Studies of optical properties of Au nanoparticles

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Studies of Optical Properties of Au Nanoparticles

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This thesis is dedicated to my parents.

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Summary

It is the intent of this work to study the optical properties of Au nanoparticles. The Au nanoparticles have been synthesized with two different methods: 1) direct-deposit self-assembly method; and 2) electrodeposition method. The direct-deposit self-assembly method, in which an ultrathin Au film was deposited on top of the substrate using electron-beam evaporation followed by rapid thermal annealing, is fully compatible with modern complementary-metal-oxide-semiconductor (CMOS) technology and has the advantage of low cost and high throughput. While, using the electrodeposition method, Au nanoparticle array can be deposited on a heavily-doped Si substrate through direct electroreduction of bulk AuCl_4^- ions. The obtained nanoparticles are with good control of coverage and aggregation. The synthesized Au nanoparticles have been characterized by the techniques of atomic force microscopy (AFM), scanning electron microscope (SEM), energy-dispersive x-ray spectroscopy (EDX), spectroscopic ellipsometry (SE) and spectrophotometry.

A detailed optical study of the Au nanoparticles on Si substrate synthesized with the direct-deposit self-assembly method has been performed using ellipsometric analysis based on the effective medium approximation (EMA) and Lorentz-Drude optical dispersion model. The effective dielectric function of the nanoparticles is best presented by a Drude term and three Lorentz oscillators, which are used to model the free electron transition, surface plasmon resonance (SPR) and interband transitions, respectively. The two oscillators at 1.26 and 2.22 eV are attributed to the splitting of

the plasmon resonance of the spatially limited free electrons inside the nanoparticles. The splitting of the plasmon resonance could be due to the influence of various factors such as the near-field interactions between adjacent nanoparticles, image charge effect of the substrate, imperfect spherical shapes of the nanoparticles, and etc.

To better understand the splitting of surface plasmon resonance of self-assembled Au nanoparticles on Si substrate observed from the dielectric functions of the nanoparticles, the dependence of the two Lorentz oscillators on structural properties are studied: the oscillator at ~ 1 eV models the polarization parallel to the substrate, while the other at ~ 2 eV represents the polarization perpendicular to the substrate. Both the parallel and perpendicular resonances are red-shifted when the nanoparticle size increases. The red shifts in both resonances are explained by the image charge effect of the Si substrate.

A comprehensive study on the image charge effect on the dielectric function of Au nanoparticle self-assembled on Si substrates without and with a SiO₂ layer (3, 10 and 30 nm in thickness) has been carried out. For Au nanoparticles on Si substrate without a SiO₂ layer, a splitting in SPR band in the imaginary part of the dielectric function ϵ_2 is observed, i.e., besides the typical SPR peak at ~ 2 eV, a pronounced peak at ~ 1 eV emerges. The splitting is attributed to the interaction between the nanoparticle and its image charge induced in the Si substrate. However, the splitting in the SPR band is greatly suppressed for a 3 nm SiO₂ layer and could not be observed for a 10 nm SiO₂ layer. On the other hand, the formation of a continuous Au film can also result in the disappearance of the Lorentz oscillator. Moreover, the image charge effect also significantly enhances the interband transitions.

Absorbance spectra of Au nanoparticles self-assembled on fused silica substrate synthesized by the direct-deposit self-assembly method have been determined using spectrophotometry measurement. Surface plasmon resonance peak of Au nanoparticles is identified in the absorbance spectra. The peak wavelength can be adjusted by controlling the synthesis conditions and or changing the dielectric environments. Either red-shifts or blue-shifts of the surface plasmon wavelength could be observed depending on the changes of the structural properties of the nanoparticles. On the other hand, the presence of the SiO₂ capping layer causes a red shift in the surface plasmon wavelength as a result of the change in the dielectric environment of the Au nanoparticles.

Modeling of absorbance of Au nanoparticles self-assembled on fused silica substrate has been performed based on Lorentz-Drude dispersion function and Maxwell-Garnett effective medium approximation. The contribution of the surface plasmon resonance and the two interband transitions to the absorbance are well modeled with three Lorentz oscillators, respectively. Influence of the structural properties on the SPR and interband transitions has been examined. In addition, the dielectric function of the Au nanoparticles has been extracted from the absorbance modeling, and it is found to be consistent with the result yielded from the spectroscopic ellipsometric analysis. Furthermore, the effect of dielectric medium on the SPR band as well as interband transitions has been investigated based on the modeling analysis.

The optical properties of Au nanoparticles on a heavily-doped Si substrate synthesized through direct electroreduction of bulk AuCl₄⁻ ions have been studied also.

