas to confine the optical field to spatial scale far below the diffraction limit. Localized SP has also been utilized to improve the absorbance of Si solar cells [70]. Light scattering from metal nanoparticle arrays placed on top of a thin-film semiconductor layer can effectively fold the path of sunlight into the layer, strongly enhancing its effective absorption. Okamoto K. et al reported surface plasmon enhanced InGaN light emitter [71]. The PL enhancements are attributed to strong interaction between quantum wells and SPs. This discovery make quantum wells and SP coupling promising for developing solid state light sources with high emission efficiencies.

1.2.2 Propagating Surface Plasmons

The difficulty that the optical technology faces is the problem of classic diffraction limit. However, nanoscale electronic/photonic devices require that light must be confined and routed in dimensions much smaller than its wavelength to allow for sufficient miniaturization of chips. Propagating SP offer the solutions to eliminate the concern of diffraction limit by using radiative EM waves guiding along the plasmonic waveguides. Therefore, plasmonic devices actually are only limited in their size by the dimensions of the input-output coupler and the transmitting medium not the excitation light spot size or wavelength.

A variety of structures, such as metallic multilayer system, i.e. metal-insulator-metal (MIM) and insulator-metal-insulator (IMI), metal stripes, nanowires, nanoparticle chains have been fabricated to serve as propagating waveguides.

Verhagen E et al [45] reported that a nanoscale gap between two metal surfaces (MIM) can confine propagating SPPs to very small dimensions. They demonstrate the near-field probing of these SPPs, propagating with a 50 nm thick silicon nitride waveguide with Ag cladding layers for frequencies ranging from the blue to the near-infrared. Barnes W.L. et al [51] showed the coupled SPPs can provide effective transfer of excitation energy from donor molecules to acceptor molecules on opposite sides of metal films up to 120 nm thick in an IMI system. This discovery indicates that propagating SP may extend the subwavelength-scale manipulation of light of in the application of photochemistry, for example, channeling energy from absorbing species to reaction centers.

Ag and Au nanorods and nanowires have been reported another promising propagating plasmon waveguides [72, 73]. Light can be coupled in at one end of the rod/wire and observed emerge from the other, proving that plasmons did propagate along the rod/wire. Plasmon propagation also can be bent or split using appropriate plasmonic structures. In fact, plasmons can be manipulated in the same way that light has been manipulated in optics but with smaller size of optical components below the diffraction limit.

An alternative way to produce propagating SPP is using nanoparticle chains instead of using metallic multilayer system or metal stripes and wires. The interparticle coupling responsible for the giant local field enhancement at the gap between nanoparticles can form coherent propagation of SPPs with both transverse and longitudinal modes. Brongersma et al [74, 75] reported that at resonance the group velocity of longitudinal wave is twice the value of the transverse wave resulting from the stronger EM coupling for longitudinal waves than for transverse waves. Weber W.H. and Ford G. W. [76] also showed the same results as observed by Brongersma that the propagating SPPs radiate

along metal nanoparticle chains by dipolar interactions. Waele R D et al [77] demonstrated that plasmon resonant nanoparticle chains exhibit a nanoscale localized response to unfocused light that can be controlled by tuning the incident wavelength. These observations suggest that plasmon chains are nanoscale receivers and concentrators of light analogous to multielement radio wave antennas. This analogy inspires new design rules for other photonic functionalities, like guiding and redirecting light at the nanoscale. Knoester J. et al [78] theoretically studied the optical response of graded linear arrays of metal nanoparticle chains in which the center-to-center distances and the radii of the spheres change linearly along the chain. When light propagating from smaller to larger spheres the optical signal can be localized in a controlled way at an arbitrary subset of a few neighboring spheres by adjusting the incident light wavelength while when light propagating from larger to smaller spheres the optical signal does not show the regular change in optical response.

In all, as a rapidly developing multidiscipline, plasmonics has yielded scientifically and technologically significant phenomena based on light-metal interactions. In such a relative new area, there are still many chances to explore the new, useful applications as well as technologies.

1.3 Motivation and objectives

My PhD study at the Nanyang Technological University coincides with the establishment of the School of Physical and Mathematical Sciences (SPMS). I had the opportunity to build a home-made PLD system for our group, which extended the capability of the Group

into thin film fabrication. I started from designing, drawing, talking to vendor and as well as putting all components together and testing the system. Because the School was in a temporary location in the basement of School of Biological Sciences and there was no suitable lab for the PLD system, the system was eventually set up at the Singapore Institute of Manufacturing Technology (SIMTech) and it had to be relocated one more time at SIMTech due to the renovation of the lab before it was moved to the present new SPMS Building in 2008. This gave me a rare opportunity as a graduate student to be involved in setting up a research lab on my own and I had learnt a lot of this expedition. Although most of the efforts and results were not written into the thesis, the experience I gained will no doubt benefit me in the long term. Later on I moved to study metallic nanostructures, which is also a new direction for the Group. There are many simulation and theoretical studies of metallic plasmonic structures. However experimental work, especially those in the optical region is critically lacking due to the fact that the spot size of lasers focused using normal confocal technique is too big for such study. The work presented in the thesis was mostly related to plasmonics.

Semispherical-shells, also called nanobowls, are of great scientific and technological interest for many applications such as containers for microencapsulating and controlled delivery, catalysis and photonic crystals and devices, separation technology and so on [79-82]. Metallic nanobowls are especially interesting for plasmonic applications. The parameters of nanobowls, i.e. the bowl size, bowl wall thickness, interspacing between two nearest bowls and material species, offer four additional approaches to tune optical properties.

Both chemical and physical methods have been used to fabricate nanobowl arrays based on monolayer self-assembly of polystyrene spheres, also known as nanosphere

lithography (NSL) method. However, the nanobowl arrays fabricated by wet chemical method show inhomogeneous distribution of nanobowls with uncontrollable interspacing [79, 80]. The nanobowl arrays produced by physical method always contain the holes at the bottom of the nanobowls and the wall surfaces of the bowls are not smooth [81, 82]. These prevent the systematic study of plasmonic properties of metallic nanobowl system. Therefore, improved methods with much better control of the parameters are called for. Starting from setting up a PLD system, combined with NSL method, we have successfully developed a technique to fabricate nanobowl arrays with controllable parameters. This is also our motivation to systematically study the SERS effects and plasmonic properties of metal nanobowls.

The bowl size can be controlled by choosing the size of polystyrene spheres which are commercially available with the size from a few nanometers to a few hundred micrometers; the bowl wall thickness can be controlled by deposition parameters of the PLD system, such as laser power intensity, deposition duration, repetition rate and target-substrate distance; the interspacing of the nanobowls is determined by the interspacing of PS spheres and can be controlled by pre-heating the monolayer PS template at its glass temperature or using plasma etching; the material species can be controlled by using different material targets. Our objectives on this research project consist of two main aspects: first, to investigate the SERS effects on two main material species, i.e. Ag and Au nanobowls; second, to study the bowl size and bowl wall thickness effects on plasmonic properties of Ag and Au nanobowls. We also attempt to fabricate metal nanobowl based hybrid structures and investigate their plasmonic structures. Based on both experimental and simulated results, the Ag and Au nanobowls exhibit the great potentials in the applications of both sensing and waveguiding.

1.4 Organization

The rest of the thesis is organized as follows:

Chapter 2 reviews SP theory by solving Maxwell equations. Both bound/localized and radiative/propagating SP are described and derived by Drude model. A newly developed theory, plasmon hybridization (PH) theory, is also introduced as it provides the physical insight into the nature and origin of a plasmon.

Chapter 3 describes the fabrication method of metal nanobowls in detail. The fabrication method combines pulsed laser deposition (PLD) technique and nanosphere lithography (NSL) method.

Chapter 4 shows the experimental results of SERS effects on metal nanobowls. Five molecule species with low concentration are used as probe molecules. Both Au and Ag nanobowls exhibit the capability to be the efficient SERS-active substrates. The results of SERS effects on hybrid structure based on metal nanobowls are also presented.

Chapter 5 presents both the experimental and simulating results on plasmonic properties of metal nanobowls. The bowl wall size and bowl wall thickness effects are investigated.

Chapter 6 shows my other work during my Ph.D study which is based on the home-made PLD system.

Chapter 7 summarizes the main achievements and presents the future work.

Chapter 2

Theory of Surface Plasmon

In quantum physics, a plasmon is a quasiparticle that results from the quantization of plasma oscillations. Plasmons are collective oscillations of the free electron gas density and can couple with photons to form another quasiparticle called plasma polaritons. Surface plasmons (SPs), also known as surface plasmon polaritons (SPPs) are those plasmons that are confined to surfaces. They are the resonant interaction between the electromagnetic field of the light and the free electron oscillations at metal surfaces, which can propagate along the metal surface as a wave [83-86]. Such resonant interaction can be theoretically interpreted and predicted using classical electromagnetism by solving Maxwell's equations: solutions of Maxwell's equations applied along an interface between a metal with a negative permittivity and an insulator with a positive permittivity.

2.1 Electromagnetics of Plasmons

The electromagnetic analysis for surface plasmons (SPs) is the problem of solving Maxwell's equations subject to certain boundary conditions. Maxwell equations are four equations, describing Faraday's law of induction, Ampere's law, and Gauss's laws of electric and magnetic fields, respectively, and can be written as below:

$$\begin{aligned}
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} &= \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \\
\nabla \cdot \mathbf{D} &= \rho \\
\nabla \cdot \mathbf{B} &= 0
\end{aligned} \tag{2.1}$$

where $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic field densities and are measured in units of [volt/m] and [ampere/m], respectively; $\mathbf{D}$ and $\mathbf{B}$ are the electric and magnetic flux densities and are measured in units of [coulomb/m²] and [weber/m²] or [tesla], respectively; ρ and $\mathbf{J}$ are the volume charge density and electric current density of any external charges and are measured in units of [coulomb/m³] and [ampere/m²], respectively.

In the absence of external source, Maxwell's equations can be written as below:

$$\begin{aligned}
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} \\
\nabla \cdot \mathbf{D} &= 0 \\
\nabla \cdot \mathbf{B} &= 0
\end{aligned} \tag{2.2}$$

The optical properties of materials including dielectrics and conductors can be explained by the plasmon mode by considering the motion of an electron in the presence of electric field of the incident light. The force equation of an electron can be read as below:

$$\begin{aligned}
\sum \mathbf{F} &= m \frac{d^2 \mathbf{x}}{dt^2} = e\mathbf{E} - m\omega_0^2 \mathbf{x} - m\gamma \frac{d\mathbf{x}}{dt} \\
\frac{d^2 \mathbf{x}}{dt^2} + \gamma \frac{d\mathbf{x}}{dt} + \omega_0^2 \mathbf{x} &= \frac{e\mathbf{E}}{m}
\end{aligned} \tag{2.3}$$

Where the item of $m\omega_0^2 \mathbf{x}$ denotes a spring like restoring force due to the binding of the electron to the nucleus and $m\gamma \mathbf{v}$ denotes a friction-type force proportional to the velocity of

the electron, $\mathbf{v}$. ω_0 is related to spring-like resonant frequency and γ is a measure of the rate of collisions between electrons per unit time, which is normally of the order of 10^{13} Hz. Such model can describe three types of materials in terms of the limits of ω and γ .

- i For dielectrics, $\omega_0 \neq 0$, $\gamma \neq 0$;
- ii For conductors, $\omega_0 = 0$, $\gamma \neq 0$;
- iii For collisionless plasmas, $\omega_0 = 0$, $\gamma = 0$.

Assuming the electric field $\mathbf{E}(t)$ of incident light in equation (2.3) is a sinusoidal wave with frequency ω , $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$, then a particular solution of equation (2.3) describing the oscillation of the electron is $\mathbf{x}(t) = \mathbf{x}_0 e^{-i\omega t}$ and $\mathbf{x}(t)$ must satisfy:

$$-\omega^2 \mathbf{x}(t) - i\gamma\omega \mathbf{x}(t) + \omega_0^2 \mathbf{x}(t) = \frac{e\mathbf{E}}{m}$$

Therefore, the solution is:

$$\mathbf{x}(t) = \frac{\frac{e\mathbf{E}}{m}}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.4)$$

The corresponding velocity of the electron will also be sinusoidal $\mathbf{v}(t) = \mathbf{v} e^{-i\omega t}$.

$$\mathbf{v}(t) = \frac{d\mathbf{x}(t)}{dt} = -i\omega \mathbf{x}(t) = \frac{i\omega \frac{e\mathbf{E}}{m}}{\omega^2 + i\gamma\omega - \omega_0^2} \quad (2.5)$$

The polarization per unit volume $\mathbf{P}$ can be found from equation (2.4). Supposing that there is the total number of N dipoles per unit volume and the individual electric dipole moment is $\mathbf{p} = e\mathbf{x}$. Therefore, the polarization per unit volume will be:

$$\mathbf{P} = N\mathbf{p} = Nxe = \frac{Ne^2 \mathbf{E}}{\omega_0^2 - \omega^2 - i\gamma\omega} = \epsilon_0 \frac{Ne^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \mathbf{E} \equiv \epsilon_0 \chi(\omega) \mathbf{E} \quad (2.6)$$

The bulk plasmon frequency of the material is defined as:

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 m} \quad (2.7)$$

$$\text{therefore, } \chi(\omega) = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.8)$$

The electric flux density will be then:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 (1 + \chi(\omega)) \mathbf{E} = \epsilon_0 \epsilon_r \mathbf{E} \equiv \epsilon(\omega) \mathbf{E}$$

where the effective permittivity $\epsilon(\omega)$ is:

$$\epsilon(\omega) = \epsilon_0 + \frac{\epsilon_0 \omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.9)$$

The real and imaginary components of this complex dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ are given by:

$$\epsilon'(\omega) = \epsilon_0 + \frac{\epsilon_0 \omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (2.10)$$

$$\epsilon''(\omega) = \frac{\epsilon_0 \gamma \omega \omega_p^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

According to the limits of ω and γ , we can list the dielectric functions for different types of materials in the table 2.1. Table 2.2 lists dielectric functions of 14 commonly used metals with different units [87].

For conductors, the velocity of electrons is given by

$$\mathbf{v}(t) = \frac{d\mathbf{x}(t)}{dt} = -i\omega \mathbf{x}(t) = \frac{i\omega \frac{e\mathbf{E}}{m}}{\omega^2 + i\gamma\omega - \omega_0^2} \stackrel{\omega_0=0}{=} \frac{i e\mathbf{E} / m}{\omega + i\gamma} \quad (2.11)$$

The electric flux density $\mathbf{J}$ representing the flow of electric charge is defined

by $\mathbf{J} = \rho \mathbf{v}$, where ρ is the volume density, and $\rho = eN$, therefore $\mathbf{J} = eN\mathbf{v} = eN \frac{i e\mathbf{E} / m}{\omega + i\gamma}$.

