Large Area Plasmonic Structure Fabrication and Tuning of Surface Plasmon Resonance

LIU CAIHONG

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Large Area Plasmonic Structure Fabrication and
Tuning of Surface Plasmon Resonance

BY

LIU CAIHONG
(M. Sc., Xiamen University, P. R. China)

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Plasmonics has attracted the great research interest of a wide range of scientists due to its extensive applications in the fields of novel optical devices, sensing applications, light generation and spectroscopy. Currently, numerous researches are being carried out to investigate the plasmonic properties of various nanostructures with different shapes and constituent materials. The research reported in this thesis mainly aims to fabricate large-area metallic nanostructures and to investigate the tunability of SPR by bimetallic layers.

Both laser interference lithography (LIL) and colloidal lithography are applied to fabricate large area plasmonic nanostructures. LIL has the advantages of being a non-contact process in air and is able to achieve large-area and maskless nanolithography at a high speed with low system investment. Around centimeter square periodic metal structures can be achieved by the LIL technique. Single layer Au and Ag/Au bimetallic layer nanodot arrays are fabricated by LIL followed by electron beam deposition and lift-off processes. Colloidal lithography adopts a simple and flexible self-assembly process using latex microspheres to produce a particle mask for metal deposition. A large area of ~0.8 millimeter square nanoparticle array can be achieved. Various types of nanoparticle arrays with different particle sizes or metal film thicknesses are successfully produced by the colloidal lithography technique. The physical and optical properties of these fabricated nanostructures are examined by OM, SEM, AFM and UV-Vis spectroscopy.

To the best of our knowledge, there is yet no extensive research on the surface plasmon behavior of hybrid nanodots localized on quartz substrates. In this thesis, we
Summary

focus on gold and silver bimetallic nanostructures and study the SPR peaks of these thin films and dot arrays. It is observed that for gold thin film on quartz substrate, the optical spectral peak is blue shifted when a thin silver film is coated over it. Compared to the plasmon band in the single metal gold dot array, the bimetallic nanodot array shows a similar blue shift in its spectral peak. These shifts are both attributed to the electromagnetic interaction between the gold and silver atoms. A simplified spring model is adopted to qualitatively explain the phenomena observed. This study offers a novel way for hybrid materials to be used to tune the SPR peaks of noble metals. Moreover, several variables, such as consistency of monolayer, particle size and metal film thickness on plasmonic effect of these fabricated nanostructures are studied in relation to tuning the SPR peaks. The SPR peak shifts observed in the optical transmission spectra are qualitatively explained using various interaction models. These characterizations have the potential to allow us to extend the applications incorporating plasmonic resonance tuning.
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Chapter 2

$\delta_d$  Decay length in the dielectric

$\delta_m$  Decay length into the metal

$\varepsilon$  Dielectric function

$\omega$  Angular frequency

$\omega_p$  Plasma frequency

$\gamma_0$  Electron relaxation rate

$\tau$  Free electron gas relaxation time

$\varepsilon_m$  Metal permittivity

$\varepsilon_d$  Dielectric permittivity

$\theta$  Incident angle

$N$  Number density

$n$  Integer number

$D$  Grating dimensions

$\lambda$  Wavelength

$\alpha_i$  Polarizability

$a, b, c$  Axes of ellipsoidal particle

$L_i$  Geometrical depolarization factors

$d$  Interparticle spacing
List of symbols

Chapter 3

\( \lambda \)  
Wavelength

\( \theta \)  
Two light waves intersect angle

Chapter 4

\( \theta \)  
Inclination angle

\( j_w \)  
Water influx

\( j_p \)  
Respective particle influx

\( j_e \)  
Water evaporation flux

\( v_c \)  
Array growth rate

\( l \)  
Evaporation length

\( h \)  
Array thickness

\( a \)  
Triangular nanoparticles perpendicular bisector

\( d_{ip} \)  
Inter-particle spacing

\( D \)  
Sphere diameter

\( d_m \)  
Deposited mass thickness
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1.1 Background

Ever-increasing demand for faster information transport and processing has driven the scaling down of electronic devices continuously. Besides considerable nanofabrication challenges, further size reduction of nano-electronic circuits is governed by the constraints of quantum information processing and energy consumption [1]. Optical interconnect attracts much research interest as an important component of future computer chips due to its much larger data carrying capacity and faster data processing speed [2]. Unfortunately, their implementation is hampered by the large size mismatch between electronic and dielectric photonic components. Miniaturization of photonic devices, to guide and confine electromagnetic waves into a size scale compatible to highly integrated electronic circuits, poses one of the technical challenges for the information technology industries [1]. Plasmonics is based on surface plasmon resonance (SPR) for unique optical properties of nano-scale metallic structures [3-5]. By manipulating light in nano-scale metallic structures, it can provide us with a feasible solution to overcome this technical limit by integrating electronic and photonic technologies together (Fig. 1.1).

Nanostructured metallic thin film layers show complex and interesting optical properties [6-9]. The most striking phenomenon is electromagnetic (EM) wave resonance due to the collective oscillations of the conduction electrons, which is called surface plasmons (SPs) [10, 11]. SPs can take various forms, ranging from freely propagating electron density waves along metal surface, to localized electron oscillations on metal
nanoparticles or nanostructures [1]. Therefore, SPs provide the ability to confine light to very small dimensions, and thus offer the potential to carry optical and electrical signals through the same thin metal circuitry.

Exploitation of SPs promises many interesting applications in nanophotonics, data storage, non-linear optics, surface-enhanced Raman spectroscopy, fluorescence spectroscopy and biochemical sensors [12-14]. These include plasmonic chips that function as ultra–low loss optical interconnects, plasmonic circuits and components that can guide light within ultra-compact optically functional devices [13, 15].
nanolithography at deep subwavelength scale [16, 17], superlenses that enable optical imaging with unprecedented resolution [18, 19] and new light sources with unprecedented performance [14]. To fulfill the potential applications offered by plasmonics, more research needs to be carried out in these areas. Some of the challenges that face plasmonics research in the coming years are as follows: (i) to demonstrate optical frequency subwavelength metallic wired circuits with a propagation loss that is comparable to conventional optical waveguides; (ii) to develop highly efficient plasmonic organic and inorganic LEDs with tunable radiation properties; (iii) to achieve active control of plasmonic signals by implementing electro-optic, all-optical and piezoelectric modulation and gain mechanisms to plasmonic structures; (iv) to demonstrate 2D plasmonic optical components, including lenses and grating couplers, that can couple single mode fiber directly to plasmonic circuit; and (v) to develop deep subwavelength plasmonic nanolithography over large surfaces [14].

In this thesis, we focus on the large area plasmonic nanostructure fabrication and investigation of the tuning of the surface plasmon resonance.

1.2 Fabrication techniques of plasmonic nanostructures

To generate strong surface plasmon resonance effect, metallic nanostructures need to be around the size of half of the wavelength of light. For visible light spectra, 200 - 400 nm nanostructures need to be fabricated. The study of plasmonic properties relies on advanced nanofabrication techniques to create effective metallic nanostructures. Metallic nanostructure fabrication techniques are usually classified as bottom-up and top-down
approaches depending on the elementary processes used to realize new architectures. Bottom-up processes tend to involve the chemical deposition of materials using electrolysis or the reduction of ionic compounds contained in solution, and a variety of shapes can be produced [7]. Direct chemical synthesis of metallic particles is the dominant bottom-up technique. Core/shell [8], rods [9, 10] and wires [11] are among the many shapes that can be fabricated in addition to spheres. The most widespread approach in nanostructure fabrication uses standard top-down process. Top-down fabrication generally starts with a substrate covered by thin layers of dielectric or plasmonic materials, and the surface patterning comprises different steps of lithography combined with dry or wet etching processes [20].

Developing lithography process is a growing interest to fabricate nanoscale devices for nanotechnology applications. The commercialization of nanoscale devices requires the development of low-cost and high-throughput nanofabrication technologies which also allow design changes frequently. Since the fabrication of high-quality lithography masks is time consuming and expensive, maskless nanolithography, such as electron-beam lithography (EBL) [20], focused ion-beam lithography (FIB) [21] and scanning-probe lithography (SPL), can reduce the fabrication cost and play an important role in industry, research, and emerging applications in nanoscale science and engineering. However, the main shortcoming of the maskless lithography is low throughput, which is mainly due to slow scanning process [22, 23]. Although multi-axial electron-beam lithography and zone-plate-array lithography [24-26] are developed to improve the throughput, they suffer from lens aberration and diffraction limit, respectively. For SPL, its throughput is two to three orders of magnitude lower than that required for practical
nanofabrication applications, even though it has made a noticeable throughput improvement [23]. It is because of the limited feedback bandwidth available to control the tip-sample distance at higher speeds, which leads to a slow scan of the tips [27]. Plasmonic lithography is a promising way to obtain nanometer-scale features beyond the diffraction limit of far-field optical lithography [16, 17]. However, the difficulty to control the nanoscale gap precisely should be solved before plasmonic lithography could be widely applied [17].

In plasmonic research, e-beam lithography (EBL) and focused ion beam (FIB) lithography are the preferred methods for fabricating high-resolution metallic nanostructures of arbitrary shapes. Periodic nanostructures, in general, are fabricated over small areas and characterized with a micro-spectrometer. Standard spectrometry equipment without any focusing optics can be used for characterization of large area samples but the fabrication process would take very long time with serial lithography tools, such as EBL or FIB [28]. In order to overcome these problems faced, we employed either laser interference lithography (LIL) or colloidal lithography combined with physical deposition of metal thin film and lift-off in this thesis.

1.3 Research focus and contributions

The main objective of this research project is to fabricate large-area plasmonic nanostructures on quartz substrate with low-cost and high-throughput and tune the surface plasmon resonance by bimetallic (Ag/Au) nanostructures. In the project, both laser interference lithography (LIL) and colloidal lithography are applied to fabricate plasmonic
nanostructures. The plasmonic effects of the fabricated nanostructures are investigated by analyzing their UV-Visible spectra. The goal of the project is to compare the plasmonic effects of a single metal structure and a bimetallic structure when another metal layer is added over the same pattern and to explain the observed band shift in transmission spectrum qualitatively using a simplified model. The bimetallic hybrid structure would eventually lead us to tune the plasmonic resonance frequency of noble metal nanostructures.

1.3.1 Large-area nanodot array fabrication by LIL

The main metallic nanostructure fabrication methods, such as EBL and FIB, have the drawbacks of low speed and high cost, which are unsuitable for future industrial applications. Therefore, a maskless and high-throughput fabrication technique - laser interference lithography (LIL) for large-area parallel surface patterning on a photoresist layer and then transferring the nano-patterns down to a thin metallic film via a lift-off approach or metal etching, is employed in this project [29, 30].