The optical properties of the nanoparticles were determined from ellipsometric analysis. The Lorentz-Drude model was used to represent the effective dielectric function of the Au nanoparticles. A prominent peak at ~ 1.7 eV is identified in the imaginary part ϵ_2 , which is attributed to the surface plasmon resonance. However, no splitting of SPR band has been observed, which may be due to the oxidized Si substrate during the electrodeposition process. On the other hand, there are also two minor peaks located at ~ 3.1 and ~ 4.2 eV, respectively, which are related to the interband transitions. The interband transitions are greatly suppressed, which could be due to the modified lattice structures of the nanoparticles. Furthermore, a detailed comparison of the optical properties of Au nanoparticles synthesized using the two techniques (i.e., direct-deposit self-assembly and electrodeposition) has been presented.

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Nomenclatures

AFM	Atomic Force Microscopy
CTAB	Cetyltrimethylammonium bromide
CMOS	Complementary Metal Oxide Semiconductor
CNT	Carbon Nanotube
DDA	Discrete Dipole Approximation
EB	Electron-Beam
EDX	Energy-Dispersive X-ray spectroscopy
EMA	Effective Medium Approximation
FDTD	Finite-Difference Time-Domain
HF	Hydrogen Fluoride
IC	Integrated Circuit
IR	Infrared
ITO	Indium Tin Oxide
LC	Liquid Crystal
LSPR	Localized Surface Plasmon Resonance
MSE	Mean-Square Error
N ² FC	Nanyang NanoFabrication Center
NP	Nanoparticle
PECVD	Plasma Enhanced Chemical Vapor Deposition
PDMS	Polydimethylsiloxane
PMMA	Poly(methyl methacrylate)
RTA	Rapid Thermal Annealing

SAM	Self-Assembled Monolayer
SE	Spectroscopic Ellipsometry
SEM	Scanning Electron Microscope
SERS	Surface-Enhanced Raman Scattering
SPM	Scanning Probe Microscopy
SPP	Surface Plasmon Polariton
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
TERS	Tip-enhanced Raman spectroscopy
UV	Ultraviolet
UV/Vis/NIR	Ultraviolet/Visible/Near-infrared

Chapter 1 Introduction

This thesis presents a study of optical properties of Au nanoparticles. This chapter introduces the background, motivation, objective and major achievement of this work. Details of this study will be presented in the following chapters.

1.1 Brief introduction to Au nanoparticles

Over the past few decades, nanotechnology, the study of manipulating matters on an atomic and molecular scale, is beginning to be seen in our daily life [1]. It deals with structures sized between 1 to 100 nm in at least one dimension, and involves operation, analysis and control materials or devices of least one dimension within that regime. A variety of fullerenes [2, 3], carbon nanotubes [4, 5] and metal and semiconductor nanoparticles [6, 7] have been synthesized and proposed as potential building blocks for optical and electronic devices. These types of nanomaterials and nanoscale devices exhibit novel physical properties, which are not shown on a macroscale. For instance, fullerenes composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube, have been the research subject due to their unique chemistry and technological applications. In addition, allotropes of carbon with a cylindrical nanostructure are defined as carbon nanotubes (CNTs). The significant

length-to-diameter ratio gives rise to novel properties, such as extraordinary strength and hardness, unique electrical properties, efficient thermal conductivity and so forth [8].

Metal nanoparticles have attracted great interest in which they can be easily synthesized and modified chemically [7, 9, 10]. Their optical properties are markedly different from those of the bulk counterpart if their dimensions are scaled into several nanometers. Unlike semiconductor nanoparticles where quantum confinement effects play a critical role in modifying their optical spectra, metallic nanoparticles experience their major changes in optical spectra which can be explained in classical dielectric theory [11]. The most exciting observation is that metal nanoparticles exhibit strong plasmon extinction in the visible spectrum. In atoms or molecules subjected to electromagnetic fields, resonances show up in spectra as narrow peaks of absorption, emission or scattering [12].

Au nanoparticle is at the heart of a widespread interest in the subject of metal nanoparticles research, owing to its peculiar optical and electrical properties. It can provide highly luminescent from visible to near-infrared range, which is probably useful in biological labeling, light emitting diodes, and optoelectronic logic gates [13-15]. It can also be involved in some applications, in which the recombination and transport of charge carriers are through the nanoparticle [16, 17]. In addition, the fast nonlinear optical response and tunable surface plasmon resonance (SPR) of the Au nanoparticle have facilitated novel devices and applications such as optical switch, molecular detectors, and biosensors [18]. Furthermore, the high absorption cross section makes Au nanoparticle a good candidate of photothermal agent [19, 20].