Table 2.1 Frequency dependent dielectric function for different type of materials

	$\varepsilon(\omega)$	$\varepsilon'(\omega)$	$\varepsilon''(\omega)$
Dielectrics $\omega_0 \neq 0, \gamma \neq 0$	$\varepsilon_0 \left(1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)$	$\varepsilon_0 + \frac{\varepsilon_0 \omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$	$\frac{\varepsilon_0 \gamma \omega \omega_p^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$
Conductors (Drude Model) $\omega_0 = 0, \gamma \neq 0$	$\varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right)$	$\varepsilon_0 - \frac{\varepsilon_0 \omega_p^2}{\omega^2 + \gamma^2}$	$\frac{\varepsilon_0 \gamma \omega_p^2}{\omega(\omega^2 + \gamma^2)}$
Collisionless Plasmas $\omega_0 = 0, \gamma = 0$	$\varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2}\right)$	$\varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2}\right)$	0

Table 2.2 Bulk plasmon frequency ω_p , damping frequency γ

<i>metal</i>	$10^2 \gamma$ (μm^{-1})	ω_p (μm^{-1})	γ (μm)	ω_p (μm)	γ (eV)	ω_p (eV)	$10^{14} \gamma$ (Hz)	$10^{14} \omega_p$ (Hz)
Al	6.60	11.90	15.15	0.08	0.08	14.69	0.20	35.44
Au	2.15	7.28	46.51	0.14	0.03	8.98	0.06	21.68
Ag	1.45	7.27	68.97	0.14	0.02	8.97	0.04	21.65
Mo	4.12	6.02	24.27	0.17	0.05	7.43	0.12	17.93
Cu	0.73	5.96	136.61	0.17	0.01	7.36	0.02	17.75
Pb	16.30	5.94	6.13	0.17	0.20	7.33	0.49	17.69
W	4.87	5.17	20.53	0.19	0.06	6.38	0.15	15.40
Pd	1.24	4.40	80.65	0.23	0.02	5.43	0.04	13.10
V	4.89	4.16	20.45	0.24	0.06	5.13	0.15	12.39
Pt	5.58	4.15	17.92	0.24	0.07	5.12	0.17	12.36
Ni	3.52	3.94	28.41	0.25	0.04	4.86	0.11	11.73
Fe	1.47	3.30	68.03	0.30	0.02	4.07	0.04	9.83
Co	2.95	3.20	33.90	0.31	0.04	3.95	0.09	9.53
Ti	3.82	2.03	26.18	0.49	0.05	2.51	0.11	6.05

Ohm's law describes the conductivity properties of a material and is given by

$$\mathbf{J} = \sigma(\omega)\mathbf{E} \quad (2.12)$$

Therefore, the frequency-dependent conductivity for a conductor is described by:

$$\sigma(\omega) = \frac{i\epsilon_0 \frac{e^2 N}{\epsilon_0 m}}{\omega + i\gamma} = \frac{i\epsilon_0 \omega_p^2}{\omega + i\gamma} = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} \quad (2.13)$$

2.2 Surface Plasmon

In order to examine the properties of surface plasmon polaritons (SPPs), we apply Maxwell's equations (2.1) to a simple model which consists of a single flat interface between a conductor (metal) and a dielectric as shown in Figure 2.1. The dielectric function ϵ depends only on one spatial coordinate, namely z -direction. The non-absorbing half space (for $z > 0$) has a positive real dielectric constant ϵ_2 , while the conducting half space (for $z < 0$) has a dielectric function of $\epsilon_1(\omega)$ which consists of a negative real part and a positive imaginary part, i.e. $\epsilon_1(\omega) = \epsilon_{1R} + i\epsilon_{1I}$.

Figure 2.1 Geometry for SPP propagation at a single interface between a metal and a dielectric.

2.2.1 Transverse Magnetic and Transverse Electric Waves

First we need to find the wave equations for $\mathbf{E}$ and $\mathbf{H}$. The Maxwell's equations constitute a set of coupled, first order, partial differential equations for $\mathbf{E}$ and $\mathbf{B}$. They can be decoupled by applying the curl to first and second equations in equation (2.1):

$$\begin{aligned}
\nabla \times (\nabla \times \mathbf{E}) &= \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = \nabla \times \left(-\frac{\partial \mathbf{B}}{\partial t}\right) \\
&= -\frac{\partial}{\partial t} (\nabla \times \mathbf{B}) = -\mu\epsilon \frac{\partial^2 \mathbf{E}}{\partial t^2}
\end{aligned} \tag{2.14}$$

$$\begin{aligned}
\nabla \times (\nabla \times \mathbf{H}) &= \nabla(\nabla \cdot \mathbf{H}) - \nabla^2 \mathbf{H} = \nabla \times \left(\frac{\partial \mathbf{D}}{\partial t}\right) \\
&= \frac{\partial}{\partial t} (\nabla \times \mathbf{D}) = \frac{\partial}{\partial t} (\nabla \times \epsilon \mathbf{E}) \\
&= \epsilon \frac{\partial}{\partial t} (\nabla \times \mathbf{E}) = -\epsilon \frac{\partial^2 \mathbf{B}}{\partial t^2} = -\mu\epsilon \frac{\partial^2 \mathbf{H}}{\partial t^2}
\end{aligned} \tag{2.15}$$

Since $\nabla \cdot \mathbf{E} = 0$ and $\nabla \cdot \mathbf{H} = 0$, we can get the wave equations for $\mathbf{E}$ and $\mathbf{H}$ as below:

$$\nabla^2 \mathbf{E} = \mu\epsilon \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{2.16}$$

$$\nabla^2 \mathbf{H} = \mu\epsilon \frac{\partial^2 \mathbf{H}}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} \tag{2.17}$$

The next step is to find the solutions to wave equations (2.16) and (2.17) by using appropriate boundary conditions. The complex wave vector $\boldsymbol{\beta}$ is called the propagation constant of traveling wave and equals the component of wave vector in the direction of SPPs propagation, i.e. $\boldsymbol{\beta} = k_x$. The SPPs propagation direction is along the x -direction and therefore its harmonic time dependence plane wave can be read as:

$$\mathbf{E}(\mathbf{x}, \mathbf{y}, \mathbf{z}, t) = \mathbf{E}_0 e^{i(\boldsymbol{\beta} \cdot \mathbf{x} - \omega t)} \tag{2.18}$$

$$\mathbf{H}(\mathbf{x}, \mathbf{y}, \mathbf{z}, t) = \mathbf{H}_0 e^{i(\boldsymbol{\beta} \cdot \mathbf{x} - \omega t)} \tag{2.19}$$

And $\mathbf{E}_0 = E_x \hat{x} + E_y \hat{y} + E_z \hat{z}$, $\mathbf{H}_0 = H_x \hat{x} + H_y \hat{y} + H_z \hat{z}$

Substituting them into first two Maxwell's equations in (2.1), we obtain

$$\begin{aligned}
\text{(i)} \quad & \frac{\partial \mathbf{E}_z}{\partial y} - \frac{\partial \mathbf{E}_y}{\partial z} = i\omega\mu_0 \mathbf{H}_x \\
\text{(ii)} \quad & \frac{\partial \mathbf{E}_x}{\partial z} - i\beta \mathbf{E}_z = i\omega\mu_0 \mathbf{H}_y \\
\text{(iii)} \quad & i\beta \mathbf{E}_y - \frac{\partial \mathbf{E}_x}{\partial y} = i\omega\mu_0 \mathbf{H}_z \\
\text{(iv)} \quad & \frac{\partial \mathbf{H}_z}{\partial y} - \frac{\partial \mathbf{H}_y}{\partial z} = -i\omega\varepsilon_0\varepsilon_r \mathbf{E}_x \\
\text{(v)} \quad & \frac{\partial \mathbf{H}_x}{\partial z} - i\beta \mathbf{H}_z = -i\omega\varepsilon_0\varepsilon_r \mathbf{E}_y \\
\text{(vi)} \quad & i\beta \mathbf{H}_y - \frac{\partial \mathbf{H}_x}{\partial y} = -i\omega\varepsilon_0\varepsilon_r \mathbf{E}_z
\end{aligned} \tag{2.20}$$

For homogeneity in the y direction $\frac{\partial}{\partial y} = 0$, solutions for $\mathbf{E}_x, \mathbf{E}_y, \mathbf{E}_z, \mathbf{H}_x, \mathbf{H}_y$ and $\mathbf{H}_z$ are as below:

$$\begin{aligned}
\text{(i)} \quad & \mathbf{H}_x = \frac{i}{\omega\mu_0} \frac{\partial \mathbf{E}_y}{\partial z} \\
\text{(ii)} \quad & \mathbf{H}_y = \frac{i}{\omega\mu_0} \left(\frac{\partial \mathbf{E}_x}{\partial z} - i\beta \mathbf{E}_z \right) \\
\text{(iii)} \quad & \mathbf{H}_z = \frac{\beta}{\omega\mu_0} \mathbf{E}_y \\
\text{(iv)} \quad & \mathbf{E}_x = -\frac{i}{\omega\varepsilon_0\varepsilon_r} \frac{\partial \mathbf{H}_y}{\partial z} \\
\text{(v)} \quad & \mathbf{E}_y = \frac{i}{\omega\varepsilon_0\varepsilon_r} \left(\frac{\partial \mathbf{H}_x}{\partial z} - i\beta \mathbf{H}_z \right) \\
\text{(vi)} \quad & \mathbf{E}_z = -\frac{\beta}{\omega\varepsilon_0\varepsilon_r} \mathbf{H}_y
\end{aligned} \tag{2.21}$$

If $\mathbf{E}_x = 0$, we call these transverse electric (TE: s-polarization) waves; and if $\mathbf{H}_x = 0$, we call these transverse magnetic (TM: p-polarization) waves. Therefore, this system allows two sets of solutions with different polarization properties of the propagation waves.

$$\mathbf{E}_i = A_i e^{-k_i |z|} e^{i(\beta_i x - \omega t)} \quad (2.22)$$

$$\mathbf{H}_i = A_i e^{-k_i |z|} e^{i(\beta_i x - \omega t)} \quad (2.23)$$

where the index i describes the media: $i = 1$ for $z < 0$, and $i = 2$ for $z > 0$.

For TM waves, only the field components $\mathbf{E}_x$, $\mathbf{E}_z$ and $\mathbf{H}_y$ are non-zero. For the metal in Figure 2.1 ($z < 0$)

$$\begin{aligned} E_{x1} &= -i \frac{1}{\omega \epsilon_0 \epsilon_1} \frac{\partial H_{y1}}{\partial z} = -i A_1 \frac{1}{\omega \epsilon_0 \epsilon_1} k_1 e^{i\beta x} e^{k_1 z} \\ E_{z1} &= -\frac{\beta}{\omega \epsilon_0 \epsilon_1} H_{y1} = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_1} e^{i\beta x} e^{k_1 z} \end{aligned} \quad (2.24)$$

$$H_{y1} = A_1 e^{i\beta x} e^{k_1 z}$$

And for the dielectric ($z > 0$), the three non-zero components are

$$\begin{aligned} E_{x2} &= -i \frac{1}{\omega \epsilon_0 \epsilon_2} \frac{\partial H_{y2}}{\partial z} = i A_2 \frac{1}{\omega \epsilon_0 \epsilon_2} k_2 e^{i\beta x} e^{-k_2 z} \\ E_{z2} &= -\frac{\beta}{\omega \epsilon_0 \epsilon_2} H_{y2} = -A_2 \frac{\beta}{\omega \epsilon_0 \epsilon_2} e^{i\beta x} e^{-k_2 z} \end{aligned} \quad (2.25)$$

$$H_{y2} = A_2 e^{i\beta x} e^{-k_2 z}$$

The boundary conditions require that the tangential electric fields and magnetic fields are continuous at the interface, $z = 0$:

$$\begin{aligned} \mathbf{E}_{x1} = \mathbf{E}_{x2} &\Rightarrow \frac{A_1 \mathbf{k}_1}{\varepsilon_1} = -\frac{A_2 \mathbf{k}_2}{\varepsilon_2} \\ \mathbf{H}_{y1} = \mathbf{H}_{y2} &\Rightarrow A_1 = A_2 \end{aligned} \quad (2.26)$$

therefore, we can get the surface plasmon condition as

$$\frac{\mathbf{k}_1}{\varepsilon_1} + \frac{\mathbf{k}_2}{\varepsilon_2} = 0 \quad (2.27)$$

The wave equation for H_y gives the relation of k_i and propagation constant β

$$\begin{aligned} k_1 &= \sqrt{\beta^2 - k_0^2 \varepsilon_1} \\ k_2 &= \sqrt{\beta^2 - k_0^2 \varepsilon_2} \end{aligned} \quad (2.28)$$

Substitute equation (2.28) into (2.27), the surface plasmon condition can also be expressed as

$$\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (2.29)$$

Similarly, for TE waves, only the field components $\mathbf{H}_x$, $\mathbf{H}_z$ and $\mathbf{E}_y$ are non-zero. For the dielectric in figure 2.1 ($z > 0$)

$$\begin{aligned} \mathbf{H}_{x1} &= i \frac{1}{\omega \mu_0} \frac{\partial \mathbf{E}_{y1}}{\partial z} = i A_1 \frac{1}{\omega \mu_0} k_1 e^{i\beta x} e^{k_1 z} \\ \mathbf{H}_{z1} &= \frac{\beta}{\omega \mu_0} \mathbf{E}_{y1} = A_1 \frac{\beta}{\omega \mu_0} e^{i\beta x} e^{k_1 z} \\ \mathbf{E}_{y1} &= A_1 e^{i\beta x} e^{k_1 z} \end{aligned} \quad (2.30)$$

And for the metal ($z < 0$), the three non-zero components are

$$\begin{aligned}
H_{x2} &= i \frac{1}{\omega \mu_0} \frac{\partial E_{y2}}{\partial z} = -i A_2 \frac{1}{\omega \mu_0} k_2 e^{i\beta x} e^{-k_2 z} \\
H_{z2} &= \frac{\beta}{\omega \mu_0} E_{y2} = A_2 \frac{\beta}{\omega \mu_0} e^{i\beta x} e^{-k_2 z} \\
E_{y2} &= A_2 e^{i\beta x} e^{-k_2 z}
\end{aligned} \tag{2.31}$$

The boundary conditions also require that the tangential component of electric field and magnetic field are continuous at the interface, $z = 0$.

$$\begin{aligned}
\mathbf{H}_{x1} = \mathbf{H}_{x2} &\Rightarrow A_1 \mathbf{k}_1 + A_2 \mathbf{k}_2 = 0 \\
\mathbf{E}_{y1} = \mathbf{E}_{y2} &\Rightarrow A_1 = A_2
\end{aligned} \tag{2.32}$$

This leads to $A_1(k_1 + k_2) = 0$. As the confinement to the surface requires $\text{Re}[k_1] > 0$ and $\text{Re}[k_2] > 0$, this condition can be satisfied only if $A_1 = A_2 = 0$ which is contradict with the reality. Hence, TE polarized surface oscillations do not exist and only TM polarized surface plasmon polaritons exist.