LIL is a technique of writing periodic or quasi-periodic patterns on photosensitive material using two coherent interference laser beams. LIL is capable of quick generation of dense features over a wide area. The period of the nanopatterns can be tuned to desired values by changing the angle between the mirror and the sample holder. In the project, we adopted double exposure procedures to achieve a two dimensional photoresist nanodot array. Patterned nanodot arrays of area 5 mm × 5 mm are achieved under the current
available system. The patterned area will be greatly enlarged if higher power lasers are used.

Because wet chemical etching is isotropic and dry etching requires reactive ion plasma (RIE) tools, a lift-off process is adopted when transferring the patterns to the metal film. Moreover, double-layer photoresist lift-off is adopted in order to overcome the sidewall effect of a single layer photoresist lift-off. The bi-layer resist lift-off process can ensure good quality structure fabrication, although it increases the process complexity. The combination of LIL and bi-layer resist lift-off techniques shows potential in low cost, large area plasmonic nanostructure fabrication. Both Au and bimetallic Ag/Au nanodot arrays are achieved by the same procedure with different metal thin film depositions. This method can be applied in the fabrication of other metallic nanostructures besides gold and silver as well.

1.3.2 Large-area nanoparticle array fabricated by colloidal lithography

In additional to LIL, colloidal lithography is also applied to fabricate large-area nanostructures. As one of the self-assembly techniques, colloidal lithography uses colloidal sphere arrays as lithographic masks or templates to fabricate nanostructures. Compared to other nanofabrication techniques, e.g. EBL, colloidal lithography has been applied widely because of its unique features: it is inexpensive, inherently parallel and enables high-throughput nanofabrication [31-33].

In the fabrication, a large-area and self-assembled colloidal spheres mask is formed on a quartz substrate by a spin coating method. Without controlling any additional
parameters other than spin speed and time, the maximum yield obtained in our experiments obtained is close to 800,000 µm². Both Au and bimetallic Ag/Au nanoparticle arrays on quartz substrates are fabricated following the metal deposition and sphere lift-off processes. Moreover, various sphere masks are flexibly achieved by changing the particle diameter and the metal film thickness, thus different metallic nanopatterns are obtained accordingly.

1.3.3 Tuning of surface plasmon resonance by sphere size and film thickness

The influences of sphere size and metal film thickness on plasmonic effect of these colloidal lithography fabricated nanostructures are studied. We compare their UV-visible spectra and qualitatively explained any observable shift in optical transmission spectra using different interaction models. These characterizations have the potential of allowing us to develop industrial applications by incorporating plasmonic resonance tuning.

1.3.4 Tuning of surface plasmon resonance by bimetallic structures

To the best of our knowledge, there has yet being any research on the surface plasmonic effect of hybrid particles localized on quartz substrate. In this project, we focus on gold and silver bimetallic structures and study SPR peaks of the films and particles arrays which are fabricated by LIL or colloidal lithography. The transmission spectra of fabricated thin films and particles arrays are analyzed by UV-Vis spectroscopy. The
results show that the SPR peak position of gold is blue shifted when silver films or particle structures are added over the same pattern. Thus, it offers a new way to design and fabricate hybrid materials or structures for tuning the SPR peaks of noble metal thin film. The peak shift is attributed to the interaction between the gold and silver atoms. A simplified model was adopted to qualitatively explain the phenomena observed.

1.4 Organization of the thesis

This thesis is divided into five chapters and their contents are listed as follows:

Chapter One gives a brief introduction to surface plasmon and its significance and applications, and reviews the fabrication techniques of metallic nanostructures. The objective and contributions of this study are also addressed.

Chapter Two introduces the basic mechanism and theoretical background of the surface plasmon. Moreover, the factors for tuning surface plasmon resonance are introduced by theoretical analysis.

Chapter Three describes the detail procedure of the fabrication of Au and bimetallic Ag/Au nanostructures by combining LIL and bi-layer resist lift-off process. The details of the lift-off process are discussed including single layer lift-off, bi-layer resist lift-off. The other part, a main contribution, is SPR tuning by the fabricated bimetallic Ag/Au nanostructures. The phenomenon observed in the experiments is qualitatively explained using a spring model.
Chapter 1 Introduction

Chapter Four describes the colloidal lithography and the colloidal sphere self-assembly methods. The detail procedure of the fabrication of metallic nanostructures is described. Three types of spheres, with diameters of 500, 770 and 1000 nm are each used to form monolayer masks, and subsequently used to fabricate metallic or bimetallic nanostructures for various size and thickness. The SPR tuning by the fabricated nanostructures are characterized and explained.

Chapter Five provides conclusions and recommendation for future work.
References:


CHAPTER 2  Theoretical Background

2.1 Fundamentals of surface plasmons (SPs)

2.1.1 Basic properties of surface plasmons

Surface plasmon polaritons (SPPs), often referred to as surface plasmons (SPs), are resonant electromagnetic fields which are strongly confined to metallic surfaces that enable them to sustain coherent electron oscillations. These electromagnetic surface waves arise via the coupling of the electromagnetic fields to the electron plasma oscillations of the conductor [1, 2].

SPs at the interface between a metal and a dielectric material have a combined electromagnetic wave and surface charge character as shown in Fig. 2.1. They are transverse magnetic in character ($H$ is in the $y$ direction), and the generation of surface charge requires an electric field normal to the surface. This combined character also leads to the field component perpendicular to the surface being enhanced near the surface as shown in Fig. 2.1 (a) and decays exponentially with a distance away from it as shown in Fig. 2.1 (b). However, the absorption of loss in the metal (ohmic loss) causes the amplitude of the propagated wave to decrease gradually. The attenuation is dependent on the dielectric function of the conductor at the frequency of the SPs [3, 4]. Due to its surface wave character, the perpendicular field of a surface plasmon polariton decays exponentially with distance from the surface, into the metal and dielectric layers [5]. The field in this perpendicular direction is said to be evanescent, and prevents power from propagating away from the surface.
the metal $\delta_d$ is in the order of half the wavelength of the incident light; whereas the decay length into the metal $\delta_m$ is determined by the skin depth, and is often orders of magnitude smaller than $\delta_d$ [6].

FIG. 2.1 The combined electromagnetic wave and surface charge character of SPs at the interface between a metal and a dielectric material. (a) The field component is perpendicular to the surface being enhanced near the surface and (b) decaying exponentially with distance away from it.
2.1.2 Localized surface plasmons (LSPs)

Localized surface plasmons (LSPs), a type of SPs, are charge density oscillations confined to metallic nanoparticles (sometimes referred to as metal clusters) and metallic nanostructures [1]. Localized surface plasmons are non-propagating excitations of the conduction electrons of the metallic nanostructures coupled to the electromagnetic field. We will see that these modes arise naturally from the scattering problem of a small and sub-wavelength conductive nanoparticle in an oscillating electromagnetic field. The curved surface of the particle exerts an effective restoring force on the driven electrons, so that a resonance can arise, leading to field amplification both inside and in the near-field zone outside the particle. This resonance is called the localized surface plasmon or short localized plasmon resonance [7]. Another consequence of the curved surface is that plasmon resonances can be excited by direct light illumination of appropriate frequency irrespective of the wave vector of the exciting light. In contrast, an SPP mode can only be excited if both the frequency and wave vector of the exciting light match the frequency and wave vector of the SPP [8, 9].

A typical example is shown in Fig. 2.2, where the conduction electrons of a spherical gold colloid oscillate coherently in response to the electric field of the incident light [1]. Excitation of LSPs by an electric field (light) at an incident wavelength, where resonance occurs, results in strong light scattering, in the appearance of intense SP absorption bands, and an enhancement of the local electromagnetic fields. The frequency and intensity of the SP absorption bands are characteristic of the type of materials
(typically, gold, silver, or platinum), and are highly sensitive to the size, size distribution, and shape of the nanostructures, as well as to the environment which surrounds them [10].

![Schematic drawing of plasmon collective oscillation of a spherical gold colloid, showing the displacement of the conduction electron charge cloud relative to the nuclei.](image)

**FIG. 2.2** Schematic drawing of plasmon collective oscillation of a spherical gold colloid, showing the displacement of the conduction electron charge cloud relative to the nuclei [1].

### 2.2 Drude model

In order to understand the optical properties of metal film and nanostructures, the metallic material properties have to be calculated using solid state theory. A simple model for metal, the Drude model, was developed by Paul Drude (1900) based on the kinetic gas theory [7]. It has described successfully many (but not all) properties of metals despite its drastic assumptions. In the model, a gas of free electrons of number density $N$ moves against a fixed background of positive ion cores. The details of the lattice potential and electron-electron interactions are not taken into account. Instead, one simply assumes that some aspects of the band structure are incorporated into the effective optical mass $m$ of
each electron. The electrons oscillate in response to the applied electromagnetic field, and their motion is damped via collisions occurring with a characteristic collision frequency $\gamma_0 = 1/\tau$. $\tau$ is known as the relaxation time of the free electron gas.

Based on the assumptions, the dielectric function $\varepsilon(\omega)$ of the free electron gas is obtained by solving a motion equation for an electron of the plasma sea subjected to an external electric field. It is well predicted by the Drude model, and the resulting equation is shown in Eq. 2.1 [11].

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma_0)} \approx \varepsilon_\infty - \frac{\omega_p^2}{\omega^2} + i \frac{\gamma_0 \omega_p^2}{\omega^3} \tag{2.1}$$

where $\omega_p$ is the plasma frequency and $\gamma_0$ is the electron relaxation rate. $\varepsilon_\infty$ includes the contribution of the bound electrons to the polarizability and should have the value of 1 if only the conduction band electrons contribute to the dielectric function.

### 2.3 Dispersion curve for SP mode

The interaction between the surface charge density and the electromagnetic fields results in the momentum of the SP ($h k_{SP}$) being greater than that of a free-space photon of the same frequency ($h k_o$) [6]. By solving Maxwell’s equation under appropriate boundary conditions [4], we can obtain the expression for the frequency-dependent SP wave vector, $k_{SP}$.

$$k_{SP} = k_o \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \tag{2.2}$$
where $\varepsilon_m$ is the frequency dependent permittivity of the metal, and $\varepsilon_d$, the permittivity of the dielectric. For SP to be possible, $\varepsilon_m$ and $\varepsilon_d$ must have opposite signs. This condition is satisfied for metals because $\varepsilon_m$ is negative.