1.2 Brief introduction to Surface Plasmon Resonance

Plasmon resonance can be denoted as surface plasmon resonance (SPR) for planar surface and localized surface plasmon resonance (LSPR) for nanoscopic metallic particles. In order to generate the SPR, the presence of a large amount of free electrons at the interface of two materials is required [21]. This condition always implies that one of these materials is a metal where free electrons are abundant. The emergence of SPR at the metal-dielectric interface can be interpreted as propagating electron density waves strongly bound to the interface, which can be modeled by Maxwell's equations. However, the excitation of SPR is not straightforward, due to the requirement for matching of the wavevector, k_{sp} , of the surface plasmon wave with that of light producing it [11]. To overcome this limitation, a special geometry has been proposed by Kretschmann, where light is shone onto the metal side whose thickness is in the range of the penetration depth of light into metal [22]. In the case of metal nanostructures, the SPR is exhibited as the collective oscillation of free conduction electrons in the nanoparticles under the excitation of external electromagnetic field. Owing to the exceedingly small dimensions, light can easily penetrate through the whole nanoparticle, which results in redistribution of conduction electrons with respect to the positively charge ions that form the metallic lattice. Therefore, metal nanoparticles can be considered as resonators, and if excited resonantly their oscillation amplitude can be amplified by orders of magnitude, in the appearance of intense surface plasmon absorption bands, and an enhancement of the local electromagnetic fields [23]. The frequency (i.e., position of the absorption maximum), intensity and bandwidth of the surface plasmon absorption bands depend

on the size, size distribution, shape, surface coverage, and surrounding environment of the given nanoparticles [24-27]. Unlike SPR, no special geometry is required for localized surface plasmons, and LSPR are excited by characteristic wavelength of light absorption [11].

The photonic applications of the metallic nanoparticles are mainly based on the exploitation of near-field coupling of LSPR, which is the enhancement of local field induced under the resonance plasmon generation condition leading to the enhancement of various light-induced linear and nonlinear optical processes within nanoscopic volume of the media around and between the nanoparticles [11]. The most significant advantage of employing LSPR in the nano-optical device is converting photons to electromagnetic modes of radiation that are not diffraction limited (i.e., feature dimensions can be tighter than $\lambda/2$) and can be used as optical elements (mirrors, waveguides, or switches) within their propagation range (i.e., few hundreds μm) [28]. Plasmonic waveguide has been proposed by Maier *et al.*, which uses a closely-packed array of metal nanoparticles to guide an electromagnetic wave in the dimensions much smaller than the wavelength of light [29]. Another application presented by metal nanoparticles is the apertureless near-field microscopy, in which a sharp metallic probe is illuminated and the scattered light is detected at far field [28]. High resolution of a few nanometers without aperture can be achieved due to the enhanced optical field at and near the tip-sample region [30].

The exploitation of SPR for various sensing applications is of great interest to researchers as well. For example, the tunable surface plasmon band based on varying

the refractive index of the surrounding medium can be used to detect the molecules attached to metallic nanoparticles and nanostructures. This kind of assays were conducted in dispersions, and on metallic nanoparticles immobilized on substrates, where the environmental changes can be controlled by the interaction between the ligand and molecules or the self-assembled capping monolayer [28]. In addition, the aggregation of surface plasmon particles through specific links makes excellent colorimetric assays, as the links can be removed during the melting transition, and the resulting spectrum can be completely reversible [31, 32]. The optical labeling of single molecule and/or multiple targets can be realized by using ultrabright, non-bleaching nanoparticles prepared with a scattering peak at any color of the visible spectrum [28]. The induced extremely high scattering flux and stability make metallic nanoparticles a much better candidate in various biological applications [33, 34]. Last but not least, the strong signal enhancements in other optical techniques like surface-enhanced Raman scattering (SERS), and surface plasmon resonance spectroscopy by employing the metallic nanoparticles, have been well discussed [35-37].

1.3 Motivation

In view of the important roles of Au nanoparticles in the intriguing SPR applications, the optical properties of Au nanoparticles deserve more thorough investigation. Au nanoparticles can be synthesized by many techniques, which have their own advantages and disadvantages [16, 38-40]. Among them, direct-deposit self-assembly, i.e., deposition of an ultrathin Au film with electron-beam evaporation

followed by rapid thermal annealing (RTA), is considered to be one of the promising techniques. It is fully compatible with the existing CMOS technology and is able to control the size, shape and distribution of Au nanoparticles by adjusting the initial metal film thickness, annealing temperature and duration [16]. In addition, this method provides a higher throughput compared to its counterparts. On the other hand, production of a large array of Au nanoparticles can also be achieved through solution-based and electrodeposition processes [38, 40]. Both techniques can result in a high throughput of metal nanoparticles with a narrow distribution of diameter. However, there are some critical issues that restrict the further development of these two methods. For the solution-based method, poor adhesion to the substrate and difficult control in coverage and aggregation are the bottlenecks of this technique [40]. Although electrodeposition method has overcome these limitations, the choice of substrate (i.e., conductive substrate) and incompatibility with CMOS techniques make it less attractive.