2.2.2 Surface Plasmon Dispersion Relation

Now we consider the dispersion relations of SPPs at the interface between a Drude metal and air with TM polarized incident light. In the case of a Drude semi-infinite metal with negligible collision frequency in the air ($\epsilon_2 = 1$ and $\epsilon_1 = 1 - \frac{\omega_p^2}{\omega^2}$), equation (2.29) can be replaced with

$$\beta = \frac{\omega}{c} \sqrt{\frac{1 - \frac{\omega_p^2}{\omega^2}}{1 + 1 - \frac{\omega_p^2}{\omega^2}}} = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}} \tag{2.33}$$

The two solutions are the dispersion relation between frequency ω and propagation constant β :

$$\omega_1^2 = \frac{\omega_p^2}{2} + c^2 \beta^2 + \sqrt{\frac{\omega_p^4}{4} + c^4 \beta^4} \quad (2.34)$$

$$\omega_2^2 = \frac{\omega_p^2}{2} + c^2 \beta^2 - \sqrt{\frac{\omega_p^4}{4} + c^4 \beta^4} \quad (2.35)$$

The dispersion curves are pictured in figure 2.2, with bulk plasma frequency $\omega_p = 15\text{eV}$. The upper solid line (in blue) represents solution ω_1 , the normal dispersion of light in solid as $\omega \geq \omega_p$, which is called the radiative mode. The lower solid line (in red) represents solution ω_2 , the bound surface plasmon polaritons as $\omega < \omega_p$, which is called the non-radiative mode. The bound mode of SPPs dispersion curve always lies at the right of the light line. The SPPs can not be excited as propagation constant β is always larger than incident light wave vector and the momentum and energy conservations can not be satisfied at the same time. The straight black line represents the light line in the air. Between the regime of the bound and radiative modes, a frequency gap region with purely imaginary β_l prohibiting propagation exists. The dashed line corresponds to characteristic surface plasmon frequency which indeed is the limiting form of a SPPs when $\beta \rightarrow \infty$. The derivation is shown below:

$$\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega^2} \text{ and } \beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}},$$

$$\beta^2 = k_0^2 \frac{(1 - \omega_p^2/\omega^2)\varepsilon_2}{1 - \omega_p^2/\omega^2 + \varepsilon_2} = k_0^2 \frac{(\omega^2 - \omega_p^2)\varepsilon_2}{\omega^2(1 + \varepsilon_2) - \omega_p^2}, \text{ and}$$

$$\text{Hence, } \omega^2 = \frac{\omega_p^2(1 - \varepsilon_2 k_0^2 / \beta^2)}{1 + \varepsilon_2 - \varepsilon_2 k_0^2 / \beta^2}$$

When $\beta \rightarrow \infty$, above expression can be approximated to $\omega^2 \approx \frac{\omega_p^2}{1 + \epsilon_2}$, and such frequency

is defined as the characteristic surface plasmon frequency

$$\omega_{SP} = \frac{\omega_p}{\sqrt{1 + \epsilon_2}} \quad (2.36)$$

Figure 2.2 Dispersion relations of SPPs at the interface between a Drude metal ($\omega_p = 15\text{eV}$) with negligible collision frequency and air. The frequency ω is normalized to the plasma frequency ω_p .

2.2.3 Propagating Surface Plasmon Polaritons

In the previous discussion, we assume that the incident light is normal to the interface. When incident light has an angle with respect to the interface as shown in Figure 2.3, we also can derive the more general SPPs dispersion relations.

$$\beta = k_i \sin \theta_i = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}$$

$$k_i = \frac{\omega}{c} \sqrt{\epsilon_2} = k_0 \sqrt{\epsilon_2}$$

Therefore, we have

$$\beta = k_0 \sqrt{\epsilon_2} \sin \theta_i, \text{ where } \sin \theta_i = \sqrt{\frac{\epsilon_1}{\epsilon_1 + \epsilon_2}} \quad (2.37)$$

Figure 2.3 Schematic diagram of surface plasmon on a metal-dielectric interface with incident angle θ_i .

As mentioned in section 2.2.2, SPPs dispersion curve lies to the right side of the light line in the medium ϵ_2 ($\beta > k_0 \sqrt{\epsilon_2}$), the SPPs are bounded to the interface and remain nonradiative. For the bound mode, the localized electromagnetic field can be applied to the applications of electromagnetic field enhancement, for example, surface enhanced Raman scattering. However, it is also possible to create the guided radiative SPPs along dielectric-metal interface by compensating the momentum difference between the propagation constant and surface plasmon wave vector.

One way to compensate such momentum mismatch Δk_x is grating coupling, where the incident wave vector impinges on metal surface with shallow grating of grooves or holes. More generally, all metal surfaces with random surface roughness or manufactured ordered scatters can generate propagating SPPs [88]. Equation (2.38) describes the compensation as:

$$\beta = k_i \sin \theta_i \pm \Delta k_x = \beta_{sp} \quad (2.38)$$

Another method to produce propagating SPPs is using a multilayer system, for example a three-layer system consisting of a thin metal film sandwiched between two insulators of different dielectric constants, i.e. IMI structure [89], or a three-layer system consisting of a thin insulating film sandwiched between two different metals, i.e. MIM structure [90]. Figure 2.4 shows SPPs dispersion of an IMI structure: prism coupling using attenuated total internal reflection (ATIR). There are two bounded/non-radiative SPPs at the metal-air interface and metal-prism interface. In between the light line in air and in prism, the SPPs at metal-air interface lies in the left side of light line in prism. This means that the bounded SPPs generated at metal-air interface can couple with prism surface and form the propagation/radiative SPPs. There are generally two configurations of prism coupling, also known as Kretschmann and Otto methods [62]. Kretschmann configuration is coating a thin metal layer on hypotenuse of the prism. The light incident from prism side at an angle greater than the critical angle of total internal reflection (TIR) tunnels through the metal film and excites SPPs at the metal-air interface. Otto configuration is leaving a thin air gap between the prism and the metal film. Similarly, TIR light wave tunnels through the air gap and excites radiative SPPs at the metal-air interface. However, such phase-matching methods are inherently leaky waves because the excited radiative SPPs

lose energy not only by the absorption of metal but also by the leakage of radiation into the prism. The theoretical analysis is described in the following paragraphs.

Figure 2.4 Prism coupling in an IMI three layer system and SPPs dispersion.

Surface plasmons are known solutions of Maxwell's equations applied along an interface between a metal with a negative permittivity and an insulator with a positive permittivity as described in section 2.2. These solutions are traveling waves that are generally bound to the interface and are exponentially decaying in both media. The excitation of surface conduction electrons suffer both from free-electron oscillation and interband damping. Therefore the damping frequency γ of the metal contributes to the imaginary part of dielectric function ($\varepsilon_1(\omega) = \varepsilon_R + i\varepsilon_I$) and so does the imaginary part of propagation constant ($\beta(\omega) = \beta_R + i\beta_I$), leading to energy attenuation of traveling SPPs. The propagation length is defined as $L = (2\text{Im}[\beta])^{-1}$. At the same time a large field confinement to the interface fall off as $e^{-k_i z}$ with $k_i = \sqrt{\beta^2 - \varepsilon_i k_0^2}$. The skin depth is defined

as $\delta = 1/k_i$ at which the electromagnetic field attenuates to $1/e$, leading to a strong concentration of the electromagnetic surface plasmon field near the interface.

For metal with damping frequency of γ , the dielectric function can be expressed with $\epsilon_1 = -\epsilon_R - i\epsilon_I = -(1 - \frac{\omega_P^2}{\omega^2 + \gamma^2}) - i \frac{\gamma\omega_P^2}{\omega(\omega^2 + \gamma^2)}$ as presented in table 2.1, then the propagation constant can be expressed as a complex function as $\beta = \beta_R + i\beta_I$, where

$$\beta_R = k_0 \sqrt{\frac{\epsilon_2(\epsilon_R^2 - \epsilon_R\epsilon_2 + \epsilon_2^2)}{|\epsilon_1 + \epsilon_2|^2}} \quad (2.39)$$

$$\beta_I = \frac{1}{2} \frac{\epsilon_2^2 \epsilon_I}{\beta_R} \frac{k_0^2}{|\epsilon_1 + \epsilon_2|^2} \quad (2.30)$$

In an IMI asymmetric structure, which is a metal film with permittivity of $\epsilon_m = \epsilon_R + i\epsilon_I$ sandwiched between two dielectric media of permittivity ϵ_1 and ϵ_2 ($\epsilon_1 > \epsilon_2$), there are four modes that are solutions of the dispersion relation [91]. Two of them are radiative leaky waves resulting from the coupling between the SPPs waves associated with each boundary, also called Fano modes. The other two modes are bound to each of the interfaces ($\epsilon_m / \epsilon_i, i=1,2$) and connected to their fields decaying exponentially into the media.

In addition to using grating coupling and multilayer system to produce propagating SPPs, metal nanoparticle chain arrays have been employed to excite propagation SPPs [74-78, 92, 93]. For a linear metal particle chain with equally spacing as seen from Figure 2.5, the dispersion relation for coupled plasmon modes can be derived by solving the Maxwell equations.

Figure 2.5 Linear metal particle chains with transverse and longitudinal dipole polarizations.

Equation (2.31) is the dispersion relation derived from reference [74] and the dispersion curve is shown in Figure 2.6 [74].

$$\omega^2 = \omega_0^2 + 2\gamma_i \omega_1^2 \cos(kd) \quad (2.31)$$

Figure 2.6 Dispersion relations for plasmon modes in a linear metal particle chain [74].

The solid lines in Figure 2.6 represent transverse (T) mode and longitudinal (L) mode. The bandwidth of the L branch $\Delta\omega_L$ is twice as large as that of the T branch $\Delta\omega_T$. The group velocity, the slope of the dispersion curve is given by:

$$v_{g,i} = \frac{d\omega}{dk} = \frac{d\omega^2}{dk} / \frac{d\omega^2}{d\omega} = \frac{2\gamma_i \omega_i^2 d \sin(kd)}{\omega} \quad (2.32)$$

where γ_i is a polarization-dependent constant for which $\gamma_T = 1$ and $\gamma_L = -2$. Substituting polarization-dependent constants into equation (2.32), we can find that at resonance, both T and L waves reach maximum and the L group velocity is twice as large as T group velocity, resulting from the stronger electromagnetic coupling for L waves than for T waves. Therefore, for a linear metal particle chain, L mode is preferred to take place.

2.3 Plasmonic hybridization mode

Surface plasmon oscillation also can be supported by various geometries of metallic nanoparticles with dimensions from a few up to several hundred nanometers. For spherical metal nanoparticles, Mie scattering theory [94] is exact to describe their optical response and plasmonic properties for any size. But for non-spherical metal geometries or arbitrarily shaped metal nanoparticles, the optical response becomes complicated because factors such as size, geometry, metal-dielectric particle structure as well as coupling effects must be considered.

Nordlander P. and Halas N. J. et al presented a hybridization method to describe plasmon response of complex nanostructures of arbitrary shape [67, 95, 96]. Analogous to molecular orbital theory that the molecular energy can be split into highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LOMO) when the molecules are excited, the plasmonic hybridization model can be understood as the interaction or hybridization of elementary plasmons supported by nanostructures of elementary geometries [67].

Nordlander P. and Halas N. J. et al used nanoshell structure as an example to present the hybridization model, as shown in Figure 2.7 [67]. A plasmonic system, nanoshell, can be taken as the assembly of a sphere and a cavity, which are the elementary geometries.

The surface plasmon frequency for a sphere and cavity are $\omega_{sp,S} = \frac{\omega_p}{\sqrt{3}}$ and $\omega_{sp,C} = \sqrt{\frac{2}{3}} \omega_p$, respectively. The interaction between the two energy levels leads to the splitting of plasmon resonances into two new resonances: the lower energy symmetric or bonding plasmon, $|\omega_- \rangle$ and the higher energy antisymmetric or antibonding plasmon, $|\omega_+ \rangle$. The strength of the interaction between the sphere and cavity is determined by the thickness of the metal shell layer.

Figure 2.7 Energy diagram of hybridization mode between a sphere and a cavity [67].

Since plasmons are incompressible irrotational deformations of the conduction electron gas of the particle, in the plasmonic hybridization method the plasmons can be treated as incompressible deformations of the conduction electron gas confined by the positive background charge of the metal ions of the nanoparticles [67, 95, 96]. For concentric nanoshells, the energies of symmetric and antisymmetric plasmon can be expressed by

$$\omega_{l\pm}^2 = \omega_p^2 \left[1 \pm \frac{1}{2l+1} \sqrt{1+4l(l+1)x^{2l+1}} \right] \quad (2.33)$$

where l is spherical harmonics of order, x is the ration of inner shell radius a to outer shell radius b . Figure 2.8 shows the relation of plasmon frequency as a function of x for concentric nanoshell with l from 1 to 5.

Figure 2.8 Relation of frequency as a function of nanoshell size.

From Figure 2.8 we can clearly see that the plasmon frequencies of nanoshell are very sensitive when x changing from 0.70 to 1, i.e. at a very thin shell thickness. For symmetric plasmon mode, the plasmon frequency increases with the spherical harmonics of orders l , while this is opposite for antisymmetric plasmon mode.

Chapter 3

Fabrication of Metal Nanobowls

Metal nanoparticle substrates are extensively studied in recent decade. They can be fabricated by various methods including dispersing the colloidal metal particle solutions on a substrate, vapour deposition of nanoparticles, electron-beam lithography as well as nanosphere lithography [36, 37, 97, 98]. The main drawback for substrates using these methods is that they are not cost-effective for batch fabrication, which limits their practical applications and at the same time spurs the efforts to produce cheaper, repeatable, stable, tunable and biocompatible SERS substrates. More recently, specifically-shaped nanostructures have been synthesized as a new generation of SERS substrates that can tune localized surface plasmon resonance (LSPR) properties for specific applications. Au nanorings [99] with gradually decreased ratio of the ring wall thickness to radius exhibited red-shifted surface plasmon resonance (SPR); Au nanocrescent moons [32] combined with the features of both nanoring and nanotips presented the ultrasensitive biomolecular detection by local electromagnetic field enhancement at the sharp edge; nanoporous Au [33] showed ability in SERS sensing; Ag nanocubes, nanobars and nanorice [35] revealed the orientation dependence on incident laser polarization and the effect of nanostructure aspect ratio and corner sharpness on the plasmon resonance frequency.

3.1 General Methods to Fabricate Nanobowls

There are two major kinds of methods to fabricate nanobowls: one is chemical method, another is physical deposition method. Both methods are aided by the polystyrene nanospheres. The chemical method is to form the target material in the interstitial spaces of three dimensional close-packed polystyrene (PS) sphere arrays through chemical solution reactions, and then to produce shell structures by removing the PS spheres. For example, cobalt-ferrite nanobowl arrays [80] were fabricated by reduction of a cobalt and iron salt solution mixture; conducting polymer nanobowl sheets [79] were generated by chemical polymerization. The physical deposition method is to deposit a thin layer of target material on PS sphere arrays and form shell structures that follow the spherical shape of PS spheres, and finally produce the nanobowl arrays by removing PS spheres. Wang X.D [81, 82] et al have reported the successful fabrication of large scale ordered TiO_2 nanobowl arrays by atomic layer deposition (ALD) on large scale close-packed PS template. Compared to the chemical method, the physical deposition method can apply to a wide range of coating materials, and can have more accurate control of nanobowl wall thickness.

However the nanobowls reported by Wang X.D. et al intrinsically leave a hole at the bottom of each bowl resulting from the shadowing effect of contact point between the PS sphere and the substrate. The nanobowl rims are also not smooth and flat after the extraction of PS spheres. For the application of surface plasmon, the complete and smooth bowls are preferred as they have better defined and more controllable properties.

We developed a method which combines nanosphere lithography (NSL) method with the pulsed laser deposition (PLD) technique. The nanobowls produced by such method are

freestanding with smooth edge and uniform wall thickness, and free of holes at the bowl bottom. These nanobowls are also aggregation free which eliminate the influence of nanoclusters. By selecting the different size of the PS spheres, we can accurately control the size of the nanobowls; by selecting the species of material targets, we can fabricate a wide range of nanobowls, from complex oxides to semiconductor and to metals; by controlling the pulsed laser deposition duration and laser power, we can easily tune the wall thickness of the nanobowls. Therefore, this method is versatile. This method is also cost-effective for batch fabrication as only a thin layer of metal is consumed. Figure 3.1 shows the schematic diagram of nanobowl preparation process. The first step is to prepare a substrate which is first coated with a layer of photoresist by a spincoater and then with a self-assembled monolayer of PS spheres. The photoresist layer is later used to lift and transform PS monolayer deposited with a metal layer onto a new substrate. This avoids the appearance of the holes at the contact point between the PS sphere and the substrate and is the key development of the method.