The SP wave vector $k_{sp}$ is plotted in Fig. 2.3. It can be seen that the momentum of surface plasmons is larger than that of the plane wave. Consequently, the surface plasmon polariton cannot radiate light into the dielectric medium, and be excited by conventional illumination from the adjacent dielectrics. Due to ohmic loss in the metal, characterized by the imaginary part of the dielectric function of the metal, the energy carried by a surface plasmon polarization (SPP) decays exponentially as the SPP propagates along the planar dielectric-metal interface. The high energy mode shown in Fig. 2.3 should be neglected because these modes also propagate into the bulk and thus are not true surface modes. Therefore, the optical properties of metals are dominated by excitations of electrons from deeper lying bands.
2.4 Surface plasmon excitation

As seen from the SPP dispersion relations, the SPP wavevector is larger than the photon wavevector in the adjacent dielectric medium; thus, light illuminating a smooth surface cannot be directly coupled to surface polaritons. Special experimental arrangements have been designed to provide conservation of the wave vector. The photon and SPP wavevectors can be matched using either photon tunnelling in the total internal reflection geometry (by prism) or diffraction effects (on grating or on surface defects) as shown in Fig. 2.4. There are three main techniques by which the missing momentum can be provided. The first makes use of prism coupling to enhance the momentum of the incident light [12, 13]. The second makes use of a periodic corrugation in the surface of the metal [14]. The third involves scattering from a topological defect on the surface, such
as a subwavelength protrusion or hole, which provides a convenient way to generate SPs locally [10, 15].

FIG. 2.4 SPP excitation configurations: (a) Otto geometry (b) Kretschmann geometry, (c) diffraction on a grating, and (d) diffraction on surface features [5].

In the prism coupling technique, incident light passes through an optically dense medium, in this case, a prism, to increase its wave vector momentum. Under suitable wavelength and angles, total internal reflection (TIR) can be achieved where the incident beam reflects off at an interface between the optically dense glass and less dense dielectric (Otto configuration as shown in Fig. 2.4 (a)) or metallic layer (Kretschmann configuration as shown in Fig. 2.4 (b)). Although no light comes out of the prism in TIR, the electrical
field of the photons extends about a quarter of a wavelength beyond the reflecting surface. The coupling gap provides the evanescent tunnel barrier across which the radiation couples, allowing the surface plasmons to be excited at the dielectric metal interface [5].

The second method to overcome momentum mismatch is periodic corrugation, such as grating coupling, as shown in Fig. 2.4(c). This involves incident light being directed towards a grating with spatial periodicity similar to the incident irradiation. The incident beam is either diffracted away from the grating or produces an evanescent mode that travels along the interface. This evanescent mode has wave vectors parallel to the interface with reciprocal lattice vectors added or subtracted from it. Numerically, these reciprocal lattice vectors are described with \( \frac{2n\pi}{D} \), where \( n \) is an integer and \( D \) gratings dimensions, and they represent different modes [18].

On a rough surface, the SPP excitation conditions can be achieved without any special arrangements. Diffraction of light on surface features can provide coupling to the SPP modes on both the air–metal and glass–metal interfaces (Fig. 2.4(d)). This is possible since in the near field region all wave vectors of the diffracted components of light are present [3, 18, 19]. Thus, SPPs can be excited in conventionally illuminated rough surfaces. The problem with random roughness is the irregular SPP excitation conditions resulting in the low efficiency of light-to-SPP coupling. This is a non-resonant excitation and there is a strong presence of the reflected excitation light close to the surface. Depending on the metal film thickness and depth of the defect, SPPs can be excited on both interfaces of the film. Such non-resonant SPP excitation processes result in a complex field distribution over the surface due to interference of SPPs excited on different interfaces of the film and the illuminating light [19].
2.5 Localized surface plasmon resonance tuning

2.5.1 Single metal nanoparticles

The interaction of a metal nanoparticle with the electromagnetic field can be analyzed using the simple quasi-static approximation provided that \( d \ll \lambda \), where \( d \) is the nanoparticle diameter and \( \lambda \) the radiation wavelength of the electromagnetic field. The resonant electromagnetic behavior of metal nanoparticles is due to the confinement of the conduction electrons to the small particle volume. For particles with a diameter \( d \ll \lambda \), all the conduction electrons inside the particle move in phase upon plane-wave excitation, leading to a buildup of polarization charges on the particle surface. These charges act as an effective restoring force, allowing for a resonance to occur at a specific frequency—the particle dipole plasmon frequency. For larger particles, the spectral response is modified due to retardation effects and the excitation of higher-order (quadrupole and higher) modes, the spectral signature of which can be calculated by retaining higher orders of the Mie theory scattering coefficients [2, 7].

In general, the spectral position, damping, and strength of the dipole as well as of the higher-order plasmon resonances of single metal nanoparticles depend on the particle material, size, geometry, and the dielectric function of the surrounding host [1]. For theoretical considerations, a large variety of naturally occurring or synthesized shapes of nanoparticles is often approximated via spheres or spheroids, for which analytically exact solvable solutions exist to all orders [1, 20, 21]. For a spherical metal nanoparticle of
radius \( a \) embedded in a non-absorbing surrounding medium of dielectric constant \( \varepsilon_m \), the quasistatic analysis gives the following expression for the particle polarizability \( \alpha \):

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

with the complex \( \varepsilon = \varepsilon(\omega) \) describing the dispersive dielectric response of the metal.

It is apparent that the polarizability experiences a resonant enhancement under the condition that \(|\varepsilon + 2\varepsilon_m|\) is a minimum, which for the case of small or slowly-varying \( \text{Im}[\varepsilon] \) around the resonance simplifies to

\[
\text{Re}[\varepsilon(\omega)] = -2\varepsilon_m.
\]

This relationship is called the Fröhlich condition and the associated mode (in an oscillating field) the dipole surface plasmon of the metal nanoparticle.

For a sphere located in air consisting of a Drude metal with a dielectric function which could be derived from Eq. (2.1),

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

the Fröhlich criterion is met at the frequency \( \omega_0 = \omega_p / \sqrt{3} \) further expresses the strong dependence of the resonance frequency on the dielectric environment [7]. The spectral position of this resonance is seen to red shift with increasing \( \varepsilon_m \) due to the buildup of polarization charges on the dielectric side of the interface, thus weakening the total restoring force [22].
For ellipsoidal particles with principal axes $a$, $b$, and $c$, an analogous expression can be found in the quasistatic approximation via introducing geometrical depolarization factors $L_i$ along these axes [1, 20], leading to

$$\alpha_i = \frac{4}{3} \pi abc \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L_i (\varepsilon - \varepsilon_m)}, \quad \sum L_i = 1. \quad (2.6)$$

For spherical particles, $L_1 = L_2 = L_3 = 1/3$. For spheroidal particles ($L_1 = L_2$), the plasmon resonance thus splits into a strongly red shifted long-axis mode (polarization parallel to the long axis) and a slightly blue shifted short axis mode (polarization perpendicular to the long axis) [20].

### 2.5.2 Coupling between localized plasmons

We have seen that the localized plasmon resonance of a single metallic nanoparticle can be shifted in frequency from the Fröhlich frequency defined by Eq. (2.4) via alterations in particle shape and size. In particle ensembles, additional shifts are expected to occur due to electromagnetic interactions between the localized modes. For small particles, these interactions are essentially of a dipolar nature, and the particle ensemble can in a first approximation be treated as an ensemble of interacting dipoles. When considering the effects of such interactions in ordered metal nanoparticle arrays, we assume that the particles of size $a$ are arranged within ordered one- or two-dimensional arrays with interparticle spacing $d$. We further assume that $a \ll d$, so that the dipolar approximation is justified, and the particles can be treated as point dipoles [7].

Two regimes have to be distinguished, depending on the magnitude of the interparticle distance $d$. For closely spaced particles, near-field interactions with a distance
dependence of $d^{-3}$ dominate and the particle array can be described as an array of point dipoles interacting via their near-fields. In this case, strong field localization in nano-sized gaps between adjacent particles has been observed for regular one-dimensional particle chains [23]. The field localization is due to a suppression of scattering into the far-field via excitation of plasmon modes in particles along the chain axis, mediated by near-field coupling.

One can intuitively see that interparticle coupling will lead to shifts in the spectral position of the plasmon resonance compared to the case of an isolated particle. Using the simple approximation of an array of interacting point dipoles, the direction of the resonance shifts for in-phase illumination can be determined by considering the Coulomb forces associated with the polarization of the particles. As sketched in Fig. 2.5, the restoring force acting on the oscillating electrons of each particle in the chain is either increased or decreased by the charge distribution of neighboring particles. Depending on the polarization direction of the exciting light, this leads to a blue shift of the plasmon resonance for the excitation of transverse modes, and a red shift for longitudinal modes.
For larger particle separations, far-field dipolar coupling with a distance dependence of $d^{-1}$ dominates. This coupling via diffraction has been analyzed for both two-dimensional arrays akin to gratings [24, 25] and one-dimensional chains with interparticle distances larger than those for which near-field coupling is observed [26]. For the example of two-dimensional gratings of gold nanoparticles with various lattice constants, far-field coupling has pronounced influences on the plasmon line shape, both in terms of resonance frequency as well as spectral width. The latter is due to a drastic dependence of the decay time on the grating constant via its influence on the amount of radiative damping as successive grating orders change from evanescent to radiative in character.
References:


CHAPTER 3 SPR Tuning of Metallic Nanodot Array Fabricated by LIL

3.1 Introduction

Thin metal films with rough surfaces exhibit optical enhancement properties due to strong electric fields that result from light induced surface plasmons (SPs) [1]. Noble metal particles of subwavelength sizes can sustain resonances of collective electron oscillations known as localized surface plasmons (LSP) [2]. Noble metal structures with SPs and LSP resonance modes have a wide range of applications for their unique properties, such as imaging with subwavelength resolution [3, 4], chemical and biological sensors [5, 6, 7], and novel photonic devices [8, 9]. It is therefore a highly interesting research scope to tune the surface plasmon resonance (SPR) peaks to desired positions since the wavelength and intensity of SPR are highly sensitive to the nanostructure material, size, shape, period as well as surrounding environment.