The conventional optical study of the Au nanoparticles is mainly focused on the absorption and scattering effect extracted from extinction spectra through either experimental measurement or numerical simulation [24, 41-44]. The obtained optical properties, especially the SPR band, are found to be strongly dependent on the size, shape and dielectric environment of the nanoparticles. This is called the extrinsic effect. On the other hand, the optical constants and dielectric function of the Au nanoparticle are also under the influence of intrinsic effect, which means the variation of n and k (or ϵ_1 and ϵ_2) are related to the nanoparticle itself [45]. However, few studies on the experimental determination of the dielectric function of Au nanoparticle

have been reported. In addition, in some circumstances, more than one SPR band may be simultaneously observed according to the symmetric axes of excitation, i.e., anisotropic nanoparticles, whose excited longitudinal and transverse waves are different [24, 46]. Moreover, some researchers reported that near-field coupling between neighboring nanoparticles may give rise to the SPR band splitting [47, 48]. Besides the coupling effect, the influence of the substrate can also be significant [49, 50]. The substrate effect is normally considered as an additional mirror image of the nanoparticle inside the substrate. The modified polarization upon additional image charge can be calculated in order to estimate the strength of particle-substrate interaction [51]. Nevertheless, the effective dielectric function study on the effects of the near-field coupling and image dipole is so far limited. Furthermore, the image charge effect on the interband transitions and the effect of a SiO₂ supporting layer on the evolution of the SPR have been less covered.

In the investigation of optical properties of Au nanoparticles, the study on the SPR band is believed to be the most essential part. The SPR band can be revealed as a strong optical absorption peak in the visible range of the spectrum. Its dependence on the size and shape of the nanoparticle, the interparticle distance, and the refractive index of the surrounding medium has been widely reported [24-27]. On the other hand, for the SPR applications, precise control over the SPR band is critical. Abundant proposals regarding the tunable SPR band has been published over the years and many of them are achieved in the solution-based environment, which has limited the usage of such methods [52-56]. Therefore, techniques which can be used in integrated circuit (IC) fabrication will certainly enhance the exploitation the SPR applications in the

complementary metal-oxide-semiconductor (CMOS) technology. Furthermore, unlike the SPR band of the nanoparticles, the study on structural dependence of other band structures, i.e., interband transitions, has been found insufficient. The interband transitions, which correspond to the transitions from valence bands to the states above the Fermi level and between different bands, are also significant in the optical study.

1.4 Objective and scope of research

In this thesis, Au nanoparticles were prepared by two different methods: (1) direct-deposit self-assembly, and (2) electrodeposition. The main objective of this thesis is to investigate the optical properties of the Au nanoparticle and its dependence on the intrinsic and extrinsic effect. The scope of the research and the approach are as follows:

- (1) Synthesis of Au nanoparticles using two different methods: a) direct-deposit self-assembly, and b) electrodeposition. Different sizes, shapes, and distributions are achieved by varying the synthesis methods and conditions.
- (2) Characterization of the Au nanoparticles using scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX), and atomic force microscopy (AFM). The obtained structural and chemical properties are used for the analysis of optical properties.
- (3) Experimental determination of the optical properties of Au nanoparticle, including the optical constants and dielectric function. The optical properties of

Au nanoparticles synthesized with the two techniques are determined using spectroscopic ellipsometric (SE) analysis

- (4) Investigation of the splitting of the surface plasmon resonance band of the Au nanoparticles on Si substrate.
- (5) A comparative study of the dielectric function of Au nanoparticles self-assembled on Si substrate without and with a SiO₂ layer.
- (6) Investigation of the dependence of the surface plasmon resonance band on the structural properties of Au nanoparticles self-assembled on the fused silica substrate using spectrophotometry measurement.
- (7) Study on the dependence of interband transitions of Au nanoparticles on the structural properties.
- (8) Modeling of absorbance of Au nanoparticles self-assembled on fused silica substrate.

1.5 Major achievement of the thesis

The major achievement of this thesis is listed as follows:

- (1) Optical properties of Au nanoparticles on Si substrate prepared by direct-deposit self-assembly method has been determined based on the SE analysis.
 - a) Dielectric function and optical constants of Au nanoparticles have been experimentally determined in the photon energy range of 1.1 ~ 4.1 eV.

- b) Surface plasmon resonance band and interband transitions of Au nanoparticles have been identified in the dielectric function.
 - c) Structural dependence of the dielectric function of the Au nanoparticles has been investigated.
 - d) Split of the surface plasmon resonance band into two bands has been observed.
 - e) The two surface plasmon resonance bands are well modeled by two Lorentz oscillators.
 - f) Dependence of the two SPR bands on the structural properties has been examined.
 - g) A comparative study of the dielectric function of Au nanoparticles on Si substrate without and with a SiO₂ layer has been made.
 - h) Contributions of the Lorentz oscillators to the dielectric function of the Au nanoparticles have been studied.
 - i) Influence of structural properties of Au nanoparticles on the surface plasmon resonance band and interband transitions are determined.
- (2) Optical properties of Au nanoparticles produced on fused silica substrate have been obtained using spectrophotometry measurement.
- a) The SPR wavelengths of Au nanoparticles with different structural properties have been identified in the absorbance spectra.
 - b) Influence of average size (in both horizontal and vertical dimensions) of the nanoparticles on the movement of the SPR wavelength has been determined.
 - c) Influence of the thickness of the Au islands thin film has been studied.