Figure 3.1 Schematic diagram of nanobowl preparation process.

3.2 Large Scale PS Sphere Arrays Fabrication

The quality of nanobowls depends on each step of fabrication process. The first step is to prepare large scale close-packed PS sphere monolayer on photoresist pre-coated Si substrates. We have tried two methods. The first is to spin PS latex onto the substrates. This method requires the superhydrophilicity of the substrates as the larger the contact of latex with the substrate the higher possibility to prepare large scale close-packed PS sphere monolayer. Normally the photoresist coated substrates are treated by oxygen plasma etching for 10 minutes so that the wettability of photoresist layer is changed from hydrophobic to superhydrophilic. The concentration of PS latex aqueous solution is another important factor to be considered because too high concentration leads to large area of PS multilayer while too low concentration leads to small area of PS monolayer with many defects. All sizes of PS latexes purchased from Polysciences, Inc. have a solid 2.5% w/v in water. This weight-to-volume ratio is too high and the PS latex aqueous solution needs to dilute to an appropriate concentration. We found the appropriate concentration is ten times more than the concentration at which all spheres in the solutions are assumed to monodisperse on a given area (1 cm $\times$ 1 cm). Table 3.1 is the calculation chart for 5 mL appropriate concentrations of various sizes. One to two drops of diluted PS solution are dripped and spread across the entire photoresist pre-coated substrates and then left undisturbed for a while following which it is spin-coated at different revolution speed (rpm, revolution per minute) and dwelling time. Table 3.2 compares the results for 3 μ m diluted PS solutions under different dwelling time and rpm. Recipe 9 (dwelling time of 45 min and spin rate of 2500 rpm) shows the best results with large area of monolayer. The reason for waiting before spinning is to let the polystyrene in the solution settle down on

the photoresist, and form the self-assembled monolayer at the boundary first. In our experience, such method is more suitable for preparing monolayer with the size larger than $1\text{ }\mu\text{m}$ as it is very easy to form PS multilayer for smaller sizes.

Table 3.1 calculation chart of appropriate concentrations for various sizes of PS spheres

	0.1 μm	0.2 μm	0.35 μm	0.5 μm	1 μm	3 μm
Particles/mL of purchased latex	4.55×10^{13}	5.68×10^{12}	1.06×10^{12}	3.64×10^{11}	4.55×10^{10}	1.68×10^9
Particles/mL needed (1 cm $\times$ 1 cm)	1.0×10^{10}	2.5×10^9	8.16×10^8	4.0×10^8	1.0×10^8	1.11×10^7
Volume needed to dilute to appropriate concentration	10 μL	20 μL	40 μL	60 μL	100 μL	330 μL

Table 3.2 Experimental results comparison under different conditions, such as waiting time, spin rate

No.	Time waited/min	Spin Rate/rpm	Results
1	15	1000	Large area of multilayer
2	30	1000	Large area of multilayer
3	45	1000	Large area of multilayer
4	30	1500	Monolayer isolated in the middle of sample
5	45	1500	Monolayer together with multilayer
6	60	1500	Monolayer together with quite a lot of multi-layer
7	25	2500	Large area of isolated monolayer with multilayer
8	35	2500	Large area of isolated monolayer
9	45	2500	Larger area of monolayer with few multilayer
10	25	3000	Monolayer isolated in the middle with multilayer

The second method is to form large-scale PS monolayer floating on the water surface and fish out the monolayer with a photoresist pre-coated substrate. Compared to previous

method, this method is more reproducible and effective. First, apply 3-5 μL diluted PS solutions onto the surface of a clean Si wafer (size: 2 cm $\times$ 2 cm) which was soaked in 10% sodium dodecyl sulfate (SDS) for 24 hours. The Si wafer is then slowly immersed in a glass vessel filled with Milli-Q water. The PS monolayer starts to form and float on the surface of water. To reduce the water surface tension, 4 μL of 2% SDS is added to the glass vessel. Finally, the monolayer is lifted off by photoresist pre-coated substrates. Such method avoids the formation of multilayer and is very suitable to prepare PS monolayer with the size smaller than 1 μm . This can be easily understood by recognizing the density of PS, 1.05 g/mL, which is comparable to the water density. The bigger the sphere the heavier the weight, thus large size of PS spheres can not float on the water surface but form suspension in water. The PS monolayer with different size exhibits different colors, the smaller the size, the darker the color and the larger the size, the more shiny the monolayer.

The two methods are complementary as for PS size smaller than 1 μm we can choose the second method, and for those larger than 1 μm we can use the spin-coating method.

3.3 Setting up a pulsed laser deposition system

After dispersing a PS monolayer on the photoresist pre-coated substrate, a thin layer of metal material must be deposited on top of it, and this is the second step to prepare nanobowls shown in Figure 3.1. The deposition technique used is pulsed laser deposition. PLD is an extremely versatile technique for preparation of a wide range of thin films and multilayer structures, such as metals, intermetallic compound, simple oxides, complex oxides and polymers. Nowadays with the stimulation and evolution of nano science, many

nanoscale thin films for semiconductor devices have been successfully fabricated by PLD. One of its great advantages is the low start-up cost, and the thin films produced by PLD have the comparable quality to molecular beam epitaxy (MBE) that cost 10 times as much. Another advantage of PLD is its ease of use. In addition, the ablation process can be easily controlled by laser parameters. We design and set up such a PLD system which is characterized with three rotational target holders, adjustable target-to-substrate distance, in situ substrate heating, and reaction gas supply. These features make it possible to fabricate functional thin films as well as nanostructures with good quality.

A PLD system consists of three major parts: the laser, optics and the PLD chamber with vacuum system. Figure 3.2 shows the schematic diagram of our PLD system and the pictures of the equipment.

Figure 3.2 Schematic diagram of homemade PLD chamber and pictures of PLD equipment.

In general, the laser wavelength between 200 nm to 400 nm is the most useful range for PLD because most materials used as targets exhibit strong absorption in this wavelength region and therefore the penetration depth into the targets is correspondingly small. The small penetration depth benefits the fabrication of high quality films as only a very thin layer of target surface is ablated. It also decreases the ablation power threshold. Third harmonic generation Nd^{3+} : YAG solid laser (355 nm) and KrF excimer laser (248 nm) are most commonly used as the laser source for a PLD system. During my Ph.D. project, third harmonic generation Nd^{3+} : YAG solid laser was employed to produce laser induced periodic structures on Si wafers and KrF excimer laser was used to grow high quality thin films and various nanostructures.

The optics is another major part of a PLD system which directs and focuses the laser beam. The materials for these mirrors, lenses, beam splitters and laser windows must be transparent to the laser wavelength so that majority of the laser energy can be conveyed to ablate the targets. The set-up of optics is flexible and mainly depends on the location of the laser source and the chamber. Using multi-sets of optics one laser source can even

simultaneously supply several chambers. In our case, the KrF laser port is higher than the laser window of the PLD chamber, and we had to use two mirrors to adjust the height of laser beam. As shown in Figure 3.2, the output laser goes through an aperture with the size of $1.5 \times 3 \text{ cm}^2$ that is the area of strongest laser beam profile, and then is reflected twice down to the center of laser window of the PLD chamber. Finally, the laser beam is focused on the target with a UV-grade fused silica focal lens. For safety, the optical components of the KrF excimer laser were enclosed in anodized aluminium housing.

PLD chamber is the third major part of a PLD system. The diversity of chamber design makes PLD with a variety of features and functions that other physical deposition system can not achieve. Our chamber is designed with following 4 features: first, three in-situ changeable and rotational targets. The size for target is 1 inch in diameter, and this feature makes it possible to prepare superlattice films with three kinds of compounds. Second, adjustable target-to-surface distance. This is an import parameter for film growth. Third, in-situ heating substrate up to $800 \text{ }^{\circ}\text{C}$ under the vacuum. It provides the energy for the deposited particles to grow epitaxially or have a better crystallinity. Forth, gas flow. More and more research groups have reported that the background gas atmosphere can facilitate to grow various nanostructures, such as nanorods, nanowires and nanopillars. Individual or mixed oxygen, nitrogen and helium can be flowed into the deposition chamber. All these features promise the production of good quality of thin films or nanostructures.

The main parameters for PLD technique include laser wavelength, laser density, laser pulse duration, target rotation rate, target-to-substrate distance, substrate heating temperature, deposition duration and background pressure. By tuning these parameters, an optimum preparation conditions can be found to prepare desired thin films as well as nanostructures.

3.4 Nanobowl Fabrication

After coating with a layer of metal film on PS monolayer on photoresist pre-coated substrate, the third step is to separate the original substrate and metal coated PS monolayer. This is done by immersing the sample in the acetone for 20 seconds, and then flipping it over and putting it on a new clean substrate. Carefully sliding the original substrate away from the new substrate leaves the sample with the PS monolayer inside the metal film shell. After drying, the sample is ultrasonicated in chloroform for 30 seconds. Finally, the sample is rinsed in deionized water and dries in air. Figures from 3.3 to 3.5 show various nanobowls with different material species, size or bowl wall thickness fabricated by our methods.

Figure 3.3 SEM images of different metal nanobowls with 1 μm bowl size. The scale bar is 1 μm .

Figure 3.4 SEM images of 3 μm bowls of La-Ca-Mn-O, 1 μm bowls of Ag, 0.5 μm bowls of Au and 0.356 μm bowls of Ni. The scale bar is 1 μm .

Figure 3.5 SEM images of nanobowls with different wall thicknesses.

Our method can be used to fabricate thin films and nanostructures made of almost any material by simply selecting the appropriate target. One outstanding advantage of the PLD technique is that the composition of the deposited thin film is the same as that of the target. This feature is especially beneficial for fabricating complex oxides, such as colossal magnetoresistance materials (CMR), La-Ca-Mn-O, and high T_C superconductor Y-Ba-Cu-O as well as doping materials. In our study, metal targets such as Ag, Au, Ni and Pt, oxides such as La-Ca-Mn-O and ZnO were used to form nanobowls or other nanostructures. Figure 3.3 shows 1 μm nanobowl arrays with different materials. Such method can also control the size of nanobowls by choosing different size of PS spheres. For PS with the size of 1 μm or below we use dispersing method to generate the PS sphere monolayer while for PS sphere with the size larger than 1 μm we use spin-coating method to generate PS sphere monolayer. Figure 3.4 shows 3 μm bowls of La-Ca-Mn-O, 1 μm bowls of Ag, 500 nm bowls of Au and 365 nm bowls of Ni. The wall thickness is another very important factor to affect the plasmonic properties of the nanobowls. PLD technique can control the thickness of deposited thin films by controlling the laser parameters such as laser density, repetition rate and deposition duration. Figure 3.5 shows different bowl sizes with different bowl wall thicknesses.

Chapter 4

SERS for Metal Nanobowls

Surface enhanced Raman scattering/spectroscopy (SERS) [30-42, 100] refers to the observation that for certain molecules adsorbed on specially prepared metal surfaces a Raman signal is detected with the intensity enhanced by a factor of 10^5 to 10^6 . Increases in the intensity of Raman signal can be even as high as 10^8 and 10^{14} for some special metal nanostructures, such as nano crescent moon [32], nano star [66], nanorice, nanocube [35], nanoshell [68] and hybrid nanostructures [67]. The huge intensity enhancement shows the importance of SERS: both surface selectivity and sensitivity. SERS effects are based on Raman spectroscopic technique and therefore we start this chapter from the principle and operation of Raman spectroscopy.

4.1 Principle and Operation of Raman Spectroscopy

When light interacts with atoms or molecules, the photons will undergo either elastic scattering or inelastic scattering. The elastic scattering of light photons is called Rayleigh scattering, such that the scattered photons have the same frequency (energy) and wavelength as the incident light. Most photons are elastically scattered and therefore the intensity of Rayleigh scattering is very strong. While only a small fraction of photons,

about one in ten million photons, are inelastically scattered such that the scattered photons have a frequency shift (energy difference) from the incident light.

This phenomenon of inelastically scattered photons was first observed by C. V. Raman and K. S. Krishnan in liquids [101] and by G. S. Landsberg and L. I. Mandelstam in crystals (quartz) [102] in 1928. Since then Raman scattering was entitled for inelastic scattering of light with the name of the Indian physicist Chandrasekhara Venkata Raman. Raman scattering is a powerful tool to study excitations of molecules and molecular structures as well as chemical compounds because the frequency shift from the incident laser reflects molecular vibrational and rotational energies and the chemical species that depend on atomic masses and bond strength.

4.1.1 Principle of Raman Scattering

The interaction between light and matter is actually the interaction between an electromagnetic (EM) wave of frequency ν_0 with the molecules of a gas, liquid or solid. The electron orbits within the constituent molecules oscillates periodically with the same frequency (ν_0) as the incident EM wave, leading to a periodic separation of charge within the molecules, which is called an induced dipole moment. The resultant induced, alternating dipole moment acts as a source of radiation and results in light scattering phenomena including both elastic and inelastic scattering. The strength of the induced dipole moment, P , is given by

$$P = \alpha E_0 \quad (4.1)$$

where α is the polarizability and E_0 is the electric field strength of incident EM wave. The polarizability is an intrinsic property of a material that depends on the molecular structure and chemical bonds. The electric field of incident EM wave can be written as

$$E = E_0 \cos 2\pi\nu_0 t \quad (4.2)$$

where ν_0 is the frequency of incident EM wave. Substituting equation (4.2) into (4.1) yields the time-dependent induced dipole moment

$$P = \alpha E_0 \cos 2\pi\nu_0 t \quad (4.3)$$

The polarizability α consists of two parts: static polarizability α_0 and a sum of terms having the periodic time dependence of the normal frequencies of the system under consideration.

$$\alpha = \alpha_0 + \sum \alpha_n \cos 2\pi\nu_n t \quad (4.4)$$

The polarizability then is written as

$$\begin{aligned} P &= \alpha_0 E_0 \cos 2\pi\nu_0 t + E_0 \sum \alpha_n \cos 2\pi\nu_0 t \cos 2\pi\nu_n t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + 1/2 E_0 \sum \alpha_n \{ \cos 2\pi(\nu_0 - \nu_n) t + \cos 2\pi(\nu_0 + \nu_n) t \} \end{aligned} \quad (4.5)$$

Equation (4.5) shows that induced dipole moments take place at three distinct frequencies, namely, ν_0 , $(\nu_0 + \nu_n)$ and $(\nu_0 - \nu_n)$. The first item represents the Rayleigh scattering (elastic scattering) whose scattered frequency is same as the incident EM wave frequency ν_0 . The second term containing other two frequencies represents Raman scattering whose frequency is shifted to lower or higher frequencies and is therefore inelastic process. The lower/down shifted frequency $(\nu_0 - \nu_n)$ is referred to as Stokes scattering, and the higher/up shifted frequency $(\nu_0 + \nu_n)$ is referred to as anti-Stokes scattering. Figure 4.1 shows the schematic diagram of the quantum theoretical description of Raman scattering. The electrons in the molecules are first excited to a virtual state which is an intermediate state between the ground state E_0 and first excited state E_1 of the

system by absorbing a photon of the incident EM wave and then go back to ground state E_0 by emitting another photon. The Rayleigh scattering corresponds to the transitions starting and ending at the same vibrational energy level. Stokes Raman scattering corresponds to the transitions starting at the ground state and ending at a higher energy level, for example the 1st vibrational energy level. Anti-Stokes Raman scattering corresponds to the transitions starting from a higher energy level, for example the 1st vibrational energy level, and ending at a lower energy level, for example, the ground state. As most of the molecules are staying at the ground state, the probability of Stokes Raman scattering is far larger than that of anti-Stokes Raman scattering, although both of them have the same absolute Raman frequency shift. The energy difference between the excitation and emission is defined as the Raman frequency shift that corresponds to the vibrational energy (phonon energy) of the molecules. Thus, Raman frequency shift is an inherent characteristic of the material and is independent of the incident radiation. This is the essential distinction to Fluorescence effect which strongly relies on incident EM wave.