A number of research groups have studied the development of novel structures, such as core/shell nanoparticles, nanorods, nanospins and nanostars which exhibit a number of interesting optical properties [10-13]. Moreover, a theoretical hybridization model for the plasmon response of complex nanostructures has been developed for some structures, such as multi-layer nanoshell [14] and nanoparticles near metallic surfaces [15]. The interplay between LSP and surface plasmon resonance (SPR) has also been extensively studied [16-18]. However, most theoretical models and experiments are focused on different structures with a single noble metal. For SPR tuning by hybrid materials, the studies mainly focus on bimetallic colloidal nanoparticles and bimetallic
thin films for biosensor applications. Bimetallic colloidal nanoparticles (Au-Ag, Au-Pt, and Ag-Pt) and nanostructures of gold and silver [19, 20] have been investigated to obtain desirable SPR peaks. The SPR of noble metal thin films has been widely used in biosensing, i.e. silver is preferred for its narrow resonance curve which results in high signal to noise ratio (SNR); gold has the advantage of having good chemical resistance. Silver and gold bimetallic thin films have therefore been frequently adopted to improve the resolution and adhesion for biosensing applications [21, 22]. The thickness of each double metal layer is also an important factor in tuning the SPR peak. Meanwhile, the role of substrate metal (gold or silver) in enhanced SPR imaging with gold nanoparticles has been theoretically studied [23]. It shows the interplay between LSP and SPR for two different noble metals.

To the best of our knowledge, there is yet any extensive research on the surface plasmon behavior of hybrid nanodots localized on quartz substrates. In this thesis, we focus on gold and silver bimetallic nanostructures and study the SPR peaks of the film and dot arrays. This study offers a novel way for hybrid materials to be used to tune the SPR peaks of noble metals. The spectral peak shift is attributed to the electromagnetic interaction between gold and silver atoms. A simplified spring model is adopted to qualitatively explain the phenomena observed.
Chapter 3 SPR Tuning of Metallic Nanodot Array Fabricated by LIL

3.1.1 Laser Interference Lithography (LIL)

3.1.1.1 Principle of LIL

When two monochromatic waves are superposed, the resulting intensity is the sum of two individual intensities of these two waves. It is well known as the wave interference [24]. Practically, the interference of two coherent light waves generates sinusoidal varying standing wave patterns. LIL is a lithographic technique using a laser as the light source to record the periodic patterns onto a layer of light sensitive polymer materials, such as photoresist [25, 26]. It is a maskless and simple patterning method to fabricate periodic, quasi-periodic and spatially coherent structures over a large area [27-30]. Figure 3.1 shows a schematic illustration of the resulting fringes generated by interference of two light beams that forms a standing wave. The resulting patterns are a series of gratings with a certain periodic length. The factors that affect the period of the structures are the light wavelength $\lambda$ and the angle $\theta$ at which the two light waves intersect, as given by Eq. (3.1).

$$\text{Standing wave period } P = \frac{\lambda}{2 \sin(\theta)} \quad (3.1)$$
3.1.1.2 Lloyd’s mirror setup

There are several different setups for laser interference lithography and each setup has its own advantages and disadvantages. Figure 3.2 shows the schematic drawing of a simple setup for laser interference lithography by Lloyd’s mirror configuration. A laser beam from a laser source is directed to a spatial filter by a set of mirrors. The spatial filter consists of an objective lens and a pinhole with its diameter approximately equal to or smaller than the focused laser beam size. The function of the spatial filter is to filter out the high frequency noise so that a uniform Gaussian beam profile can be obtained.
Meanwhile, it also acts as a beam expander whereby the beam diameter after the pinhole increases thus giving uniform beam intensity. The expansion of the laser beam diameter by the spatial filter gives a closely approximated plane wave over the exposure area [26].

![Schematic drawing of a Lloyd’s mirror setup for laser interference lithography of periodic structures on photoresist.](image)

**FIG. 3.2** Schematic drawing of a Lloyd’s mirror setup for laser interference lithography of periodic structures on photoresist.

In front of the spatial filter, there is a rotating stage with a mirror mounted perpendicularly to the sample holder. A part of the expanded beam is reflected by the mirror onto the sample held at 90° to the mirror surface and interferes with the other portion of the beam that falls directly on the sample to create a grating-like standing wave, which is recorded on the photoresist layer of the sample. Due to the fact that the mirror is at a right angle with respect to the sample surface, light beams always reflect at the same angles as the original incident beam. Therefore, altering the angle of the incident beam by rotating the rotation stage varies the period of the pattern as mentioned in Eq. 3.1. In this case, different values of standing wave periods can be obtained and thus periodic structures with different dimensions can be created.
The period of the fringes can be as low as half of the light wavelength of the incident laser beam. Therefore, depending on the types of laser used, structures of sub-micron dimensions can be produced. The use of LIL technique enables the size of gratings or periodic structures created on the photoresist to be as small as half of the incident beam wavelength. The applications of LIL include the patterning of magnetic media materials and MRAM (Magnetic Random Access Memory) devices, structuring of polymers and creating distributed feedback (DFB) structures for quantum dot lasers. However, the utilisation of the LIL technique to create microlens arrays is a new field, which requires intensive study.

3.1.2 Lift-off process

There are two common methods to produce metal or oxide nanostructures for semiconductors, namely; lift-off and etching. Lift-off is known as an additive process as opposed to etching, which is a subtractive process. In the lift-off process, a sacrificial photoresist layer is printed using an inverse mask pattern. The metallic or oxide pattern is created by blanket coating the photoresist pattern with metal or oxide and washing away the sacrificial layer. Any material which was deposited on the sacrificial layer is removed, while any material which was in direct contact with the substrate remains behind. In the etch process, a metallic pattern is fabricated by the first blanket coating the substrate with a metal or oxide layer, then patterning photoresist with the desired mask pattern and etching away the metal or oxide which is not covered by the photoresist. Wet chemical etching is common but these processes are isotropic and can easily undercut the photoresist. Dry etching is also available but requires reactive ion plasma tools. Moreover, toxic gas of Cl₂ needs to be used during dry etching of metals, such as gold and silver.
3.1.2.1 Single-layer photoresist lift-off

The obvious advantage of a standard photoresist lift-off is its process simplicity, because it involves only one masking step and the photolithography process is completely standard. Figure 3.3 outlines the basic steps involved in single-layer photoresist lift-off.
(a) Photoresist coating

*Photoresist is spin-coated onto the substrate*

(b) Exposure and development

*A pattern is defined on photoresist by lithography followed by development*

(c) Metal deposition

*Metal film is coated on to the surface by E-beam evaporation*

(d) Liftoff

*Photoresist and metal film above photoresist are “liftoff” by immersing the structure in acetone*

(e) Sidewall removal

*Sidewalls from deposited films are removed by gentle swipe of clean-room swab.*

**FIG. 3.3** Procedure for single-layer lift-off process

The main disadvantage is the sidewall effect. Metallic film is deposited on the sidewall of the photoresist. This part of the metal film remains adhered to the substrate even after the resist is removed. This sidewall makes the lift-off step more difficult, since it is harder for acetone to come into contact with the photoresist “behind” the sidewall. Depending on how robust the film and substrate are, sidewalls from the deposited film can be removed using a gentle swipe of a clean-room swab or a directed stream of acetone from a squeeze bottle. As a rule, the substrate should be immersed in acetone.
until all the film has been lifted off and there are no traces of film particulates – once the particles dry on the substrate, they are notoriously difficult to be removed.

Another problem associated with this method is that the sidewall resulting from photolithography may not be perfectly perpendicular to the substrate, as shown in Fig. 3.4. This problem is made worse for the LIL-based photoresist patterns. Due to the Gaussian shape of the laser beam intensity, it is very difficult to get patterns with sharp and straight edges. The cross-sectional view of post-LIL exposure lift-off is shown in Fig. 3.4.

![Photoresist coated - After LIL Exposure and Development - Au Layer Deposition](image)

**FIG. 3.4** Cross sectional view of LIL-based lift-off process flow.

The sidewall of the patterns turns out to be in a bump shape, which makes it easier for the deposited metal to form a continuous film layer. This metal film layer covers all the photoresist patterns and thus makes it difficult for acetone to permeate into the structure to remove the photoresist.

All these disadvantages lead to the application of the bi-layer photoresist lift-off process.
3.1.2.2 Bi-layer photoresist lift-off process

Bi-layer lift-off metallization techniques offer significant advantages in resolution, removal, process simplicity, undercut control and yield over conventional single-layer lift-off processes. Because of its ease of applications, long shelf life and lower tool cost, the polydimethylglutarimide (PMGI) bi-layer process has become an attractive method for semiconductor devices [31]. PMGI is virtually insoluble in typical photoresist solvents, so no intermixing occurs, permitting the imaging resist to be applied and prebaked directly on the top of the PMGI layer. This property makes PMGI resists uniquely suited for many critical and non-critical bi-layer lift-off processes [32]. In this experiment, a bi-layer lift-off process is applied, as it requires the least process steps and is recommended for most lift-off applications. The procedure for bi-layer lift-off process is shown in Fig. 3.5.
(a) PMGI coating
_Prebreak substrate, followed by PMGI coating and a second prebake._

(b) Photoresist coating
_Photoresist is spin-coated onto PMGI, followed by prebake._

(c) Exposure and development
_A pattern is defined on the photoresist by lithography, followed by development._

(d) Undercut
_TMAH is used to develop PMGI isotropically, creating an undercut profile on the sidewall._

(e) Metal deposition
_Metal film is coated to the surface by E-beam evaporation._

(f) Lift-off
_Bi-layer photoresist structure is lifted-off; leaving only desired metal film on substrate._

FIG. 3.5 Procedure for bi-layer lift-off process
In this simplified process, the PMGI layer develops nearly isotropically to produce bi-layer reentrant resist profiles. The amount of undercut is precisely controlled by the PMGI prebake conditions as well as through the choice of proper developers, develop time and develop mode. There are several types of PMGI, e.g. SF3, SF6, SF9. These resists differ from one another in cyclopentanone concentration, which is the main constituent in PGMI [32]. PMGI slow, medium and fast resists are well suited for use with tetramethylammonium hydroxide (TMAH) 0.26N, (2.38%) developers. PMGI fast resists are also compatible with less aggressive developers, such as TMAH 0.237N, (2.2%) developers which offer enhanced process control by reducing develop undercut rate [32].

For the gold or silver metallic deposition process, PMGI has high thermal stability (Glass Transition Temperature Tg ~190ºC), which makes it compatible with the high temperature deposition processes. Finally MicroChem’s Remover PG is used to lift-off the bi-layer resist stack. Remover PG is a solvent stripper designed for efficient and complete removal of PMGI, PMMA, SU-8, and other resist films on Si, SiO₂, GaAs, and many other substrate surfaces. Remover PG may also be used as a lift-off solvent [33].