- d) Influence of dielectric medium around the nanoparticles on the SPR wavelength has been investigated.
 - e) Modeling the absorbance of Au nanoparticles based on optical dispersion function and effective medium approximation has been carried out.
- (3) Optical properties of Au nanoparticles synthesized with electrodeposition method have been obtained using spectroscopic ellipsometric analysis.
- a) Structural properties of Au nanoparticles can be controlled by adjusting the distance between anode and cathode electrodes, and the duration of deposition.
 - b) Optical properties of the nanoparticles are well modeled by three Lorentz oscillators and a Drude term.
 - c) Dependence of the SPR band and interband transitions on the structural properties of nanoparticles has been investigated.
 - d) Contributions of the SPR band and interband transitions to the dielectric function have been determined.
 - e) A detailed comparison of the optical properties of Au nanoparticles synthesized with the two techniques (i.e., direct-deposit self-assembly and electrodeposition) has been studied.

1.6 Organization of the thesis

This thesis is mainly focused on the studies of optical properties of Au nanoparticles.

In **Chapter 1**, the basic concept of surface plasmon resonance associated with metal nanoparticles and its potential applications are briefly introduced. The motivation, objective and scope of the research and the major achievement of this thesis are also given in this chapter.

In **Chapter 2**, a literature review of the research on Au nanoparticles is presented. It begins with discussion of the direct-deposit self-assembly method and other common techniques for the preparation of Au nanoparticles (see Section 2.2). After that, the common techniques used to characterize the structural, material, and optical properties of Au nanoparticles are reviewed (see Section 2.3 and 2.4). Finally, the applications of Au nanoparticles in photonic and sensing applications are discussed in detail.

In **Chapter 3**, a comprehensive study on the optical properties of Au nanoparticles on Si substrate prepared by direct-deposit self-assembly technique is presented. A non-destructive method is developed to determine the dielectric function and optical constants of the Au nanoparticles self-assembled on the Si substrate using spectroscopic ellipsometry (see Section 3.2). In this chapter, the SPR band and the interband transition are investigated by examining the dielectric function of the nanoparticles (see Section 3.3). In addition, the split of plasmon resonance band into two bands is found to be related to various factors. Based on the investigation of the dependence of the two plasmon resonance bands on the structural properties, together with a comparative study of the dielectric function of the Au nanoparticles on Si substrate without and with a SiO₂ layer, the effect of image charge effect of Si

substrate on the split of SPR band can be determined. On the other hand, its influence on the interband transitions has also been studied (see Section 3.4 and 3.5).

In **Chapter 4**, absorbance spectra of Au nanoparticles self-assembled on fused silica substrate are obtained from spectrophotometry measurement. The dependence of the SPR wavelength on the average size (in both horizontal and vertical dimensions) is studied. The influence of the thickness of the Au thin film and the dielectric medium around the nanoparticles is also investigated (see Section 4.3). Furthermore, the modeling of absorbance of Au nanoparticles based on the Lorentz-Drude model and effective medium approximation is performed, and the result is found to be consistent with ellipsometric analysis (see Section 4.4). In addition, the effect of dielectric medium on the SPR band and interband transition has been determined from the modeling of the absorbance of Au nanoparticles.

In **Chapter 5**, optical properties of Au nanoparticle synthesized by electrodeposition method has been modeled with three Lorentz oscillators together with a Drude term. The morphology of the nanoparticles can be manipulated by varying the process parameters. A prominent and two minor peaks observed in the imaginary part ε_2 are attributed to the surface plasmon resonance and two interband transitions, respectively, and they are found to be dependent on the structural properties of the nanoparticles (see Section 5.1). Furthermore, a comparative study on the optical properties of Au nanoparticles fabricated by the two techniques (i.e., direct-deposit self-assembly and electrodeposition) has been presented (see Section 5.2).

In **Chapter 6**, the research work carried out in this thesis is summarized. Recommendations for future work are also given in this chapter.

Chapter 2 Literature Review

2.1 Introduction

Noble metallic nanoparticles have attracted great attention in the exploitation of SPR [27, 28, 57]. The SPR can be interpreted as collective oscillations of electrons in the nanometer scale metallic systems, which can be caused by the strong resonance in the optical region of electromagnetic spectrum [23]. When they interact with light, surface plasmons lead to highly enhanced nanolocalized optical fields at the metallic surface [58]. Their intense colors have led to the applications in the stained windows as early as the Middle Ages [24]. The resonance behavior can be witnessed when sunlight obliquely strikes glass windows in churches and cathedrals attributed to the presence of gold, silver, and copper nanoparticles [12].

Over the past few decades, a great deal of effort has been devoted into the understanding of the properties of SPR in metallic nanoparticles. The size dependence of the SPR is due to the size dependence of the dielectric function ϵ of the metallic nanoparticles. It is defined as the intrinsic size effect [24]. On the other hand, for larger-size nanoparticles, the evolution of SPR is directly related to the change of particle size. This is referred to as the extrinsic size effect [24]. The shape and position of the SPR also depends on the dielectric constant of the surrounding medium. Together, these understandings form the foundation for many of the remarkable

applications of the rapidly developing field of plasmonics [28]. In this chapter, we briefly review the synthesis, characterizations, properties and applications of Au nanoparticles.