Raman scattering is intrinsically very weak. However, the Raman signal can be enhanced by several orders of magnitude, normally from 10^3 to 10^6 , if resonance Raman scattering (RRS) takes place. As seen from right most illustrative diagram in Figure 4.1, the incident laser with energy close to an electronic absorption band excites the molecule to near one of its excited electronic states (energy level E_1), instead of exciting the molecule to a virtual energy state. The resonance between certain vibrational modes and electronic transitions results in a greatly increased Raman scattering intensity. Resonance Raman spectroscopy can examine relatively few vibrational modes at a time because RRS only contributes to the vibrational modes involved with the electronic transitions, which is very important and useful for mode-related biomolecule detection. Nonetheless, the

enhancement of Raman intensity by RRS is still limited, especially for the applications of biomolecular trace detection or even single molecule detection. In these cases, SERS becomes an alternative to meet the requirements of huge Raman intensity enhancement.

Figure 4.1 Schematic diagram of quantum theoretical description of Raman scattering process.

4.1.2 Raman Instrumentation and Operation

Two micro Raman systems were used in our experiments: WITEC CRM200 (532 nm Nd: YAG laser and 457 nm diode-pumped solid-state (DPSS) laser) and Renishaw inVia (325nm, He-Cd laser, 532 nm Nd: YAG laser and 785 nm high-performance near-infrared (HPNIR) diode laser) Raman systems. The operation of Raman spectroscopic

measurement starts with locating the sample on the piezostage under the microscope by illuminating and focusing a normal white light source (tungsten halogen lamp, 350 nm to 850 nm) to the sample. As seen from figure 4.2, the white light first reflects down by beam splitter 2 and then focuses on the sample via an objective which can be selected according to the requirement of magnification, numerical aperture (NA) as well as environment-dependent lenses, such as oil-immersion and water-immersion objectives. The reflected white light from the sample goes straight up and is directed to right by beam splitter 3, and finally is collected by a video camera which produces the optical image of the sample surface. After focusing, the sample is excited by a laser which is coupled into a single mode fiber and then directed via holographic beam splitter 1 to the sample through the same objective to excite the Raman signals. The scattered light from the sample, including both Rayleigh light and Raman scattering light are collected in backscattering mode. As Raman scattering is much weaker than Rayleigh scattering, an edge filter is used to block the Rayleigh light. Therefore, only the Raman and a very small fraction of Rayleigh signals go to the grating and are collected by a charge-coupled-device (CCD) or avalanche photodiode (APD). A Raman spectrum with the intensity as a function of wave number is then recorded by the spectrometer.

Peak position, peak intensity and full width at half maximum (FWHM) are the important parameters of a Raman spectrum as they reflect the properties of the sample. Generally, peak position is determined by the oscillation strength (similar to chemical bonding in chemistry) as well as the mass of the constituent atoms. The Raman peak position shift is related to stress which has found important applications in industry, e.g. determination of strain in SiGe devices for integration circuit (IC) fabrication; peak intensity reflects the structure and composition of the sample; peak width reflects the

crystallinity and the structure of the sample. With the aid of a piezostage that can move the sample along x, y and z direction with precision of 1-2 nm, a Raman image can be obtained by collecting the spectrum information of each point on the sample, i.e. peak position, peak intensity or peak FWHM, under the illumination of laser. Raman mapping provides intuitive, useful and conclusive information of the samples, for example the distribution of stress, composition and structure variation, optical response of the sample.

Figure 4.2 Schematic diagram of confocal Raman spectroscopy.

4.2 SERS Effects and Enhancement Factors

From chapter 4.1 we understand that Raman spectroscopy is a characterization method to identify molecular vibrational and rotational frequencies, molecular structures and chemical compounds. To overcome its intrinsic disadvantage of low intensity and expand its application in bioscience and biotechnology, SERS has been developed to detect trace biomolecules based on two accepted mechanisms of enhancement: chemical enhancement (CE), α , depending on changes to the adsorbate electronic states due to chemisorption of the analyte[103-105], and electromagnetic enhancement (EME), G , depending on surface roughness for metal films or geometry, size, orientation for metal nanoparticles. The total enhancement μ is the multiply of factors of CE and EME.

$$\mu = \alpha \cdot G \quad (4.6)$$

Between these two enhancement mechanisms, EME is dominant as CE only contributes the enhancement on one or two orders of magnitudes. The EME factor arises from enhanced optical fields due to excitation of EM resonances in the metallic structures, based on the localized surface plasmon theory as introduced in Chapter 2. To a first approximation, G can be expressed as:

$$G(r_m, \omega) = \left| \frac{E(r_m, \omega)}{E_{inc}(\omega)} \right|^4 \quad (4.7)$$

where r_m is the location of the molecule, $E(r_m, \omega)$ is the total electric field at the molecule location r_m , and $E_{inc}(\omega)$ is the electric field of incident EM plane wave. The first two powers of enhancement can be attributed to the local EM field enhancement at incident laser frequency ω_L , while the second two powers of enhancement can be attributed to the

Raman emission enhancement at the Raman frequency ω_R . These two contributions to the SERS enhancement are not always the same when the electric field has an antenna effect on metal nanostructures [40]. Thus, the total SERS enhancement factor G can be modified to:

$$G = \left| \frac{E_{loc}(\omega_L, \theta)}{E_{inc}(\omega_L)} \right|^2 \left| \frac{E_{max}(\omega_R)}{E_{inc}(\omega_R)} \right|^2 \quad (4.8)$$

where E_{loc} is the actual polarization dependent local electric field, and $E_{max}(\omega_R)$ is the maximum field at the Raman frequency that can be obtained at that point for the optimal polarization. Incident EM wave frequency ω_L and Raman frequency ω_R are not necessarily the same. If ω_R is very close to ω_L , $E_{max}(\omega_R)$ can be assumed to equal the maximum of the local electric field $E_{loc}(\omega_L, \theta)$ for the optimal polarization. Otherwise, the local electric field $E_{loc}(\omega_R, \theta)$ at the Raman frequency and the corresponding $E_{max}(\omega_R)$ are different. The modified equation (4.8) describes the antenna effects induced by the geometry of the nanostructures or the coupling effect between two kinds of nanostructures [37, 39, 40].

4.3 Experimental Results and Discussion

The metal nanobowl arrays fabricated by the method described in Chapter 3 were used as SERS substrates to detect a few kinds of commonly used molecules in bioscience and biotechnology, including rhodamine 6G (R6G), crystal violet (CV), 3-mercaptopropionic acid (3-MPA), methylene blue (MB) and brilliant cresyl blue (BCB). These probe molecules were solved or diluted in the deionized water so that the concentration of the

molecule can be varied from 1 mM/L to 1 μ M/L for difference levels of detection sensitivity. The table 4.3.1 shows the chemical formula, molecular weight and physical state of each kind of molecule.

Table 4.1 Properties of probe molecules

Name	Chemical formula	Molecular weight	Physical state
R6G	$C_{28}H_{31}N_2O_3Cl$	479.02 g/Mol	Solid
CV	$C_{25}H_{30}ClN_3$	407.99 g/Mol	Solid
3-MPA	$HSCH_2CH_2COOH$	106.14 g/Mol	Liquid
MB	$C_{16}H_{18}ClN_3S \cdot 3H_2O$	373.9 g/Mol	Liquid
BCB	$(C_{17}H_{20}ClN_3O)_2 \cdot ZnCl_2$	771.92 g/Mol	Solid

4.3.1 SERS Detection on Ag and Au Nanobowl Substrates

Figure 4.3 shows SERS spectra of CV molecules with the concentration of 1 μ M/L on Ag nanobowl substrate under the 532 nm excitation laser. Figure 4.3(a) is the SEM image of Ag nanobowl arrays, with the bowl size of 1 μ m and Figure 4.3(b) is the optical image of Ag nanobowls on Si substrate. Two positions were investigated: one position with Ag nanobowls as indicated by white frame in Figure 4.3(b) and the other position without the cover of Ag nanobowls. As shown in Figure 4.3(c), the CV SERS peaks were detected on the position with Ag nanobowls, but only Si peak was observed on the position without Ag nanobowls. This result implies that Ag nanobowl serves as the effective SERS substrates to detect low concentration molecules.

Figure 4.3 CV molecules detected from Ag nanobowl substrate: (a). SEM image of Ag 1 μm nano bowl arrays; (b). optical image of Ag 1 μm nanobowls arrays on Si substrate; (c) Raman spectra of CV molecule (concentration of 1 $\mu\text{M/L}$) on Ag nanobowl substrate. The laser wavelength is 532 nm.

Figure 4.4 Raman spectra of R6G molecules (1 $\mu\text{M/L}$) detected from both Au and Ag nanobowl substrates. The bowl size is 1 μm and the incident laser wavelength is 532 nm.

Figure 4.5 Photo emission spectra of Au nanobowls: (a). optical image of 1 μm Au nanobowl arrays on Si substrate; (b). Au photo emission intensity image; (c) Raman spectra of four positions in (b). The incident laser wavelength is 532 nm.

Figure 4.6 Photo emission spectra of Ag nanobowls. Left picture is the Ag photo emission intensity image and right diagram is Raman spectra of four positions in the left image. The incident laser wavelength is 532 nm.

Figure 4.4 shows SERS spectra of R6G molecule with the concentration of 1 $\mu\text{M/L}$ obtained from both Ag nanobowl and Au nanobowl substrates. Au nanobowl also can serve as effective SERS substrate to detect low concentration molecules. The SERS signals from low concentration molecules such as R6G, CV, BCB and MB have also been detected on the smaller sizes of metal nanobowl substrates, i.e. 80 nm, 200 nm, 356 nm and 465 nm.

It is noted that there is a strong background of the Raman spectra measured from both Au and Ag nanobowl substrates. This can be attributed to the photo emission from Au and Ag nanobowl structures under the green laser excitation (532 nm). Figure 4.5(a) is the optical image of Au nanobowl arrays on Si substrate with the bowl size of 1 μm and Figure 4.5(b) is the Au photo emission intensity image obtained by mapping the background intensity from 540 to 640 nm in an area of 4 μm by 4 μm . Position 1 and 2 at the bowl rims show the strongest emission intensities as seen from Figure 4.5(c). Close to the bowl rims (position 3) the emission is still strong. At position 4, without Au nanobowls on Si substrate, only Si peak can be detected. Ag nanobowls also exhibit photo emission under the green laser excitation, but not as strong as that observed from Au nanobowls. Figure 4.6 shows Ag photo emission intensity spectra corresponding to 4 positions in the background intensity image (from 540 to 640 nm). The brighter places in the image correspond to the stronger emission intensities and vice versa.

Photoluminescence from bulk noble metals has been attributed to the radiative recombination arising from transitions between electrons in s-p conduction bands and holes in the d bands generated by optical excitation [176]. However, the nonradiative electron-hole recombination is much faster than the radiative recombination process and

thus quenching the photoluminescence from the bulk metals. Significant enhancements of such photo emission can be achieved from metal nanostructures that have been linked to the enhanced localized fields near the metal nanoparticle surface due to the SP excitation and the lightning rod effect [177, 178]. The resonant excitation of localized SPs has a strong frequency dependence on the incident light while lightning rod effect is independent of the incident light wavelength and is due to the purely geometric phenomenon of the electric field line crowing. Our experimental observations of the photo emissions from Au and Ag nanobowls indicate that the SP resonances were excited under the illumination of the green laser, and the strong EME positions are where the strong photo emission occurs. This also has been confirmed by the simulated EM field distribution on metal nanobowls shown in Chapter 5.

Figure 4.7 SERS peak intensity images of CV molecular vibrational peaks (concentration: 1 $\mu\text{M/L}$) detected from Au 1 μm nanobowl arrays on Si substrate. The incident laser wavelength is 532 nm.

SERS spectrum of CV molecules shows molecular vibrational peaks located at 915 cm^{-1} , 1182 cm^{-1} , 1368 cm^{-1} and 1569 cm^{-1} as seen from Figure 4.7. In order to investigate the exact EME sites and the SERS intensity distribution, these SERS peaks were mapped to individual peak intensity images. The four images corresponding to the four SERS peaks show no difference which indicates that the four peaks are simultaneously enhanced and their relative intensity remains. It is noted that the background intensity image presents the agreement with four SERS peak intensity images. The positions with the strongest background intensity are where four SERS peaks have the strongest peak intensities. Combined with the observation from Figure 4.5 we can conclude that the strongest SERS enhancement takes place at the bowl rims rather than other positions for Au nanobowls. Si Raman intensity image exhibits an opposite intensity distribution to background intensity image. This can be easily understood as the more Si signals are detected the less Si substrate is covered by Au nanobowls and vice versa.

4.3.2 SERS Detection on Hybrid Structures

Since hybrid structures can redistribute the EM field and create new surface plasmon modes as described in Chapter 2.3, we attempted to use the bowl structure to hybridize with other particle geometries, such as Ag tetrahedrons and Au nanospherical particles, so that to investigate how different the SERS effects on these hybrid structures as compared with only bowl structure.

As shown in Figure 4.8(a), the Ag tetrahedrons were randomly distributed in the Ag nanobowl arrays. The size of the Ag tetrahedron is about 100 nm and the size of the bowls is 1000 nm. Figure 4.8(b) shows the Raman intensity image of BCB molecules (1 $\mu\text{M/L}$) at

peak position 1652 cm^{-1} . The strongest intensity distribution does not follow the morphology of Ag nanobowl arrays. We compare SERS spectra of three positions with the Raman spectrum of 1 M/L BCB molecules on Si substrate which is used as the reference spectrum of BCB molecules. The four spectra are normalized for comparison. From Figure 4.8(b) we can see that positions 1 and 3 have the strongest intensity at peak position 1652 cm^{-1} and position 2 has the lowest one. The SERS spectra in Figure 4.8(c) also confirm this result. Position 1 resembles the Raman spectrum of BCB molecules on Si substrate; position 3 induced other two peaks at 1582 cm^{-1} and 1305 cm^{-1} whose intensities are even stronger than the peak at 1652 cm^{-1} ; while at position 2, two peaks at 1282 cm^{-1} and 1346 cm^{-1} are enhanced and several peaks between $650\text{--}1000\text{ cm}^{-1}$ that do not appear in the Raman spectrum of BCB molecules on Si substrate are excited. Because of Raman selection rule, not all vibrational transitions will be “Raman active”, i.e. some vibrational transitions will not appear in the Raman spectrum. The hybrid structure between Ag bowls with Ag tetrahedrons may tune the surface plasmon resonances to certain frequency that resonates with some BCB molecular vibrational modes. This tuning effect may change the polarizability tensor of the molecules so that to create new Raman selection rules, leading to the detection of originally Raman inactive vibrations.

Figure 4.8 SERS observation on hybrid structure of Ag bowls with Ag tetrahedrons: (a) SEM image of randomly distributed Ag tetrahedrons in Ag nanobowl, the inset is the magnified image of Ag tetrahedron; (b) Raman intensity image of BCB molecules ($1\mu\text{M/L}$) at peak position of 1652 cm^{-1} ; (c) Normalized SERS spectra of three positions in (b). The incident laser wavelength is 532 nm .