3.2 Fabrication details

Both single layer (Au) and bimetallic (Ag/Au) nanodot arrays are fabricated. The process sequence for the bimetallic structure is exactly the same as that for the single layer structure, i.e. both by using the bi-layer resist lift-off process. The only difference is that an additional layer of Ag film is deposited over the single layer metallic Au structure. The two structures would have exactly the same size and shape, with the presence of Ag as their only difference. The procedure is shown in Fig. 3.5.
3.2.1 Substrate selection and preparation

There are several types of materials that are suitable as substrates for plasmonic structures, such as glass, fused quartz and silicon. In this experiment, UV fused quartz is used as the substrate due to its excellent optical properties, which is the ideal material to transmit light at a broad band of wavelength. It has over 90% transmittance for wavelengths of light from 200 nm to 1200 nm [34]. However, despite the superior optical property, it is difficult to obtain a clean and straight cross section of the quartz substrate. Cross section becomes especially important in this experiment, because the cross-sectional undercut profile needs to be confirmed before the subsequent process is carried out. Thus, silicon substrate is also used due to the presence of a preferred crystal orientation in the silicon wafer. The cross section obtained after cutting is clean and smooth. This facilitates the studying of cross sectional profiles. It has been shown that the process parameters used to achieve the undercut profiles are comparable for both silicon and quartz substrates. After a successful undercut profile is obtained from silicon substrates, the process is transferred to quartz substrates to carry out the rest of the fabrication process, and to measure the optical properties as well. Therefore, silicon substrates are used mainly as an intermediate step, to obtain the process parameters for exposure, development and undercut. Silicon is not chosen as the substrate for plasmonic research because it is non-transparent and unsuitable for characterizing the optical transmission property.

Before the quartz and silicon samples are used, they are cleaned by solvents which consist of 3 steps. They are firstly washed with acetone, followed by isopropyl alcohol (IPA), and finally by deionized (DI) water. For each cleaning step, the substrates are
immersed in the solution inside a beaker and put in the ultrasonic machine for 30 min. The sample is then prebaked by a hot plate at 180 ºC for 3 min. to enhance the adhesion between the PMGI resist and the substrate. PMGI (SF6) resist is then spin-coated onto the substrate. A spin speed of 3500 rpm is used for 50 sec. to obtain a resist thickness of 300 nm. This is followed by another prebake at 180 ºC for 3 min. The function of the second prebake step is to dry the PMGI film and fix the undercut rate [32].

After being coated with the PMGI layer, the sample is coated with negative photoresist ma-N 1407. The sample needs to undergo a pre-exposure soft bake at 100 ºC for 1 min and 30 sec to remove the moisture and harden the photoresist. The spin coating is done at 3500 rpm for 30 sec. The resulting photoresist has a thickness of about 650 nm.

3.2.2 Exposure and development

The sample is exposed by the interference of two laser beams at the same angle, which results in the generation of periodic grating structures on the photoresist. The exposure is carried out with the Llyod’s mirror setup with a Helium Cadmium (He-Cd) continuous wave (CW) laser (Kimmon, Japan) as the laser source. The laser wavelength \( \lambda \) is 325 nm with a long coherence length of 10 cm, which makes it suitable for interference lithography purpose.

After a single exposure, an array of periodic line structure is formed. The subsequent cross exposure of the photoresist by rotating the sample by 90 degrees enables the forming of holes arrays on the quartz surface. The period of the structure is set by changing the angle of the rotating stage. In this experiment, the angle is set at 4 degrees,
which is approximately equal to a period of 2 µm according to Eq. 3.1 and gives the pillars with a diameter of approximately 1 µm. The exposure time required to fully expose the photoresist mainly depends on the laser fluence (mJ/cm²) and developing time. Develop of photoresist ma-N1407 is done by immersing the sample into the ma-D 533 developer, followed by rinsing with DI water and drying by nitrogen gun. The developer dissolves the negative photoresist that is not exposed by the laser, and has no effect on the PMGI resist underneath.

Undercut profile is achieved by using a 1.9% TMAH developer. The samples are immersed in TMAH solution upside down for 30 sec, so that the sample surface would have the maximum contact with the developer solution. TMAH dissolves PMGI isotropically. This results in an undercut in the PMGI layer below the photoresist.

3.2.3 Metal thin film deposition

Prior to the thin film deposition, particularly for sputtering or evaporation processes, a post-develop bake is recommended. This can drive off excess solvent so that there is less outgassing during the film deposition. However, the bake should not be too long or at too high temperature, otherwise the resist will reflow slightly. In this experiment, the sample is baked at 100 ºC for 5 min to dry out the liquid solvent that remains before metal deposition takes place.

Metal deposition is carried out using an electron-beam evaporator. Cr or Ti thin film is deposited to increase the adhesion between different thin film layers, i.e., between the quartz substrate and Au, and between Au and Ag thin films. For the single layer Au dots array, 2 nm of Cr is deposited onto the quartz substrate, followed by 25 nm of Au
film. For double layer Ag/Au dots array, another 2 nm of Ti and 25 nm of Ag films are subsequently deposited. Figure 3.6 illustrates the metal layers deposited in each case.

![Illustration of metal layers deposited for (left) single layer Au, (right) bimetallic Ag/Au dot.](image)

**FIG. 3.6 Illustration of metal layers deposited for (left) single layer Au, (right) bimetallic Ag/Au dot.**

### 3.2.4 Lift-off

Remover PG is used to remove the bi-layer resist stack, leaving only the metal film deposited directly onto the substrate. The lift-off time is difficult to estimate, it ranges from 20 sec to a few mins, depending on the undercut profile obtained from the previous steps. Generally, a more prominent undercut profile would result in a shorter lift-off time. The lift-off time can be controlled by observation with naked eyes. Usually, a sample is pulled out of the remover PG solution as soon as one part of the metal film is seen to be removed. The sample is then rinsed with DI water, which would flush out most of the other metal films. The end product should be a non-metallic-colored and transparent sample, which shows weak iridescent color when being examined under the light.
3.3 Characterization methods

3.3.1 Optical microscopy (OM)

FIG. 3.7 Optical microscope image of a fabricated Au nanodot array.

Figure 3.7 shows the fabricated structure which is a square array of circular metallic dots. Meanwhile, the structure exhibits an excellent uniformity over a large area with a pattern area around 5 mm × 5 mm.
3.3.2 Scanning electron microscopy (SEM)

3.3.2.1 Single layer Au thin film structures

FIG. 3.8 SEM images of Au nanodot arrays fabricated with different sizes of the Au nanodots.
The period and feature size of the fabricated dots could be flexibly tuned by lithography parameters, such as the intersection angle $\theta$ of the two laser beams and the exposure time. From Fig. 3.8 (a), the diameter of fabricated dots can be measured to be around 1.5 $\mu$m, and the period around 2.4 $\mu$m. When the angle $\theta$ is increased and by controlling the exposure time, the period becomes 1.5 $\mu$m and individual dots are around 700 nm apart from one another, as shown in Fig. 3.8 (b).

### 3.3.2.2 Double layer Au/Ag film structures

![Fig. 3.9 SEM images, tilted at 50°, of a Ag/Au dot array fabricated by LIL.](image)

As can be seen in Fig. 3.9 where the image is tilted at 50°, uniform circular array of oblate spheroids can be observed on the substrate. The Au/Ag bimetallic nanodot array structure shows similar dot size and array period as those of the single layer Au nanodot
structure. The diameter of the dot is measured to be around 900 nm, and the period is around 1.6 μm.

### 3.3.3 Atomic force microscopy (AFM)

The bimetallic dots structure is characterized and confirmed by AFM as shown in Fig. 3.10. The bimetallic structure can be confirmed by additional AFM characterization as shown in Fig. 3.10 (b). The line scan profile of the dot array shows that the height of the dots is around 50 nm, while the designed value set by the electron beam evaporator is around 54 nm. This is because a small quantity of surface metal is etched away by the PG remover during the lift-off process. This explanation is also supported by the observation of the rough surface of dots in the line scan profile. However, this small reduction of the surface metal (silver) layer does not affect the investigation of the plasmonic effect of bimetallic Ag/Au dots since most silver is still there. The bottom plane of the dot features suggests that the photoresist has been lifted-off completely. Therefore, the fabricated structure is a bimetallic dot array with a height of around 25 nm gold and 20 nm silver.
Chapter 3 SPR Tuning of Metallic Nanodot Array Fabricated by LIL

(a) 400 (nm)

(b) 55

- 55
Chapter 3 SPR Tuning of Metallic Nanodot Array Fabricated by LIL

3.3.4 UV-Vis spectroscopy

3.3.4.1 Au and Ag/Au thin films

All the transmission spectra of the thin films and dot arrays are measured with an UV-Vis scanning spectrophotometer (Shimadzu Corporation). Normal incident light is adopted in the experiment. All the transmission values are normalized to the maximum transmission value in the same curve. The transmission spectra of the single gold film of 25 nm thickness and the double layer (silver (20 nm) /gold (25 nm)) film are shown in Fig. 3.11. The typical resonance peak of noble metal materials exists on the metal thin films, even without regular nanostructures, due to the granular structures on the thin films [35, 36]. It can be seen that the spectral peak position is around 524 nm in the gold thin film while there are two peaks at the positions of 320 nm and 496 nm in bimetallic Ag/Au thin layer films. The two peaks are assigned to silver and gold, respectively, since silver
has the surface plasmon resonance at a shorter wavelength than gold of the same shape and size due to the difference in the dielectric function of these materials [37]. Therefore, the gold surface plasmon resonance peak has been blue shifted after adding the silver film over it from 524 nm to 496 nm.

As has been confirmed, the dot structure consists of two metallic layers: 25 nm of gold and 20 nm of silver, each possessing its own individual optical responses. At the same time, the two metallic layers are sufficiently close, therefore a new hybridized mode is formed due to their interactions [14].

FIG. 3.11 UV-Vis spectra of Au and Ag/Au bimetallic thin films. All the transmission values are normalized to the maximum transmission value in the same curve.
3.3.4.2 Au and Ag/Au dot arrays

To investigate the resonance influence of the additional silver to gold, the single layer gold nanodot array and the silver/gold bimetallic nanodot array are fabricated and characterized under the same experimental conditions.

The transmission spectra of the Au nanodot array and bimetallic Ag/Au nanodot array are compared in Fig. 3.12. There is a plasmon band for the gold nanodot array with the peak wavelength at 510 nm. Previous investigations have shown that arrays of particles with similar circular section (spheroids) parallel to the substrate deposited on ITO or glass display a single plasmonic resonance [17]. This band at 510 nm is attributed to the plasmon band for the Au nanodot array. The shoulders around the band may be due to the surface roughness [18]. In the transmission spectra of the bimetallic nanodot array, two plasmon bands are observed, which correspond to the Au and Ag components, respectively. As shown in Fig. 3.12, there is a relatively narrow band with peak wavelength at 324 nm and a broader band with a peak wavelength at 450 nm. Since the Au plasmon resonance wavelength is longer than that of Ag for nanodots of the same shape and size [37], it is reasonable to assign the narrow band to the Ag component and the broader band to the Au component. Comparing the Au plasmon bands in these two structures, there is a significant blue shift in Au peak wavelengths of the bimetallic nanodot array. This shift is attributed to the addition of the Ag thin film, since the only difference between these two structures is the presence of the Ag layer.
FIG. 3.12 UV-Vis spectra of Au nanodot array (dashed line) and Au/Ag bimetallic nanodot array (solid line) that are fabricated by LIL technique. All the transmission values are normalized to the maximum transmission value in the same curve.