2.2 Synthesis techniques for Au nanoparticles

Surface plasmon resonance of metallic nanoparticles has recently attracted a great deal of attention due to a wide range of potential applications. Various synthesis techniques have been proposed for different applications, and each of them has its own advantages and disadvantages [16, 38-40]. For example, for the application of plasmonic waveguides used in on-chip optical interconnects, one important consideration is the compatibility with integrated circuit (IC) fabrication. Besides, owing to the strong dependence of the SPR band on the structural properties of the nanoparticles, the morphological parameters like the size, shape and distribution of nanoparticles have to be precisely controlled in order to meet the stringent requirements imposed by the application of Au nanoparticles. The common techniques used to synthesize Au nanoparticles are reviewed in this section. First of all, the direct-deposit self-assembly method, which was employed to fabricate the nanoparticle arrays for this thesis, is discussed. After that, three other techniques (i.e., solution-based methods, electrodeposition and electron-beam lithography) are also reviewed. A discussion on the pros and cons associated with each technique is included in this section.

2.2.1 Direct-deposit self-assembly technique

Electron-beam evaporation is usually used for the direct-deposit process. In the evaporation process, high-energy electron beam directed by the magnetic field can melt and evaporate a block of the target materials, which subsequently condense on the substrate placed on the top of the chamber. This process occurs in a high-vacuum environment, in which the molecules or atoms are able to move freely and to condense on all surfaces. Thin films ranging from a few nanometers to several micrometers in thickness with high intensity and surface quality can be fabricated using electron-beam evaporation, as well as sputtering and pulsed-laser deposition. Generally, to form metal nanoparticles, the thickness of the deposited metal film is limited to several nanometers. Fig. 2-1 shows the basic procedures for the formation of metal nanoparticle. A metal wetting layer with thickness of a few nanometers is deposited onto Si wafer covered by a thin layer of thermal oxide by electron-beam evaporation. Then, a rapid thermal annealing (RTA) process is carried out for the self-assembly of the deposited clusters. The thermal energy from annealing treatment can facilitate the movement of the clusters and the formation of discrete nanoparticles. Before RTA, the as-deposited film comes naturally with some thickness perturbation and even nanoparticles start to form. As the RTA treatment is to give the atoms enough surface mobility, the film will self-assemble into a lower-total-energy state [16].

The formation of nanoparticles can be explained by the stress relaxation, dispersion force, and surface energy minimization during the annealing process. In more details, the difference in thermal expansion coefficient between the metal and

the substrate leads to the formation of hillocks, as the elastic energy associated with film stress induced during the deposition process can be reduced by breaking the film into islands along the initial perturbation [59]. In addition, the minimization of the surface energy and the dispersion force between the top and bottom interfaces can help stabilize the film [16]. Once the nanoparticles are formed, the work function difference between the metal and the extrinsic substrate generates localized depletion and accumulation region in the substrate [16].

Fig. 2-1 Process sequence for metal nanoparticle formation (from Ref.[16]).

The key advantage of such technique is that it is able to integrate with mainstream CMOS technology. Liu *et al.* has demonstrated that different metal nanocrystals (e.g., Au, W, Ag and Pt) formation on thin oxide film has been

incorporated into a simplified NMOS process to fabricate metal nanocrystal memory device [16]. Many more studies show that the self-assembly of nanocrystals consists of metal evaporation and RTA is a simple and complementary MOS friendly method [60, 61]. In addition, the flexibility in controlling the size, shape and distribution of the nanoparticles by varying the initial film thickness of the metal wetting layer, annealing temperature and duration, and also by the metal/tunnel oxide interface structure, is considered as another merit of this technique [59, 61-63]. For example, well-defined nanoparticles with round shape and narrow size distribution can be achieved when the thickness of the metal wetting layer is small [59, 63]. However, due to the increase in the thickness of initial metal layer and the annealing temperature, the controllability in the size, shape and distribution of the induced nanoparticles will be deteriorated. For instance, as the film grows thicker, nanoparticles become irregular in shape as well as in size distribution, which can be explained by the increased inter-links between nanoparticles that transform nanoparticles into irregular interlocked islands [16]. The non-spherical nanoparticles can also be related to the surface-mobility-limited growth, which occurs after significant ripening and coalescence [60].

2.2.2 Other synthesis techniques

Besides the direct-deposit self-assembly technique, other common techniques to synthesize the Au nanoparticle include solution-based (i.e., chemical colloidal) processes, electrodeposition and electron-beam lithography. In this section, these common techniques are briefly reviewed.