Figure 4.9 SERS observation on hybrid structure of Au bowls with Au nanospherical particles: (a) SEM image of Au nanobowl arrays before the filling of Au spherical particles; (b) SEM image of fully filled Au spherical particles in Au nanobowl; (c) background image from 550-1580 cm^{-1} ; (d) SERS intensity image of MB molecules (1 $\mu\text{M/L}$) at 1664 cm^{-1} ; (e) background image from 2300-3600 cm^{-1} ; (f) SERS spectrum of MB molecules on the hybrid structure. The incident laser wavelength is 532 nm.

The second hybrid structure we investigated is Au nanoparticles fully filling in Au nanobowls. Figure 4.9(a) and (b) show the SEM images of 1 μm Au nanobowl arrays before and after filling Au spherical particles. MB molecules with low concentration of 1 $\mu\text{M/L}$ were used as probe molecules to examine the SERS effects on such hybrid structure. The two background images shown in Figure 4.9(c) and (e) follow the morphology of nanobowls filled with nanoparticles as seen in (b), implying that Au photo emission intensity distribution varies with the morphology. However, SERS peak intensity image at 1664 cm^{-1} as seen from Figure 4.9 (d) does not show the similar variation with the morphology. This is distinct from the observation of singular Au nanobowl arrays as shown in Figure 4.6. The interactions between Au nanoparticles and the interactions between the Au nanoparticle and Au bowl may contribute to such discrepancy.

4.4 Conclusions

Both Au and Ag nanobowls show their capabilities to be efficient SERS substrates. The SERS peak intensity images of several probe molecules present that under the green laser excitation (532 nm), the enhancement positions for singular bowl structure and hybrid structures are different. For singular bowl structure, the strongest SERS peak intensity

takes place at the bowl rims where the strongest photo emissions occur. The SERS observation on hybrid structures between Ag nanobowls with Ag tetrahedron and between Au nanobowls with Au nanoparticles indicates that it is possible to break Raman selection rules by tuning surface plasmon resonances via the plasmon hybridization and therefore to excite the original Raman inactive vibrations. This holds the promise to detect biomolecules whose molecular vibrations are originally Raman inactive and cannot be measured by normal Raman spectroscopy.

Chapter 5

Plasmonic properties of Metal Nanobowls

In the last chapter we discussed the SERS effects on Ag and Au nanobowls as well as their hybrid structures. In this chapter we will discuss the dependence of plasmonic properties on bowl size and wall thickness effect. Numerical calculation to the solutions of Maxwell's equations is performed to investigate the electromagnetic (EM) field distribution and plasmonic properties of metal nanobowls.

5.1 Experimental Observation of EME Orientations

In Chapter 4 we observed that the strongest Au inelastic emission takes place at the Au bowl rims. The inelastic emission reflects the EM resonances, the stronger the emission the higher the EM enhancement (EME). First we examine how the EME orientation varies with the incident laser polarization. The laser wavelength used is 532 nm. The bowl size is 1 μm and bowl wall thickness is 31 nm. As seen from Figure 5.1(a), when laser polarization is horizontal as indicated by green arrow, the strongest EME takes place at the bowl rims with the orientation parallel to the horizontal direction. Similarly, when laser polarizes at 60° or 90° , the EME orientation is tuned to 60° or 90° , always parallel to the

incident laser polarizations. This behavior is also observed on individual Au nanobowl as shown in Figure 5.1(d) and (e).

Figure 5.1 Relations between EME orientations of 1 μm Au nanobowl arrays and individual nanobowl with incident laser polarization. The laser wavelength is 532 nm.

Figure 5.2 Relations between EME orientations of 1 μm Ag nanobowl arrays with incident laser polarization. The laser wavelength is 532 nm.

However, Ag nanobowls do not show the same EME orientation dependence on incident laser polarization. Figure 5.2 shows Ag inelastic emission intensity images at 0°, 30°, 60° and 90°, as indicated by green arrows. With the variation in laser polarizations,

the distribution of EME does not change much. This result implies that the strongest Ag EME orientation is independent of incident laser polarizations.

There are two configurations of nanobowl arrays as shown in Figure 5.3. Type 1 is the main axis of bowl arrays parallel to horizontal direction; and type 2 is the main axis of bowl arrays 30° with respect to horizontal direction, as shown in Figure 5.3. The two configurations result in different EME orientation patterns although both of them have the period of 60° .

Figure 5.3 Two configurations of Au nanobowl arrays and their EME orientation patterns.

We performed the experiments to test the EME orientation patterns for the two configurations. The Au bowl size is $1\ \mu\text{m}$ and bowl wall thickness is 38 nm. The EME orientations are always parallel to the incident laser polarizations as shown in Figure 5.4. The EME orientation patterns seem as periodically parallel waveguides and the directions of waveguiding can be tuned by changing the incident laser polarizations. This could be an importantly potential application to control waveguiding directions.

Figure 5.4 Au inelastic emission intensity images at different incident laser polarizations for both two configurations. The incident laser wavelength is 532 nm.

5.2 Simulation Results

It is interesting that the EME orientation dependence on incident laser polarization only happens to Au nanobowls and not Ag nanobowls under the green laser excitation. The theoretical calculation on EM field distribution can help us understand the reasons. We will start from the introduction of the simulation method and then show simulation results.

5.2.1 Simulation Methods and Software

The problem of electromagnetic analysis is considered as the problem of solving Maxwell's equations subject to certain boundary conditions. For spherical nanoparticles

with any size, Mie scattering theory [58, 94] provides a rigorous solution to Maxwell's boundary conditions of continuity at the junction between the nanoparticle and the surrounding medium that describes well the optical properties of spheres. But for non-spherical geometries, i.e. arbitrarily shaped particles, Mie scattering theory is no longer exact to account for field-retardation effects induced by factors like geometry, size and orientation of arbitrarily shaped particles. Hence, determination of the plasmon-resonant properties of arbitrarily shaped particles is to find the exact solutions to Maxwell's equations. The commonly used computational methods reported in literatures include discrete dipole approximation (DDA) [106], finite element method (FEM) [107], and finite-difference time domain (FDTD) [108, 109]. Nordlander P. and Halas N.J. et al recently present the plasmon hybridization (PH) theory to calculate plasmonic resonances of complex nanostructures which has been introduced in Chapter 2.3 [67, 95, 96].

DDA is a method for calculating the scattering and absorption properties of arbitrarily shaped nanostructures by approximating the complete nanostructures as a finite array of polarizable point dipoles. The points under the external field acquire a dipole moment. The optical properties are then simulated as the interaction of a finite number of closely spaced dipoles.

FDTD is a popular computational method for electromagnetic modeling system and is based on numerically evaluating the temporal evolution of electromagnetic fields. The time-dependent Maxwell's equations are discretized to space and time partial derivatives. The resulting finite-difference equations are solved by repeating the calculations on electric field vector components in a volume of space at a given instant in time and magnetic field vector components in the same spatial volume at the next instant in time

until the desired transient or steady-state EM field behavior is fully evolved. FDTD is able to observe both near and far field values of the EM fields at any time during the simulation.

FEM is a numerical method for finding approximate solutions of partial differential equations (PDE). The solution approach is based either on eliminating the PDE completely or rendering the PDE into an approximating system of ordinary differential equations. FEM is a powerful method for solving PDEs over complex domains that is able to model EM system by solving PDEs of Maxwell's equations but also to analyze any engineering problems linking to solve PDEs. The commercially available software, COMSOL Multiphysics, offers users to model and solve all kinds of scientific and engineering problems based on FEM, such as fluid dynamics, chemical engineering, geophysics, heat transfer, optics and photonics and so forth.

In our work we used radio-frequency (RF) module of COMSOL Multiphysics to simulate the EM distribution and plasmonic properties of metal nanobowl structure. The computational cost of calculating the optical spectra as a function of incident light wavelength ranging from 350 nm to 750 nm was significant, for example, the simulation for 500 nm metal nanobowl took 652500 s (over one week) on a 64-bit processor with 8 GB of RAM. The FDTD software, EM explorer, was also utilized to simulate 1 μm Au nanobowl EM field distribution.

5.2.2 EM field distribution and EME orientations of individual Au bowl

We compared the simulated EM field distributions of individual Au bowl with the bowl size of 1 μm and wall thickness of 30 nm by both FDTD and FEM methods. The

three-dimension simulation was obtained with a y -polarised plane wave $\vec{k}$ hitting the bowl at a zero incident angle (propagating along z direction). The Au optical constants are taken from reference [110], $(0.62 + i2.081)$ for incident light wavelength of 532 nm). The two different methods give the analogous EM field distributions as shown in Figure 5.5, indicating the accuracy and reliability of the simulation results. In the xz plane, there are three strongly enhanced EM field regions, i.e. the bowl bottom and the two ends near the bowl rim (see Figure 5.5a and d). In the yz plane, there have no obvious enhancement (see Figure 5.5b and e). In the xy plane, the two enhanced EM field regions are symmetrically distributed near the bowl rim with the EME orientations parallel to y direction which is the laser polarization (see Figure 5.5c and f). The simulated EME orientations of 1 μm Au bowl are perfectly in accordance with the experimental results as shown in Figure 5.1 and Figure 5.4.

Nanobowl structure can be seen as the assembly of numerous concentric thin nanorings with the inner ring size gradually increasing from zero to the bowl size. Aizpurua J et al reported optical properties of Au nanorings [99]. The polarization pattern of the nanoring, with the size of 100 nm and the incident wavelength of 1000 nm, showed that the strongest EME takes place at the nanoring rim with the EME orientations perpendicular to the incident laser polarization. The mechanism was explained as a strong dipolar excitation that involves the entire ring perimeter and originates from the coupling of dipolar modes at the inner and outer surfaces of the nanorings. Compared to our experimental observation for 1 μm Au nanobowls, the EME orientation was opposite. We speculate that the bowl size plays the important role in determination of the EME orientations with respect to the incident laser polarizations. For bowl sizes smaller than the

incident wavelength, the strong dipolar coupling between the outer and inner surfaces of nanobowl gives rise to the perpendicular polarization dependence, same as the nanoring; for bowl sizes larger than the incident wavelength, the dipolar coupling between the outer and inner surfaces becomes very weak, and a different mechanism is responsible for the parallel polarization dependence.

Figure 5.5 Three dimensional FDTD and FEM simulation results of EM field distributions on (a) and (d) in xz plane, (b) and (e) in yz plane, and (c) and (f) in xy plane. The arrows and dots indicate the polarization directions.

When light excites the SPs at the metal-dielectric interface, how far that the surface plasmon polaritons can propagate along the interface is mostly concerned because this distance determines the range of excitation energy transfer which may process in three ways. Dexter transfer [111], also known as electron exchange excitation transfer, has a transfer range of about 1 nm. Foerster transfer [112] is a near-field resonant dipole-dipole interaction and has a greater transfer range on the order of 10 nm. Both Dexter and Foerster transfer are non-radiative transfer. The third way is radiative transfer, which is the emission and absorption of a photon and has the longest range from 10 nm to a few hundred microns that can work as waveguide. For small nanoparticle chains as introduced in section 2.2.3, the propagating surface plasmon polaritons can be excited with both the longitudinal and transverse modes. The longitudinal mode whose propagation direction is parallel to the laser polarization is more likely to occur because the longitudinal group velocity is two times the transverse group velocity, resulting from the stronger electromagnetic coupling for longitudinal waves. This propagation behavior can be attributed to Foerster transfer, dipole-dipole interaction between the nearest two particles along the chain.

The wall thickness of the 1 μm Au nanobowls is 30-40 nm and the surface of the bowl rim can be seen as Au nanoparticles confined between the inner and outer bowl walls. Along the surface of the bowl rim, Au nanoparticles make up of the particle chains confined in the bowl wall. We used COMSOL Multiphysics software to simulate the longitudinal wave propagating in a cross chain and a linear chain, which is obtained with a y-polarised plane wave $\vec{k}$ (532 nm) hitting the Au nanoparticle chains along z direction. The particle size is 40 nm and the interspacing between two particles is 5 nm for Figure

5.6(a), 20 nm for particle (b) and (c). The EM field distributions indicate that longitudinal wave is stronger and preferred for both cross chains and linear chain. This explains why the EME orientation for 1 μm Au nanobowl is always parallel to the incident laser polarization instead of being perpendicular to the incident laser polarization.

Figure 5.6 Au nanoparticle chains with size of 40 nm in diameter and interspacing of 5 nm for (a) cross chains with y polarization and 20 nm for both (b) linear chain with y -polarization and (c) linear chain with x -polarization. Arrows indicate light polarization.

Figure 5.7 Evolution of EM field distribution and EME orientations with the increase in bowl size for individual Au bowl. The light wavelength is 532 nm and the arrows represent the incident light polarization.

Figure 5.7 shows the evolution of the EM field distribution and EME orientations for individual Au bowl with the size from 500 to 1000 nm. For 500 nm Au bowl, the EME orientations are purely perpendicular to the incident light (532 nm) polarization. For 650 nm Au bowl, the strongest EM fields are distributed near the bowl rims with the orientation perpendicular to the polarization and at the same time the less strong EM field are distributed with an elliptic ring shape. When the bowl size increases to 850 nm, the strongest EME orientations change to be parallel to the incident light polarization and the less strong EM fields are distributed at the bowl rims with the orientation parallel to the incident light polarization. When the bowl size reaches 1000 nm, the EME orientations are purely parallel to the incident light polarization. Therefore, the magnitude of the bowl size relative to the incident wavelength determines the polarization dependent properties of the Au bowl. As a result, all sizes of Au bowl arrays could be served as the plasmonic waveguiding structure with the controlled the waveguiding directions.

5.2.3 EM field distribution comparison for Ag and Au nanobowls

An interesting experimental observation is that Au nanobowl arrays have the EME orientation dependence on the incident laser polarization while Ag nanobowl arrays do not, as seen from Figure 5.1 and 5.2. To find the reasons, we used COMSOL Multiphysics software to simulate 3-dimensional EM field distributions for both Au and Ag bowls with x - and y -polarization, respectively. The incident light is along z direction and the wavelength is 532 nm. The dielectric constants are $0.05 + i3.324$ for Ag and $0.62 + i2.081$ for Au corresponding to wavelength of 532 nm [110]. For all simulations, the bowl size is 250 nm, the bowl thickness is 15 nm and the interspacing between nearest bowls is 10 nm.

The EM field distributions for number of bowls increasing from 1 to 5 are shown from Figure 5.8 to 5.12.

Figure 5.8 EM distributions in xy plane of single metal nanobowl: (a) geometry of one nanobowl; (b) and (c) are Ag nanobowl with x and y polarizations, respectively; (d) and (e) are Au nanobowl with x and y polarizations, respectively.

The EM distribution of single metal nanobowl shows that Ag and Au have similarly perpendicular EME orientation dependence on the incident light polarization as seen from Figure 5.8. But the EME positions for Ag and Au bowls are different. Strong EM fields distribute at the outer rim of the Ag bowl but at the inner rim of the Au bowl for both x and y polarizations as indicated by the white arrows. With the increase in the number of the bowls, Ag bowls begin to exhibit the distinct EM distributions and EME orientations from Au bowls (Figure 5.9-5.12). Au bowls keep the same EM field distributions and EME orientations as observed from single Au bowl no matter how many numbers of the nanobowls are investigated. That is the EM fields are distributed at the inner rims of Au nanobowls with the EME orientation perpendicular to the incident light polarizations.