3.4 SPR tuning by bimetallic structure

The observed blue shifts in the transmission spectra for Ag/Au thin film and nanodot arrays can be explained qualitatively by a simple dipole-dipole interaction model, which is a well known form of molecular system [38, 39]. The electric field of the irradiated light causes the positive and negative charges within the atom to be displaced from their equilibrium positions. For a single metal, an atom with electrons bound to the nucleus can be represented by a small mass bound to a larger mass by a spring. Each of
the charges in the atom is under the influence of the electric field and driven back and forth. For metals, electrons move freely in the lattice to form an “electron sea”. Due to the big difference in movement between atoms and electrons, the electrons are expected to contribute dominantly to the induced dipole moment.

The simplified spring model of gold and silver atoms is shown in Fig. 3.13 (a). The larger circle represents a gold atom and the relatively smaller circle represents a silver atom. The gold spring model could be adopted for a single gold nanodot, and the frequency of the spring could be considered as the resonance frequency of the gold nanodot. When the gold and silver atoms are placed adjacent to each other, the additional polarization forces act on both atoms as sketched in Fig. 3.13 (b). The top and bottom circles represent silver and gold atoms, respectively.

When the driving field is parallel to the particle surface, the repulsive forces within each atom are enhanced due to the attractive forces between the positive and negative charges in different atoms, giving rise to a correspondingly higher resonance frequency. Thus the resonance wavelength of the gold nanodot array is blue shifted in the bimetallic structure due to the interaction with the silver nanodot array.
FIG. 3.13 Sketches to illustrate the electromagnetic interaction between closely spaced atoms: (a) a gold atom (left) or a silver atom (right) and (b) a pair of closely placed atoms with the polarization of the exciting field parallel to the particle surface.
In addition, it is noted that there is a more apparent blue shift for the Au SPR peak from 510 nm to 450 nm in the nanodot arrays (Fig. 3.12) while the peak wavelength blue-shifted from 524 nm to 496 nm in the thin film (Fig. 3.11). With reference to the simplified spring model, there is an electrical attraction between adjacent atoms. Compared to the thin film structure, the nanodot array has gaps which weaken the attractive forces between isolated nanodots. Consequently, this leads to a larger unrestrained restoring force and a higher resonance frequency. This translates physically to a shorter resonant wavelength in its UV-Vis transmission spectra and therefore, a more apparent blue shift occurs.
References:


Chapter 3 SPR Tuning of Metallic Nanodot Array Fabricated by LIL


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[34] Synthetic Quartz Wafers and Quartz Substrate, retrieved from World Wide Web http://www.advantivtech.com/wafers/quartz-wafers.html


CHAPTER 4  SPR Tuning of Nanoparticle Array Fabricated by Colloidal Lithography

4.1 Introduction

4.1.1 Colloidal lithography

Colloidal lithography, as one of the self-assembly techniques, uses colloidal sphere arrays as lithographic masks or templates to fabricate nanostructures. It could also be named nanosphere lithography [1]. Compared to other nanofabrication techniques, such as e-beam lithography, it has been applied widely because of its unique features: it is inexpensive, inherently parallel and enables high-throughput nanofabrication [2-4]. Moreover, several parameters of nanopatterning which affect feature geometry can be altered with respect to colloidal fabrication techniques, e.g., colloidal and substrate materials, colloidal shape, size and monolayer distribution.

Colloidal lithography structures begin with the self-assembly of dispersed nanospheres to form a two-dimensional colloidal crystal deposition mask. A number of methods to obtain well-ordered and densely packed monolayer from water suspended spheres have been intensively reported [5, 6], such as spin coating [7], drop coating [8] and thermoelectrically cooled angle coating [9]. All of these deposition methods require that the nanospheres are able to freely diffuse across the substrate, seeking their lowest energy configuration. This is always achieved by chemically modifying the nanosphere surface with a negatively charged functional group, such as carboxylate or sulfate, which is electrostatically repelled by the negatively charged surface of a substrate, such as mica or glass. As the solvent (water) evaporates, capillary forces draw the nanospheres together,
and the nanospheres crystallize in a hexagonally close-packed pattern on the substrate [1]. The phenomenon of self-assembly is due to the ‘lateral capillary force’ between particles that is mutually attractive in nature. This force is developed when the liquid layer is deformed during evaporation and is a function of particle radius and liquid surface tension [10].

Following self-assembly of the nanosphere mask, a metal or other material is then deposited by thermal evaporation, electron beam deposition (EBD), or pulsed laser deposition (PLD) from a source normal to the substrate through the nanosphere mask to a controlled mass thickness, as shown in Fig. 4.1 (a). After the metal deposition, as shown in Fig. 4.1 (b), the nanosphere mask is removed by sonicating the entire sample in a solvent, leaving behind the materials deposited through the sphere mask to the substrate, as shown in Fig. 4.1 (c).
FIG. 4.1 Illustration showing the colloidal lithography process. (a) Formation of a monolayer of nanospheres, (b) exposed areas in mask after deposition and (c) nanostructures left after lift-off of monolayer.
In this work, we seek to fabricate a large area and well ordered array of nanostructures by self-assembly of commercially available submicron spheres using two known techniques, namely the tilt method and the spin coating method. The tilt method is straightforward and does not require any special apparatus, while in the spin coating method, the area of the monolayer can be varied by controlling the spin speed and the solid concentration in the aqueous colloidal suspension.

### 4.1.2 Tilt method for self-assembled monolayer particle fabrication

The setup for the tilt method used in monolayer fabrication is shown in Fig. 4.2.

![FIG. 4.2 Experimental setup of the tilt method of monolayer fabrication.](image)

The droplets with suspended particles are deposited on the substrate and allowed to evaporate at a controlled ambient temperature. Dimitrov et al. [11] suggested that the hydrodynamic pressure due to water flux between the bulk and the drying peripherals
leads to the laterally attractive forces between the particles. Due to the non-uniform evaporation over the surface of a droplet, to maintain its shape, the droplet creates an internal convection that pushes impurities to the edges. Thus monolayer regions are formed at the peripherals. The area of monolayer yield can be controlled by the volume of suspended particles deposited and the tilt angle of the setup [12]. The covered glass tray is then used to maintain a constant ambient. No external airflow is allowed to affect the evaporation rate.

The obvious advantage associated with the tilt method is its process simplicity. It involves minimal steps, and it is relatively easy to monitor the process parameters. This becomes obvious compared to the spin coating technique in the subsequent section. However, each sample takes a relatively long period of time for complete evaporation of the suspended particle solution using the tilt method. As the suspension is dropped onto the top of the incline, the thick suspension layer recedes at a very slow rate that is proportionate to the water influx, particle influx, water evaporation flux and incline angle [11]. As the setup should not be disturbed until the suspension has completely evaporated, the process takes a relatively long time with the samples kept in the airtight cabinet. The results for each sample can only be ascertained at the end of the evaporation period, introducing an element of uncertainty in the tuning of the parameters for the tilt method.
FIG. 4.3 Schematic drawing of the particle and water fluxes in the vicinity of the growing monolayer particle array on an inclined microslide. Here, $\theta$ is the angle of inclination, $j_w$ the water influx, $j_p$ the respective particle influx, $j_e$ the water evaporation flux, $v_c$ the array growth rate, $l$ is the evaporation length and $h$ the thickness of the array [11].

Another key disadvantage of the tilt method is the small area of surface coverage by monolayers and its non-uniformity. Among the various papers reported by different groups, the largest area ($\sim 8100 \mu m^2$) fabricated using the tilt method reported by Ng et al [11-13] is almost negligible compared with monolayers fabricated by other techniques ($\sim 91000 \mu m^2$ by spin coating).
4.1.3 Spin coating method for self-assembled monolayer particle fabrication

The spin coating method is another method commonly used to obtain well-ordered and two-dimensionally arrayed nanoparticles. During the spin coating, the colloidal suspension flows across the glass substrate at high rates to form densely packed arrays while the excess coating material is dispelled [14]. The solution concentration, ambient humidity and spin speed are all important parameters in achieving a large area particle monolayer array.

Emslie et al. proposed a model to predict the thickness of a fluid during the spin coating [15]. In the model, the decreasing fluid height is inversely proportional to the square of the spin speed. An illustration of a two-step spinning effect with different spin rates is shown in Fig. 4.4 [16]. It is important to point out that the monolayer begins to form when the thickness of the suspension film becomes sufficiently thin for the spheres to start protruding from the suspension film surface. At this point, the particles are subjected to an immersion capillary force, which originates from the deformation of the liquid surface [17]. For a slow spin speed, the high solution thickness leads to a relatively large amount of water remaining on the substrate at the end of this period, and thus immersion capillary forces can be neglected. For a high spin speed, the centrifugal force is initially too strong and the solvent evaporates so fast that a large number of particles are expelled away from the substrate and a bi-layer array is formed at the substrate center. Therefore, to produce a large area of ordered monolayer array, the conditions must include the suspended colloidal particles being able to wet the substrate and both the spin rate and time must be carefully optimized. The speed for the first step is slower, used to
control the thickness of the suspension by the centrifugal force. For the second step, a faster spin rate can reduce the thickness of the liquid suspension through the solvent evaporation.

FIG. 4.4 Illustration showing two-step spinning and its effects at different spin rates [16].

The key advantages of the spin coating method are its high throughput and relatively simple preparation. The coating of monolayer particles can be achieved in a few minutes, including complete evaporation of the suspension solution as the excess spheres are spun off from the spin coater at a high speed.

The issue that lies in the spin coating technique is the various parameters that must be accurately controlled. Not only must the ambient conditions be relatively constant,
the parameters to be monitored include spin time, spin rate and the amount of particle to be deposited on substrate for spinning [16].

### 4.2 Experimental details

The schematic diagram of the experimental process is shown in Fig. 4.1. In this study, both the tilt method and the spin coating method are studied for the formation of self-assembled colloidal spheres. The influence of the concentration of the colloidal spheres is studied by the tilt method first. Large area monolayer sphere fabrication is carried out by the spin coating method. Three types of polystyrene (PS) spheres of diameters of 1000 nm, 700 nm and 500 nm are self-assembled to form monolayer masks by controlling the spin coating parameters. The formed monolayer is used as masks in the deposition of a thin layer of noble metallic materials. These produced various types of noble metallic nanostructures after the lift-off process. Furthermore, the material and thickness of the metallic nanoparticles could be easily tuned during the metal coating process. Therefore, a few nanoparticle arrays can be fabricated with different sphere diameters, metallic thin film thickness and their composition.