2.2.2.1 Chemical colloidal technique

The solution-based techniques have been used for decades to synthesize metallic nanoparticles (gold, silver), due to its ability in control of the size, shape and size distribution of the nanoparticles [38, 64, 65]. This can be done by using a reducing agent together with a metal precursor to form free-standing metallic nanoparticles [66, 67]. Subsequently, the prepared nanoparticles are transferred from the solution to the desired substrate. A typical synthesis system is made by precursors, organic surfactant and solvent. By heating the reaction medium to sufficiently high temperature, the precursors chemically decompose into active atomic or molecular species. The nanoparticles are formed, and their growth is affected by the presence of organic surfactant.

Solution-based colloidal synthesis is quite common in chemistry field, as it can be used to create very monodisperse nanoparticles, which is useful for sensing applications. The most famous approach is the classical synthesis of 12 nm diameter Au nanoparticles by using the sodium citrate reduction of gold chloride in an aqueous solution [68]. In another textbook, the recipe for preparation of colloidal Au nanoparticles with diameter ranging from few nm to 64 nm has been provided by Handley [69]. Furthermore, nanoparticles of tunable shape (from spherical to nanorods with controllable aspect ratio) can be realized through colloidal synthesis, by a seed-mediated sequential growth process. For example, Jana *et al.* have illustrated the spheroidal and rod-like Au particles could be prepared in the presence of rod-like micellar template [70, 71]. Monodisperse Au nanorods can also be achieved using

citrate-stabilized seed crystals and their subsequent growth in a series of reaction solutions contains $[\text{AuCl}_4]^-$, ascorbic acid and the cationic surfactant cetyltrimethylammonium bromide (CTAB) [72].

For the SPR applications, precise control over the SPR band can be realized through solution-based approach. Pratibha *et al.* demonstrated that the SPR wavelength of the Au nanoparticles dispersed in liquid crystals (LCs) can be changed by varying the volume fraction of the nanoparticles [52]. It was reported that a strong polarization sensitivity of SPR can be achieved for self-aligned Au nanorods dispersed in reconfigurable anisotropic fluids as a result of nanorod alignment, and the SPR wavelength depends on the dispersion medium's refractive index [53]. A tunable surface-enhanced Raman scattering (SERS) substrate has been obtained through precisely controlling the spacing between silver nanoparticles by temperature [54]. Tunable SPR has been realized by regulating the interparticle spacing of two-dimensional Au-nanoparticle array embedded in an elastic polydimethylsiloxane (PDMS) membrane in terms of mechanical expansion of the highly malleable PDMS film [55]. Tunable SPR has been also achieved from one-dimensional self-assembled Au nanoparticles (e.g., nanochains) by manipulating the amount of CTAB added to control the aggregation behavior of the nanoparticles [56]. Fig. 2-2 shows the plane-view TEM image of the Au nanoparticles synthesized with chemical colloidal method (using chlorauric acid with sodium citrate solution, as citrate ions act as both a reducing agent and a capping agent) [73].

Fig. 2-2 TEM images (a-e) and summary (f) of the average sizes of gold nanocrystals synthesized using different $\text{Na}_3\text{Ct}/\text{HAuCl}_4$ precursor ratios as labeled in each image. All nanocrystals were grown in boiling water using an initial HAuCl_4 concentration of 0.25mM. (from Ref.[73])

However, there are two critical issues which restrict the further development of solution-based method: (1) poor adhesion to the substrate and (2) difficult control of particle coverage and aggregation [40].

2.2.2.2 Electrodeposition technique

Besides the solution-based method, electrodeposition is another alternative technique to synthesize metallic nanoparticles, which is interpreted as an inexpensive and versatile technique. This is an effective technique to deposit metallic nanoparticles

on conductive substrates with a thin dielectric layer in order to form particular films [40, 74, 75]. The growth mechanism is usually explained by the three-dimensional island growth (Volmer-Weber mode) [76, 77]. In more details, the growth models of electrodeposition can be classified into instantaneous and progressive nucleation, but only instantaneous nucleation can result in a narrow size distribution of the nanoparticles which happens in the early stage of synthesis [76-78]. However, both models involve kinetic, diffusion and mixed control, and diffusion zones do not overlap with each other during the process [78]. Thus, the particle coverage can be controlled by the applied voltage and thickness of the dielectric layer, while the mean particle diameter can be adjusted by deposition time, concentration and temperature of the solution [78, 79]. Fig. 2-3 shows the SEM micrograph collected after electrodeposition of Au nanoparticles.

Fig. 2-3 SEM micrograph obtained after electrodeposition of Au nanoparticles (from Ref.[40]).

Owing to its low resistivity, a heavily-doped Si substrate can be used as an electrode in the electrodeposition. The obtained nanoparticles are directly adhered to the Si substrate with good control of coverage and aggregation. On the other hand, metallic nanoparticles on Si substrate may have applications ranging from sensing to optoelectronics/phonics and surface enhanced spectroscopy [80-82]. For example, in the application of surface-enhanced Raman spectroscopy (SERS), the Si substrate exhibits a strong and easily recognized phonon band at $\sim 520\text{ cm}^{-1}$, offering a useful internal reference or standard. In the case of electrodeposition of Au nanoparticles on Si substrate, the Au nanoparticles are firmly adhered to the Si substrate, thus the nanoparticle arrays have very good long-term stability. In addition, unlike glass, there is no interfering fluorescence background from the Si substrate.