Figure 5.9 EM distributions in xy plane of two metal nanobowls: (a) geometry of two nanobowls; (b) and (c) are Ag nanobowls with x and y polarizations, respectively; (d) and (e) are Au nanobowls with x and y polarizations, respectively.

Figure 5.10 EM distributions in xy plane of three metal nanobowls: (a) geometry of three nanobowls; (b) and (c) are Ag nanobowls with x and y polarizations, respectively; (d) and (e) are Au nanobowls with x and y polarizations, respectively.

Figure 5.11 EM distributions in xy plane of four metal nanobowls: (a) geometry of four nanobowls; (b) and (c) are Ag nanobowls with x and y polarizations, respectively; (d) and (e) are Au nanobowls with x and y polarizations, respectively.

Figure 5.12 EM distributions in xy plane of five metal nanobowls: (a) geometry of five nanobowls; (b) and (c) are Ag nanobowls with x and y polarizations, respectively; (d) and (e) are Au nanobowls with x and y polarizations, respectively.

Figure 5.13 EM distributions in xy plane of five metal nanobowls with the bowl size of 500 nm: (a) and (b) are Ag nanobowls with x and y polarizations, respectively; (c) and (d) are Au nanobowls with x and y polarizations, respectively.

For two Ag nanobowls (Figure 5.9), the strongest EME positions take place at the hot spot for x polarization, i.e. the interspacing between the two bowls. The strongest EME positions for y polarization are distributed at the outer rims of the Ag nanobowls with the EME orientations perpendicular to the y direction. For three bowls (Figure 5.10), the EM distributions of Ag nanobowls become totally different from Au nanobowls for both x and y polarizations, as seen from Figure 5.10. Ag nanobowls have the strongest EME positions occurring at three hot spots instead at the inner bowl rims like Au nanobowls for both x and y polarizations. The EM interaction between the two nearest Ag nanobowls leads to the strong enhancement at the interspacings because the strongest EME positions

for individual Ag nanobowl are located at the outer rims. While for Au nanobowls, there is not strong EM interaction between the two nearest Au nanobowls as the strongest EME positions for individual Au nanobowl are distributed at the inner rims. When the number of nanobowls increases to four and even five (Figure 5.11 and 5.12), the strongest EME positions for Ag nanobowls are at the hot spots and therefore show no polarization dependence. These simulation results confirm the experimental observations that Ag nanobowls have no polarization dependence but Au nanobowls do, resulting from the different EME positions and interaction between the two nearest bowls. We also simulated the EM distributions for five-bowl arrays with the size of 500 nm as seen from Figure 5.13. It shows the identical results as those observed from 250 nm 5-bowl arrays.

5.2.4 Bowl wall thickness effect

Bowl wall thickness is another controllable parameter in our bowl fabrication and it is also a key factor to determine the plasmonic properties because the plasmon resonant frequencies are a sensitive function of the wall thickness of the nanobowl. We used COMSOL Multiphysics software to simulate the total energy density (TED) spectra as a function of incident laser wavelength from 350-750 nm for both Au and Ag nanobowls. TED is formulated by $\frac{1}{2}\epsilon\mathbf{E}\cdot\mathbf{E} + \frac{1}{2\mu}\mathbf{B}\cdot\mathbf{B}$, which can be considered as the scattering intensity when measured by experiments. The bowl size is fixed at 250 nm and the wall thickness varies between 5 nm to 50 nm.

As shown in Figure 5.14, normalized total TED spectra for wall thickness of 5 nm and 10 nm show multi-peaks for Au bowl, which may correspond to multipoles of plasmon

modes as described by Plasmon Hybridization theory in Chapter 2.3. The strongest peak shifts from 670 nm for wall thickness of 5 nm to 580 nm for wall thickness of 10 nm. The Ag bowl also presents the same blue shift behavior with the increase of the wall thickness.

Figure 5.14 Total energy density spectra as a function of incident light wavelength from 350 nm to 750 nm. The bowl size is fixed at 250 nm and the bowl wall thickness increases from 5 nm to 50 nm. Left and right diagrams represent the Au and Ag nanobowl, respectively.

With the further increase in wall thickness from 15 nm to 30 nm, the TED peaks for both Au and Ag nanobowl shift to smaller wavelength but the degree of the blue shift is gradually weakened. However, when the wall thickness increases to 35 nm, the red shift occurs. The TED peak position of Au nanobowl for the wall thickness of 30 nm is 387 nm and for wall thickness of 35 nm is 392 nm. The TED peak position of Ag nanobowl for the wall thickness of 30 nm is 386 nm and for wall thickness of 35 nm is 388 nm. When the wall thickness increases from 35 nm to 50 nm, the TED peaks for both Au and Ag nanobowl keep redshifting and the degree of shift is gradually strengthened. These simulation results indicate that the bowl wall thickness can tailor the plasmonic resonances at the optical range and exhibit a regular variation with the increase in the bowl wall thickness. This capability is very important for the application of plasmonic devices controlled by plasmonic resonance modes. The wall thickness effect on TED spectra is consonant for Au and Ag nanobowl.

5.3 Conclusions

Au and Ag nanobowls present distinct bowl size effect on EM distributions and polarization dependence. For Au nanobowls, when bowl size is much larger than the incident light wavelength, the EME orientations are always parallel to the incident light polarizations, and when bowl size is smaller than the incident light wavelength, the EME orientations are always perpendicular to the incident light polarizations. Two different mechanisms are responsible for the two observations. For Ag nanobowls, the interspacing between the two nearest bowls are the strongest EME positions. As any size of bowl arrays possesses similar hot spots that are determined dominantly by the interspacings, it is

reasonable that bowl size does not affect the EM distributions for Ag nanobowls and therefore there is no EME orientation dependence on the incident light polarization, either. The two distinct observations for Au and Ag nanobowls can have different applications. For example, the Au nanobowl arrays can be used as waveguides to vary its waveguiding direction by changing incident laser polarization; while Ag nanobowl arrays can be used as SERS sensors to detect various biomolecules at the hot spots. Adjusting bowl wall thickness can tune the plasmonic resonance frequencies within the optical range and the variation is regularly changing and therefore is controllable and desirable.

Chapter 6

Other work

During my Ph.D study, another important research direction is the fabrication of nanostructures based on pulsed laser deposition technique which has been introduced in Chapter 3. Nanostructures can be produced either by direct interaction between the pulsed laser and substrates, or by depositing ablated particles on catalyst pre-patterned substrates and then forming various morphologies of nanostructure.

6.1 Core-shell structures induced by pulsed laser ablation

6.1.1 Introduction

Laser induced periodic surface structures (LIPSS) such as ripples, ridges, and cones resulting from laser-material interaction have stimulated considerable efforts in the area of laser microprocessing for microelectronics application [113-117]. A variety of morphologies on a solid surface have been extensively reported by adjusting the laser fluence, wavelength, pulse duration, the ambient gas species and processing pressure [118-124] or with the aid of pre-patterned structure [117, 125]. Laser induced Si, the

semiconductor industrial mainstay, surface microstructure and nanostructure especially have the significance in the application of miniaturized Si-based devices [126, 127].

Nanocrystal Si (nc-Si) and nc-Si/SiO_x system have been gaining widespread interests owing to their potential application as light-emitting devices which are fully compatible with Si-based optoelectronic integrated circuits [128-133]. Quantum confinement and oxygen related defects have been proposed as the origins of intense visible PL in these low dimensional Si structures [134-140]. However, it is still an open question as for the mechanism of the PL.

In this chapter we report the simultaneous formation of Si nanostructures and nc-Si capped by SiO_x coreshell structures by using Nd³⁺: YAG third harmonic generation (TGH) (355nm) laser irradiation. It is noted that nc-Si/SiO₂ system has its own importance in semiconductor industry because SiO₂ surface is a well-established material known to passivate Si surfaces where the Si/SiO₂ system is fully compatible with current Si technology.

6.1.2 Experimental

Si (100) oriented wafers were loaded on the target holder of a pulsed laser deposition (PLD) chamber after ultrasonic cleaning in acetone and subsequently in deionized water. A focused TGH Nd³⁺:YAG laser with a focal spot size of 1mm in diameter was used as the light source to impinge on the samples. The laser beam has a wavelength of 355 nm, a laser fluence of 20mJ/mm², a pulse duration of 30 ns and a repetition rate of 10 Hz. The experiments were carried out under ambient environment. Nanostructures were formed in the laser irradiated areas. Post annealing of the laser-treated samples were performed in a tube furnace in air.

The sample morphologies after laser irradiation were studied by field emission scanning electron microscopy (FE-SEM JEOL JSM-6700F). Energy dispersive X-ray diffraction (EDX) was used to investigate the composition variations before and after annealing. Raman spectroscopy (Witec CRM200, $\lambda_{\text{laser}} = 532 \text{ nm}$) and photoluminescence spectroscopy were performed to study the crystallinity, the size distribution in nc-Si/SiO_x system as well as the light-emitting properties.

6.1.3 Results and discussion

The Si nanoparticles produced at the laser irradiated area are shown in Figure 6.1(a). The average size of the nanoparticles is about 50 nm. Figure 6.1(b) shows the SEM image of Si nanoparticles after annealing at 900C for 2 hours in air. Obviously, after the thermal treatment the nanoparticles grow bigger to an average size of 80 nm. Typical ripple structures were observed in the laser irradiated areas at lower magnification SEM image. After annealing, the Si nanoparticles in some areas of the ripples disappear due to the aggregation of grown particles, as seen from Figure 6.1(c). EDX measurement shows a variation of atomic ratio between Si and O before and after annealing. The content of O atomic percentage increases from 7% to 50% after annealing which indicates the Si nanoparticle surface is oxidized and passivated by a thin layer of SiO_x ($x < 2$) while the particles grow in size.

An interesting observation of the laser ablation is the formation of much larger particles (about 500nm) in the vicinity of laser irradiated area as seen from Figure 6.2(a). These half-micron sized particles are the result of bombarded-out Si atoms from the laser-irradiated area and are uniformly distributed on the Si substrate. The inset in Figure 6.2(a) is the high magnification image. However, the SEM images after annealing shown in

Figure 6.2(b) imply one particle in Figure 6.2(a) may contain a large number of ultrafine particles as the cluster-like morphology presents after annealing. In order to have a better understanding of such particles, Raman spectroscopic measurement ($\lambda=532\text{nm}$) was performed. Figure 6.3 shows the Raman spectra before and after annealing. The Raman peak of bulk-Si transverse optical (TO) mode is located at 520cm^{-1} with full width at half maximum (FWHM) of 7 cm^{-1} . The half-micron sized particles before annealing shown in Figure 6.2(a) present a red-shifted and asymmetric Raman peak which can be fitted by two Gaussian peaks positioned at 495cm^{-1} with FWHM of 34cm^{-1} and 516 cm^{-1} with FWHM of 11cm^{-1} . According to literature [134, 136, 139, 141], the broad low energy band centered at 495cm^{-1} results from disordered Si structure while the narrow high energy band centered at 516cm^{-1} results from Si nanocrystals of average size 4 nm. This result indicates that the half-micron sized particle is made up of a large number of nc-Si. After annealing, the nc-Si Raman peak is shifted to 517cm^{-1} and its FWHM becomes narrower compared with that before annealing. This result suggests the nc-Si grow in size after annealing. Hence annealing increases the thickness of the SiO_x layer as well as the average size of the nc-Si cores.

Figure 6.4 shows the room temperature photoluminescence band of the samples before and after annealing. The broad PL peak centered at 640nm was observed before annealing. The PL spectrum has been reported to be very sensitive to the surface chemistry of Si nanocrystals, the interface between nc-Si and SiO_x as well as oxygen related defects [133, 135, 137]. Since the experiments were carried out in ambient environment the bombarded-out Si particles may be oxidized and form the nc-Si core capped with a thin layer of substoichiometric SiO_x structure. The excitons localized at the interface between the core nc-Si and shell SiO_x as well as the oxygen vacancies are considered as the main origins of

the observed emission in our samples. After annealing, the PL peak is shifted from 640nm (red) to 760nm (infrared) and became 10 times stronger than that before annealing (see Figure 6.4). This shift is consistent with our conclusion that the nc-Si increase in size after annealing. As evidenced by EDX investigation that O content increases after annealing, the change of nc-Si surface property may also lead to the shift of the PL band.

Figure 6.1 SEM images of laser-irradiated area. (a) before annealing Si nanoparticles with average size of about 50nm; (b) after annealing Si nanoparticles with average size of about 80nm; (c) after annealing some Si nanoparticles disappear at laser induced ripple structure.

Figure 6.2 SEM images of bombarded-out Si particles in the vicinity of laser-irradiated area: (a) before annealing; (b) after annealing. The insets are the high magnification images.

Figure 6.3 Raman spectra of the bombarded-out particles before and after annealing.

Figure 6.4 PL spectra of bombarded-out particles before and after annealing.

6.2 ZnO honeycomb structures by PLD technique

6.2.1. Introduction

Macroporous materials with high surface-to-volume ratio such as honeycomb structures [142, 143], nanobowls [144-147], and hollow spheres [148, 149] are of great scientific and technological interest due to the ability to interact with atoms, ions and molecules at both their surfaces and throughout the bulk of the materials. The applications for macroporous materials involve containers for microencapsulation and controlled delivery, separation technology, gas sensors, catalysis, photonic crystals and devices [150-153]. However, the controlled pore size, shape as well as uniformity are still challenges [142-149] because these factors are directly affecting their ability to perform the desired function in a

particular application. Among these synthetic strategies, NSL method [154-157] is the most appropriate and versatile approach to produce periodic and regular template for the subsequent macroporous materials fabrication, which normally employs self-assembled monolayer of polystyrene sphere as the basic template. Here, we will demonstrate the successful fabrication of ZnO honeycomb structures on metal prepatterned Si substrates by NSL method combined with PLD technique.

ZnO has been a hot research topic partly because of its excellent properties, such as its wide bandgap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, gas sensitivity, field-emission effect, biocompatibility, and environment-friendly character [158-161] and partly because of rich morphologies of ZnO nanostructures [162-166], i.e. nanowires, nanobelts, nanocombs, nanotubes, nanopropellers which have great potential for a variety of nanoscale applications. However, fabrication of macroporous ZnO has been rarely reported so far. Due to the high surface-to-volume ratio and good biocompatibility, ZnO honeycomb structures are believed to be the potential candidates in the bioscience and biotechnology as miniaturized containers for microencapsulation, controlled drug delivery, artificial cells, catalysis and so forth [149-153]. Here, the reasons responsible for the different change of morphology and distribution of metal nanoparticles among Pt, Au, and Ag templates are presented. The growth mechanism of ZnO honeycomb structures is proposed and discussed in detail, which provides us the important information to choose the most appropriate metal pattern to produce controllable ZnO honeycomb structure under different experimental parameters in future.

6.2.2. Experimental

Pt, Au and Ag patterns were fabricated using NSL method. Six μl of ethanol and 10 μl of sodium dodecylsulphate (10%) were mixed with 3 drops of 465 nm in diameter polystyrene (PS) spheres mixture (purchased from Polysciences. Inc.) Monolayer regions were obtained by spin coating 10 μl of this mixture onto Si substrate (phosphorus-doped n-type with (001) orientation) at 3600 rpm for 2 min. Pt, Au or Ag was subsequently deposited onto the monolayers using direct current sputtering (Jeol JFC-1600 Auto-Fine Coater) with the current set to 30mA and sputtering time set to 60s. Removal of the PS spheres by sonication in chloroform for 10 s gave the Au, Pt or Ag hexagonal patterns.