For plasmonic effect investigation, metals such as Au, Ag and Al are normally used. In this study, the experimental results are compared for different values of a parameter among the created nanostructures as shown in the following list. In each case, their characterizations by SEM and UV-Vis spectroscopy are performed. All the UV-Vis spectrum measurements are recorded using un-polarized light.
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1. Spheres of three diameters: 500, 770 and 1000 nm at the same Au film thickness of 20 nm.

2. Various film thicknesses of 20, 30 and 45 nm with the same sphere diameter of 1000 nm.

3. Single Au thin film and bimetallic Ag/Au thin film deposition.

4.2.1 Preparation of substrate and microspheres suspension

The substrate selection and preparation are the same as those described in Chapter 3 section 3.2.1.

The suspension used in this study is an industrially produced latex polystyrene (PS) microsphere suspension (Duke Scientific Corporation) supplied as 1 wt. % solution in water. Sizes of spheres used are of diameters at 500, 770, and 1000 nm, respectively with size uniformity (C. V.) less than 3.0 %. Concentration of the suspension is 1:1 mix (by volume) with isopropyl alcohol (IPA).

4.2.2 Influence of solvent concentration

Three concentrations of PS spheres and solvent are initially considered. The diameter of the PS sphere is 1 µm and one drop of the sphere suspension is around 20 µl. Three types of samples are prepared according to the following solution concentrations:

1. 10 ml distilled water mixed with 1 drop PS suspension,

2. 5ml distilled water to 1 drop PS suspension,

3. Undiluted PS sphere suspension.
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(a)

(b)
FIG. 4.5 PS sphere monolayers formed by the tilt method at different dilution ratios of distilled water to PS sphere suspension: (a) 10 ml distilled water to a drop of suspension, (b) 5 ml distilled water to a drop suspension and (c) undiluted suspension.

As observed in Figs. 4.5 (a) and (b), the formed PS sphere monolayers are strips along the peripherals of the water droplet on the substrate. The average width of the monolayer strip increases from 13 \( \mu \text{m} \) to 25 \( \mu \text{m} \) when a less diluted concentration is applied. Finally, with the undiluted suspension, we can see a much larger yield with undiluted spheres suspended in liquid as shown in Fig. 4.5 (c). However it is also observed that the monolayers are broken into many separated islands with disjoints between them. In general, there are fewer well-ordered, closely packed areas of monolayer arrays.

It can be seen from the Fig. 4.5 that the average yield of consistent and closely-packed monolayers increases with the concentration of the particle solution. This is because an increase in solution concentration causes a decrease in the mobility of the
particles near the solution/substrate interface and results in a higher surface coverage [16].
In the following experiments, no distilled water-diluted colloidal suspension is used. However, to increase the wetting of the substrate and the yield of monolayer arrays across the substrates, the subsequent particle-solutions used are diluted by IPA (1:1 by volume) [13].

4.2.3 Spin coating process

The spin coating process for each sphere size is based on two parameters, spinning rate and time period. According to previous studies by Hulteen and Chen et al, we have obtained the proper range of spin rates to be around 100-1000 rpm [8]. The spin rate and spin time are optimized to obtain the large area monolayer at three sphere diameters of 500, 770 and 1000 nm.

The two-step spinning process is proposed by Ogi to maximize the monolayer yield [16]. The speed for the first step is slower, which is used to control the thickness of the suspension by the centrifugal force. Under the appropriate thickness for each sphere size, the immersion capillary force makes the spheres attract one another and form a monolayer. A fast spin speed in the second step causes the solvent to evaporate quickly. For 1 μm diameter particles, the thickness of the suspension suitable to produce a monolayer is achieved at a spin speed of around 800 rpm for 50 s, which is therefore chosen as the spin speed of the first step. The second step is used to spin off the excess suspension found at the edge of the suspension droplets. An increase of the spin speed by 200 rpm to 1000 rpm is chosen, and the spin duration for the second step is 10s. For 770
nm and 500 nm diameter particles, the spin speed in the first step is 1000 rpm for 50 s and in the second step, 1200 rpm for 10 s.

It is also found in the subsequent experiment for 770 nm and 500 nm diameter particles that the smaller the suspended particles, the faster the spin rate must be. This is due to the following two reasons. Firstly, centrifugal force is stronger for larger particles. Centrifugal force on smaller particles is not sufficiently strong in the radial direction, thus a large number of particles remain suspended in the solution during the spinning period. Therefore, a faster spinning speed is needed to cause a larger centrifugal force which compresses the suspension droplets to be thinner, causing the monolayers to be better arranged accordingly. Secondly, the immersion capillary forces act when the solution thickness is comparable to the particle size. Faster spinning speed accelerates the solvent evaporation to reach the thin liquid film for immersion capillary force [16].

4.2.4 Metal nanoparticle array formation

4.2.4.1 Metal film preparation

Metal deposition is carried out using an electron beam evaporator after the self-assembly of the spheres. A 20 nm thick Au film is deposited over the monolayer for each sphere size whereas different samples of 1000 nm diameter sphere monolayer masks are coated with 20 nm, 30 nm and 45 nm thick Au layers. For the hybrid bimetallic case, an additional 20 nm of Ag film is coated above the 30 nm thick Au film. To improve the adhesion of the Au to quartz and Ag to Au interfaces, additional 5 nm Cr film and 5 nm Ti
film are added, respectively. The consideration is the same as that mentioned in Section 3.2.3.

4.2.4.2 Chemical lift-off of particle mask

After the metal deposition, the monolayer mask is removed before further analyses. The samples are first dipped into an acetone bath and left in the ultrasonic bath for 1 min 30 sec to 2 min. This is controlled to enable sufficient time for the acetone bath to remove the sphere monolayers. However, keeping the samples in the ultrasonic bath for too long can lead to the removal of the thin metal films deposited on the substrates.

4.3 Characterizations of fabricated metallic nanoparticle arrays

4.3.1 Optical microscopy (OM) of monolayer sphere masks

Figures 4.6 shows the optical images of the hexagonally close-packed 1 μm diameter sphere masks self-assembled onto the substrate. The monolayer of large diameter spheres is found not only to be most easily formed and recreated but also has the highest yield of monolayer formation. It is found that a large monolayer area of ~ 90,000 μm² (300 μm × 300 μm) is produced for spheres of a diameter of 500 nm at the proper spin process at ambient conditions. Furthermore, a monolayer of an area of ~ 462,000 μm² (700 μm × 660 μm) for spheres of a diameter of 770 nm is obtained. An area of ~ 100,000 μm² (1000 μm × 800 μm) is also obtained for spheres of a diameter of 1000 nm. These monolayers are achieved at their respective proper spin coating processes. A larger consistent area of monolayer ensures ease of characterization and minimal erratic behavior in the characterization.
4.3.2 SEM images of fabricated metallic nanostructures

As shown in Fig. 4.1, a monolayer of hexagonally close-packed nanospheres is self-assembled on the substrate. When a metal film is deposited through the monolayer mask, the three-fold interstices allow the deposited metal film to reach the substrate, creating an array of triangularly shaped nanoparticles. Geometric calculations can define the relationship between the perpendicular bisector of the triangular nanoparticles $a$, and the inter-particle spacing $d_{ip}$, to the sphere diameter $D$ [1, 7].

$$d_{ip} = \frac{1}{\sqrt{3}} D, \quad a = \frac{3}{2} \left( \sqrt{3} - 1 - \frac{1}{\sqrt{3}} \right) D.$$  \hspace{1cm} (4.1)
The dimension of each nanostructure in the periodic array is determined by the length of the triangle’s perpendicular bisector $a$, and the deposited thickness of the particle $d_m$. Therefore, the nanoparticle size is varied by changing the sphere mask diameter $D$, and the deposited mass thickness $d_m$.

The fabricated Au nanoparticle arrays are characterized by a SEM (Hitachi). Figures 4.7 (a), (b) and (c) show SEM images of the Au nanostructures with the same thickness of 20 nm fabricated by colloidal lithography with different sphere diameters of 500 nm, 770 nm and 1000 nm, respectively. It can be seen that the lengths of the perpendicular bisector are 110 nm, 160 nm and 225 nm, respectively. These values agree with the geometric calculations very well.
FIG. 4.7 SEM images of Au nanoparticle arrays created using PS sphere monolayer mask with spheres of diameters of (a) 500 nm, (b) 770 nm, and (c) 1000 nm, respectively.
4.3.3 UV-Vis spectroscopy

The transmission spectra are measured by an UV-Vis scanning spectrophotometer (Shimadzu Corporation). Light from the source is unpolarized and irradiated normally onto the samples. All the graphs have been normalized for peak position comparison.

4.3.3.1 Different sphere diameters

Figure 4.8 shows the transmission spectra of the three different periodic Au nanostructures fabricated with the same Au thickness of 20 nm. The dash, dash dot and solid curves in Fig. 4.8 represent the transmission spectra of the nanostructures fabricated with sphere masks of diameters of 500 nm, 770 nm and 1000 nm, respectively. It can be seen that there is a different band for each curve. The corresponding peak wavelengths for each of the curves are 477 nm, 491 nm and 508 nm, respectively. As in previous investigations, the spectra show that each of the periodic triangle nanoparticle arrays fabricated by the same lithography method displays a single plasmon resonance band [1, 18]. The plasmon bands observed in each curve are attributed to the Au nanoparticle array. The shoulders around the bands may be due to the surface roughness of the Au, and the broad band may be due to the non-uniform nanoparticle size distribution [20]. It can also be seen that there is a red shift in the peak resonant wavelength, from 477 nm to 491 nm first and then to 508 nm as the sphere size increases from 500 nm to 770 and then to 1000 nm. The details of the explanation will be discussed in Section 4.4.1.
4.3.3.2 Different thin film thicknesses

Figure 4.9 shows the transmission spectra of the fabricated Au nanostructures for three different Au thicknesses at the same period. These Au nanoparticle arrays are all fabricated with a sphere mask of spheres of a diameter of 1000 nm. The dash, dash dot and solid curves in Fig. 4.9 represent the transmission spectra for nanoparticle arrays of Au of thicknesses of 45 nm, 30 nm and 20 nm, respectively. It can be seen that the corresponding peak wavelength for each curve is at 477 nm, 491 nm and 508 nm,

FIG. 4.8  UV-Vis spectra of gold nanostructures fabricated by colloidal lithography with spheres of diameters of 500 nm, 770 nm and 1000 nm, respectively.
respectively. The peak resonance wavelengths are red shifted as the Au thickness decreases. The spectral position of the Au plasmon band is red shifted up to 50 nm when the Au thickness decreases from 45 nm to 20 nm. The details of the explanation will be discussed in Section 4.4.1.