The metal prepatterned substrates were loaded onto PLD substrate holder which was then heated to 600 $^{\circ}\text{C}$ under a vacuum of 6×10^{-6} mbar. A focused KrF excimer laser (248 nm) was used as the source to ablate on the ZnO target (99.99% purity). During the deposition, oxygen background gas with pressure of 10 mbar was introduced into the PLD chamber. The laser energy is 300 mJ; the repetition rate is 20 Hz; the target-substrate distance is 5 cm and the deposition duration is 10 min.

6.2.3. Results and discussion

Figure 6.5 shows SEM images of ZnO deposited on Pt, Au and Ag templates. Regular and periodic honeycomb structures are observed on Pt template and the spacing between two adjacent cells is in accordance with the diameter of the PS spheres used (465 nm). ZnO deposited on Au template also exhibits honeycomb structures but they do not follow the periodicity of original PS sphere arrays and the cell sizes are not uniform. Compared with the cells formed on Pt template, smaller and more densely packed cells are generated on Au template. However, ZnO deposited on Ag template forms continuous thin film with big grains and fail to produce honeycomb structures.

Figure 6.5 SEM micrographs of ZnO deposited on Pt, Au and Ag templates.

The hexagonal metal patterns play an important role in growth of ZnO honeycomb structures. Initially, the hexagonal lattices of triangularly shaped metal islands were formed at the interstitials between adjacent PS spheres for all the sputtered metals. After transferring the metal templates into PLD chamber and in-situ heating to 600 °C in vacuum, changes of metal island morphology and metal particle distribution take place as shown in Figure 6.6. The Pt islands crystallized to small spherical Pt particles which were uniformly distributed over the originally triangular island sites after annealing. Such change in morphology creates a periodically catalytical environment so that to grow periodic and regular ZnO honeycomb structures on Pt template. For Au template, after

annealing the triangularly shaped Au islands crystallized to one big Au spherical particle in the center of the island site with much smaller Au particles scattered around. Since both the center and small scattered Au particles serve as the catalysts, the overall Au pattern after annealing becomes irregular which produces irregular ZnO honeycombs as a result. In contrast to Pt and Au templates, Ag template dose not change much in size and shape after annealing and fails to fabricate the ZnO honeycomb structure, which implies that Ag does not act as catalyst during the growth of ZnO by PLD.

Figure 6.6 SEM images of metal templates after annealing at 600 °C in PLD vacuum chamber: (a) Pt, (b) Au and (c) Ag.

As shown in Figure 6.6, the spherical shape of Pt and Au nanoparticles indicates that Pt and Au were in liquid phases while Ag islands were still in solid phase ^[26, 27] when annealed at 600 °C in vacuum. This seems to contradict with the fact that Ag is easier to melt than Pt and Au since Ag has a lower melting point of 962 °C than Pt and Au, which is 1772 and 1064 °C, respectively. We propose that Au and Pt nanoparticles reacted with substrate Si and formed eutectic metal-Si alloys [169, 170]. When a metal forms the alloy with Si at a certain atomic percentage, the melting temperature, called eutectic temperature, of the alloy can be much lower than that of both the metal and Si. The bulk eutectic temperatures for Pt-Si, Au-Si and Ag-Si alloys are 830, 360 and 835 °C respectively [171]. In addition, considering the depressed saturation vapor pressure at 6×10^{-6} mbar, the melting temperatures of all three metals are further reduced [172]. For Pt and Au templates, the metal-Si alloys were formed at the interface between Si substrate and metal islands and then metal islands were gradually melted to liquid droplet-like nanoparticles. As Au-Si eutectic temperature is only 360 °C, during the melting of Au islands, Au particles have a higher energy and are able to migrate along the Si surface [173], either moving toward the island center and accumulating as bigger particles or dispersing as many smaller particles around the island. In contrast with Au, Pt particles have a lower but moderate energy during the melting and the migration is tiny as a result of relatively uniform spherical particles distributed over the island sites. Despite Ag-Si has a similar eutectic temperature as Pt-Si, Ag was not melted under the same experiment circumstance. Under the same sputtering parameters, the thickness of the islands is different due to the difference in the sputtering yield [172]. The yield for Ag is the largest, giving rise to the thickest islands, followed by Au islands and Pt islands are the thinnest. The thicker Ag islands require a higher temperature to melt. Moreover, Ag is easily oxidized which reduces its catalytic

function. In reference [168], Pt, Au and Ag were used as catalysts to fabricate ZnO nanowires. After annealing at 800 °C AgO was formed, resulting in lower quality ZnO nanowires compared to Pt or Au catalyst. In our experiment, oxygen was introduced during the deposition of ZnO, which further increases the likelihood of oxidation. Therefore, Ag is not a good choice as catalyst.

The XRD pattern of Pt template annealed at 600 °C in vacuum indicates that polymorphic phase of Pt₃Si was formed, as seen in Figure 6.7. This observation proves that Pt forms liquid alloy with Si during annealing and when the alloy is cooled down below its eutectic temperature, polymorphic phase Pt₃Si begins to separate from alloy phase and final room temperature mixtures are Pt₃Si, Pt and Si [171]. Different from Pt-Si alloy, Au-Si phase diagram [171] shows that Au-Si has no polymorphic phase below its eutectic temperature, and when temperature decreases below its eutectic temperature, Au and Si are separated from liquid alloy phase. Therefore, we can not investigate AuSi alloy at room temperature, which is consistent with XRD result of Au template (see Figure 6.7).

Figure 6.7 XRD patterns of Pt and Au templates after annealed at 600 °C in vacuum.

In order to further understand the formation mechanism of ZnO honeycomb structure by PLD, we investigated the initial stage of ZnO growth. Figure 6.8(a) shows a SEM image of the first 2-minute pulsed laser deposition of ZnO on Pt catalyst prepatterned Si substrate at 600 °C in vacuum. The deposited ZnO molecules are trapped by Pt liquid droplets which serve as the site-specific-growth agents and accelerate the growth rate of ZnO islands as well. Substrate heating provides the deposited ZnO molecules the necessary kinetic energy so that they can easily migrate to the Pt sites. With the deposition time elapsing, more ZnO molecules diffuse toward the Pt catalyst sites and coalesce with adjacent protruded ZnO film as circled in Figure 6.8(a). As a result, the honeycomb cell was formed when six ZnO islands connected with each other. Another experiment was performed under the same conditions as the one shown in Figure 6.8(a) but without in-situ heating. The result is shown in Figure 6.8(b). The inset is the high magnification image, which shows that ZnO nanoparticles are uniformly distributed on the whole template resulting in a uniform film. Such observation indicates that metal liquid droplets are the prerequisite for the growth of ZnO honeycomb structures.

The crystallinity of ZnO honeycomb structure was examined by X-ray diffraction measurement. As shown in Figure 6.9, both ZnO honeycomb structures on Pt and Au templates and ZnO thin film on Ag template exhibit (002) preferred orientation. In-situ substrate heating resulted in the deposited ZnO molecules crystallizing along [002] direction which has been reported as the easy and fastest growth direction among ZnO crystallographic directions [174]. The inset is enlarged XRD pattern for three metals and Pt₃Si diffraction peak was detected again. The good crystallinity of ZnO honeycomb structures on Pt and Au templates will benefit for its potential application in biosensors

because the surface exposed to the gas molecules is same which can increase the stability and repeatability of the gas sensor [160].

Figure 6.8 SEM images of ZnO deposited on Pt templates at first 2min deposition stage: (a) in-situ heating at 600 °C in vacuum; (b) no in-situ heating in vacuum.

Figure 6.9 XRD patterns of ZnO grown on Pt, Au and Ag templates.

Figure 6.10 depicts PL measurement for all three samples which present different peak positions of the band-edge emission in ultraviolet (UV) region as well as defect-induced emissions in visible region. ZnO grown on Ag template tends to form a continuous film, and its PL spectrum exhibits the normal band-gap emission in UV region centered at 390 nm as reported in the literature [158]. ZnO honeycomb structures produced on Au and Pt templates exhibit three emissions in UV region as shown in inset. The peak positions of three UV emissions for ZnO on Pt and Au are 380, 388, 397nm and 379, 386 and 399nm, respectively. The difference in peak position may result from the different size of honeycomb cells on Pt and Au templates. It has been widely reported that different ZnO nanostructures present different UV peak positions in the range of 370-400 nm, and such peak shift is not the result of quantum confinement in the nanocrystals because these structure sizes are much larger than ZnO Bohr radius of 2.34 nm [158, 166, 175]. Therefore the morphology of ZnO nanostructure is recognized as the main factor leading to different PL spectra [158]. Defect-induced emissions in visible region result from several types of surface defects in ZnO [158], including neutral, singly charged, and doubly charged zinc or oxygen vacancies as well as zinc or oxygen interstitials. Each kind of defect corresponds to a certain defect energy level leading to the different defect-induced emission peaks in visible region. As seen from Figure 6.10, all three samples present the green and red emissions [158, 175] in visible region but with different peak position and peak density. ZnO honeycomb structure has a large surface-to-volume ratio which makes PL peaks sensitive to surface defect concentration/level.

Fig 6.10 PL spectra of ZnO grown on Pt, Au and Ag templates.

6.3 Conclusions

In conclusion, we have demonstrated the formation of Si nanostructure and nc-Si/SiO_x core/shell structure using third harmonic Nd³⁺:YAG (355nm) laser irradiation under ambient conditions. The nanoparticles formed in the laser irradiated area have an average size of 50nm. After annealing the nanoparticles are grown bigger to an average size of 80nm. In the vicinity of the laser spot, half-micron sized particles were observed, which consist of 4nm nc-Si/SiO_x coreshell structures as evidenced by Raman data. The PL measurements exhibit a broad visible emission centered at 640nm which can be assigned to defects-related PL peak, i.e. the interface between nc-Si and SiO_x as well as oxygen related defects.

We have also demonstrated the successful fabrication of periodic ZnO honeycomb structures on Pt template. Liquid phase of metal catalyst is a prerequisite for ZnO honeycomb structures growth. During ZnO deposition by PLD, the liquid spherical metal nanoparticles serve as the site-specific-growth agents and accelerate the growth of ZnO molecules over the templates. Under our current experimental conditions, Pt template is the most appropriate catalyst to produce ZnO honeycomb structure with controllable periodicity and cell size. However, by adjusting the experimental parameters Au pattern is also expected to be the effective catalysts to fabricate controllable ZnO honeycomb structures. The annealing temperature can be reduced to a point just above Au-Si eutectic temperature of 360 °C so that to avoid the migration of Au nanoparticles. While for Ag pattern, it is not inert during the annealing and requires a higher temperature to melt, and therefore it is not a good choice to serve as the catalyst. ZnO honeycomb structures present good crystallinity with (002) preferential orientation which can be attributed to in-situ substrate heating. The PL spectra of ZnO honeycomb structures are different from normal ZnO thin film, which is assigned to the different morphology and different surface defect concentration presenting in such large surface-to-volume ratio macroporous structures.

NSL method combined with PLD technology provides a feasible way to control the cell size and periodicity of the honeycomb structures. Such method also can be extended to fabricate a wide range of materials with controlled pore size and desired properties.

Chapter 7

Conclusions and Future work

Starting from setting up a PLD system, combined with NSL method, we have successfully developed a technique to fabricate semi-spherical shells, the closely packed nanobowl arrays. Such approach has the advantage of flexible and precise control on the important parameters of nanobowl structures. These parameters include bowl size, bowl wall thickness, interspacing between two nearest bowls and material species that also are the key factors to tailor the plasmonic properties of metal nanobowls. For example, the bowl size can be controlled by choosing the size of polystyrene spheres which are commercially available with the size variation from a few nanometers to a few hundred micrometers; the bowl wall thickness can be controlled by deposition parameters of the PLD system, such as laser power intensity, deposition duration, repetition rate and target-substrate distance; the interspacing of nanobowls is determined by interspacing of PS spheres and therefore can be controlled by pre-heating the monolayer PS template at its glass temperature or using plasma etching to vary the interspacing of PS spheres; the material species can be controlled by using different material targets.

The nanobowl fabrication method provides us a good chance to systematically study the plasmonic properties of metal nanobowl structures. In this thesis, we investigated two metal species, Au and Ag, both of which have been proved to be the most appropriate

candidates in plasmonic applications. Au and Ag nanobowl array showed their capability to be SERS sensor based on localized/bound surface plasmon mode. Several commonly used molecules in bioscience and biotechnology such as R6G, CV, BCB, MB and MPA-3 have been employed as probe molecules. SERS spectra of these probe molecules at a low concentration of 1 $\mu\text{M/L}$ were recorded and compared. SERS peak images suggested that Au nanobowls have the consistent SERS hot spot sites and strongest inelastic emission intensity positions while Ag nanobowls do not have the consistency. The SERS observation on hybrid structures between Ag nanobowls with Ag tetrahedrons and between Au nanobowls with Au nanoparticles indicates that it is possible via tuning surface plasmon resonances to break Raman selection rules and therefore to excite the original Raman inactive vibrations. This is a significant discovery and has the potential application to be used in biomolecules detection especially for those molecular vibrations that can not be observed governed by conventional Raman selection rules.

Au nanobowls and Ag nanobowls present distinct bowl size effect on the EM distributions and polarization dependence relation, experimentally. For Au nanobowls, when bowl size is larger than the incident light wavelength, EME orientations are always parallel to the incident light polarizations, and when bowl size is smaller than the incident light wavelength, EME orientations are always perpendicular to the incident light polarizations. Two different mechanisms are responsible for the two observations. For Ag nanobowls, the interspacing between the two nearest bowls are the strongest EME positions. As Ag nanobowl hot spots are determined dominantly by interspacing, it is understandable that the bowl size does not affect the EM distributions for Ag nanobowls and therefore there is no obvious EME orientation dependence on incident light polarization, either.

The simulation results on bowl size effect also confirm that positions of strongest EME for Au and Ag nanobowl arrays are different leading to different polarization dependence behaviors. The two distinct observations for Au and Ag nanobowls can have different applications. For example, the Au nanobowl arrays can be used as waveguides to vary its waveguiding direction by changing incident laser polarization; while Ag nanobowl arrays can be used as SERS sensors to detect various biomolecules at the hot spots. The simulation results also suggest that adjusting bowl wall thickness can tune the plasmonic resonance frequencies and the variation is regularly changing and therefore is controllable and desirable.

Although our experimental observation agrees with the simulation results by FEM and FDTD methods on plasmonic properties on both Ag and Au nanobowls, the nature and origin of the difference between Ag and Au nanobowls have not been fully understood. More experiments and simulations are necessary to carry on. The recommended future work summarizes as below:

1. Interspacing effect on plasmonic properties of metal nanobowls;
2. Surface plasmon resonance frequency tuning effects on Raman selection rule;
3. Plasmonic properties of hybrid structures based on nanobowls;
4. Plasmonics properties of multilayered nanobowl structures;
5. Real applications of metal nanobowls as well as nanobowl based hybrid structures in the area of biosensor and nanophotonics.

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To be submitted journal papers

1. **Y. Ma**, K.W. Kho, H. Zhang, Y.M. You, S. Chandrasekar, C.L. Ong, C.X. Cong, X.T. Zeng, Z.X. Shen, The SERS activity observed on metal nanobowl substrates
2. **Y. Ma**, X.T. Zeng and Z.X. Shen, Plasmonic waveguiding of Au metal nanobowls
3. **Y. Ma**, X.T. Zeng and Z.X. Shen, Bowl size and wall thickness effects on plasmonic properties of metal nanobowl arrays

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