![Graph of UV-Vis spectra](image)

**FIG. 4.9** UV-Vis spectra of metallic nanostructures fabricated by colloidal lithography at different Au film thickness of 20 nm, 30 nm and 45 nm, respectively.

### 4.3.3.3 Single Au layer and bimetallic Ag/Au

Further comparison is carried out as a continuation of our previous research on bimetallic nano-dots SPR effect [21]. We have found that when an Ag layer is stacked
upon the Au layer, the peak wavelength is blue shifted. In this work, for the Ag/Au bimetallic layers, an additional 20 nm thick Ag layer is coated above the 30 nm thick Au layer. The total structure with a height of 50 nm is compared with the 30 nm single Au layer to compare the influence on Au SPR (with and without the Ag layer). To ensure that a consistent 30 nm Au layer is coated, the samples chosen are from the same deposition batch. Figure 4.10 shows the UV-Vis spectra of metallic nanostructures fabricated by colloidal lithography for single Au layer and bimetallic Ag/Au layers. It can be seen that there is only one SPR band for the single layer Au nanoparticle structure at a peak wavelength of 487 nm, while there are two SPR bands in the bimetallic Ag/Au nanoparticles at the peak wavelengths of 370 nm and 458 nm. Since the Au SPR wavelength is longer than that of Ag [21], it is reasonable to assign the SPR band with the peak wavelength at 370 nm to the Ag component and the other SPR band to the Au component. Moreover, there is a significant blue shift in the Au peak wavelength of the bimetallic nanoparticle array. This shift is attributed to the addition of the Ag component since the only difference between these two structures is the presence of the Ag layer.
4.4 SPR tuning by fabricated nanostructures

4.4.1 SPR tuning by aspect ratio

The relationship between nanoparticle size and the localized surface plasmon resonance (LSPR) has been recognized, though not fully understood, for many years. Colloidal lithography is particularly useful in studying the optical properties of LSPR because nanoparticle size is easily varied by changing the sphere mask diameter, $D$, and the deposited mass thickness $d_m$. It is difficult to decouple size and shape effects on the
SPR wavelength. They are considered together as the nanoparticle aspect ratio \((a/d_m)\) [1]. As the aspect ratio is increased, the optical peaks are red shifted, as investigated theoretically [19] and experimentally [1, 18].

Here, two cases related to aspect ratio are studied. The first case is about the three Au nanoparticle arrays of the same Au film thickness of 20 nm fabricated with sphere diameters of 500, 770 and 1000 nm, respectively. In this case, by increasing the size of the sphere diameter \(D\), the lengths of the perpendicular bisector of the Au nanoparticle fabricated, \(a\), is increased as shown in Eq. (4.1). Thus, the aspect ratio of the Au nanoparticle increases correspondingly. The plasmon resonance peak of the Au nanoparticle array is red shifted with the increase of sphere diameter \(D\) as shown in Fig. 4.8.

The other case is that of the three Au nanoparticle arrays fabricated with various Au film thickness of 20, 30 and 45 nm, using the same sphere diameter of 1000 nm. The observed red shift of peak resonance wavelength as shown in Fig. 4.9 could also be explained by considering their aspect ratios. The nanoparticle dimension \(a\) is the same in these three arrays since the sphere mask diameter is the same. The aspect ratio is in inverse proportional to the thickness of the coated metal \(d_m\), and it increases with the decrease of \(d_m\). Therefore, the SPR peak wavelength is red shifted when the thickness decreases. These results agree with other theoretical [19] and experimental studies [1, 18].
4.4.2 SPR tuning by bimetallic structures

From the UV-Vis spectra comparison in Fig. 4.10, it can be seen that there are two SPR bands in the bimetallic Ag/Au layer nanostructure with peak wavelengths at 370 nm and 458 nm, respectively. As mentioned in Section 4.3.3, the SPR band with the peak wavelength at 370 nm can be assigned to the Ag component and the other SPR band assigned to the Au component. Therefore, the peak resonant wavelength of Au in the bimetallic Ag/Au layer is blue shifted from 487 nm to 458 nm compared with that of the single Au layer. This result shows consistency with our previous work of the nano-dot pattern SPR tuned by bimetallic film structures fabricated by laser interference lithography [22]. The blue shift can be qualitatively explained using a simple dipole-dipole interaction model, which is used to define molecular systems. When an EM wave shines on a metallic nanostructure, the electrical component of this light wave causes electrons inside the metal atoms to be displaced from their equilibrium positions. Classically, the electrons are known to be bounded to the nucleus in the same way as a small mass is bounded to a large mass by a spring. The opposite movement of charges acts as a restoring force, which causes the electrons to oscillate in resonance at their dipole frequency [22]. Although the current shape of the Au nanoparticles is triangular instead of circular, the model is still applicable. When an Ag atom is placed close to an Au atom, the additional polarization forces from the Ag atom act on both atoms. With a driving field parallel to the particle interface, the restoring forces within each atom are enhanced by the attracting forces between positive and negative charges of the different
atoms. Consequently, this leads to a higher resonance frequency. The resonance wavelength of Au/Ag bimetallic nanostructure array is thus blue shifted. This bimetallic layer structure has both Ag and Au SPR peaks at ~370 nm and 450 nm. It shows that this multi-layer metallic nanostructure fabrication presents a potentially effectively way to generate wide band multi-peak SPR effects, which has promising applications for wide band light sources, such as plasmonic solar cells to enhance the sunlight absorption from 300 nm to 3 µm for higher light-to-electricity energy conversion.
References:


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5.1 Conclusions

In this thesis, two major works have been presented. The first one is to fabricate large-area plasmonic nanostructures on quartz substrates, and the second one is to study the surface plasmon resonance (SPR) tuning of the fabricated nanostructures. Both laser interference lithography (LIL) and colloidal lithography are applied to fabricate single layer and bimetallic layer plasmonic nanostructures. A novel approach to tune the SPR band has been demonstrated by the use of a bimetallic layer plasmonic nanostructure. The main contributions and results are summarized as follows:

1. Periodic nanodots have been fabricated by laser interference lithography on quartz substrates over large areas (5 mm × 5 mm) in a short time (a few minutes). This patterning technique increases the throughput of the fabrication nanostructures compared to chemical synthesis methods and reduces the cost in nanostructure fabrication compared to electron-beam lithography (EBL) and focused ion-beam (FIB) lithography.

2. The bilayer resist lift-off process is employed to overcome the sidewall effect of the single-layer lift-off process, and inversely transfers the photoresist pattern on to the metallic layer. In this study, the metallic nanodot arrays are successfully fabricated by
combining LIL and bi-layer resist lift-off process. Single (Au) and bi-layer (Ag/Au) nanodot arrays are achieved by the same procedure with different metal depositions.

3. Several types of metallic nanoparticle arrays are flexibly fabricated by colloidal lithography. Colloidal sphere arrays as lithographic masks are used to fabricate nanostructures, so that simply changing the thickness of coated metal layer can lead to different metallic nanoparticles even by using the same monolayer sphere mask. In this study, Au nanoparticle arrays with thicknesses of 20 nm, 30 nm and 45 nm are achieved by using a sphere mask with spheres diameters of 1000 nm. Moreover, a bimetallic (Ag/Au) nanoparticle array is fabricated by an additional coating of Ag film after Au film coating.

4. A large area, up to 800,000 µm², of self-assembled monolayer polystyrene (PS) sphere mask is formed on quartz substrates by the spin coating method. Various monolayer sphere masks are flexibly fabricated by the spin coating method without controlling any additional parameters other than spin speed and spin time. In the study, PS spheres of diameters 500 nm, 770 nm and 1000 nm are self-assembled as masks for the fabrication of metallic nanoparticle structures.

5. The influence of sphere size and metal film thickness on the plasmonic effect of the nanostructures fabricated by colloidal lithography are investigated. Since it is difficult to decouple size and shape effects on the SPR wavelength, they are considered together as the nanoparticle aspect ratio. The optical peaks are red shifted as the aspect ratio increases,
which has also been shown in previous theoretical and experimental investigations. In the sphere size study, by increasing the size of the sphere diameter, the length of the perpendicular bisector of the Au nanoparticle produced is increased. Thus, the aspect ratio of the Au nanoparticles increases correspondingly. In the metal film thickness study, the aspect ratio is increased by decreasing the film thickness. Therefore, the observed red shifts with the increase of sphere size or the decrease of film thickness in the UV-visible transmission spectra are qualitatively explained.

6. Tuning of surface plasmon resonance by bimetallic plasmonic structures is demonstrated. To the best of our knowledge, there is yet no research on the surface plasmonic effect of hybrid particles localized on quartz substrates. In this thesis, the SPR peaks of single layer (Au) and bimetallic (Ag/Au) layer structures fabricated by both LIL and colloidal lithography are studied. The results show that the SPR peak position of gold is blue shifted when a thin silver film or silver particle structures with the same pattern is added. A simplified model is adopted to qualitatively explain the phenomena observed. The spectra peak shift is attributed to the interaction between gold and silver atoms. Thus, this method offers a new way to design and fabricate hybrid materials or structures for tuning the SPR peaks of noble metals flexibly.

5.2 Suggestions for future work

There are some suggestions for future studies and applications of the research presented in this thesis.
1. To increase the power of the laser employed in laser interference lithography (LIL) system to enlarge the fabricated area. Adjustments of the Lloyd’s interferometer are necessary to reduce the intensity non-equality between the original beam and the reflected beam. By enhancing the beam interference contrast, the resolution of the lithography can be improved down to sub-150 nm dimensions.

2. The shape of the nanostructures fabricated can be altered in the LIL system by changing the angle of the two exposures. Angles of 30°, 45°, instead of a 90° turning angle, will lead to oblique array nanostructures, such as nanorod arrays. So far the structures fabricated by LIL are of circular shape and only square arrays are attempted. Multiple resonance peaks in the near infra-red regime are excited by the periodical nano-feature array structures.

3. More metallic materials, such as magnetic materials (e.g. nickel) could be employed in bimetallic nanostructures to study the mechanisms of plasmon modes. The magnetic plasmonic characteristic of magnetic metal material is worth investigating in order to have a clear understanding of the inherent relations between magnetos and plasmons.

4. The fabricated nanostructures can be used for further application studies, such as in surface enhanced Raman spectroscope (SERS) and highly sensitive biosensors.