Although the electrodeposition method has overcome the two limitations introduced in the solution-based method, the restricted choice of substrates and incompatibility with CMOS technology make it less attractive.

2.2.2.3 *Electron-beam lithography*

Electron-beam (EB) lithography is recommended by many physicists as the first choice for fabrication of monodispersed metallic nanoparticle (NP) arrays with desired sizes, shapes, patterns, and interparticle distances on glass substrates [83-85]. The typical fabrication process includes [28]: 1) spin-coating of a conducting substrate (either ITO or thin metal layer covered glass slide) with a 70-100 nm electron sensitive resist, usually poly(methyl methacrylate), PMMA; 2) forming the desired

pattern by EB lithography; 3) chemical development of the exposed resist; 4) thermal evaporation of the gold (or silver) film; 5) removal of the remaining PMMA film by acetone; 6) imaging the pattern by scanning electron microscope (SEM) and/or atomic force microscopy (AFM). The typical pair-wise Au NPs fabricated by EB lithography is illustrated in Fig. 2-4.

Fig. 2-4 SEM images of particle pair samples with varying interparticle distance (center-to-center) (from Ref.[39]).

The primary advantage of EB lithography is that it can beat the diffraction limit of light and build features in the nanometer regime. It has been used as a tool to create noble metal disks and islands to examine the role of interparticle spacing in the

plasmon properties of the nanoparticle complex systematically and quantitatively. Besides, these structures and many more develop our understanding of the properties of LSPR in nanoparticles and other nanometer scale metallic structures. However, its key limitation is the throughput, i.e., the very long time it takes to expose an entire Si wafer or glass substrate. The difficulty in scale-up and the expenses involved are the disadvantages.

2.2.2.4 Other synthesis techniques

Besides the abovementioned techniques, others techniques such as laser ablation [86, 87], template synthesis [10, 88], and ion implantation and sputtering (or co-sputtering) [89, 90], have also been used for the synthesis of Au nanoparticles. Each of them has its own advantages and disadvantages. As mentioned earlier, owing to the dependence of the optical properties on the structural morphology, it is important to have the flexibility to adjust the size, shape of the nanoparticles as well as the dielectric medium during the synthesis.

2.3 Characterization techniques of Au nanoparticles

As a consequence of reducing the size and dimensionality of a material, a drastic change in electronic and optical properties can be induced. Thus, the structural and material information will provide essential information for the analysis of data obtained from the optical characterization. In Section 2.3.1, the structural

characterizations are aimed to determine the size, shape and distribution of the Au nanoparticle. In addition, the objective of the material characterizations is to reveal the atomic and chemical composition of the nanoparticles. In Section 2.3.2, the employed optical characterization techniques are discussed. The main purpose is to determine the dielectric function and optical constants of Au nanoparticles, the properties of SPR band and its dependence on the structural and environmental properties.

2.3.1 Structural and material characterizations

2.3.1.1 Atomic force microscopy

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscope, which is capable of resolving one nanometer scale. AFM operates by measuring the repulsive or attractive force between a probe and the sample. The force depends on the nature of the sample, the distance between the probe and the sample, the probe geometry, and the sample surface contamination. In contrast to scanning tunneling microscopy, which requires conductive samples, AFM is suitable for conducting as well as insulating samples. In general, AFM can operate in three working modes: contact, non-contact and tapping mode. Through this thesis, all the AFM measurements were conducted in tapping mode. Tapping mode images overcome the limitations of the conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. For the case of nanoparticles synthesized by the direct-deposit self-assembly technique, AFM is widely used to

determine the size, shape and distribution of the nanoparticle [45, 59, 63, 91]. Fig. 2-5 shows typical AFM images of Au nanoparticles.

Fig. 2-5 Typical AFM images for Au film samples with different thicknesses (from Ref.[63]).

2.3.1.2 Scanning electron microscope

Scanning electron microscope (SEM) is one type of electron microscope whose basic principle is defined as using an electron beam to produce a magnified image of the sample [47, 92, 93]. The electrons interact with the atoms at or near the sample surface producing signals about the sample's surface morphology, composition, electrical conductivity and etc [94]. The electron energy is normally 10-30 keV, but for insulating samples, the energy can be as low as several hundred eV. The SEM images are obtained by scanning the sample with a focused electron beam and detecting the secondary electrons, backscattered electrons, characteristic x-rays, light, specimen current and transmitted electrons. Secondary electrons imaging can provide high-resolution image of sample surface, backscattered electrons are often used to study the distribution of different elements in the sample, and characteristic x-rays are significant in determining the sample composition and the abundance of elements in

the sample. In addition, electron microscopes are better than its optical counterparts because of much larger magnifications and higher depth of field. Fig. 2-6 shows the SEM image of the hexagonal array of dots with a repeat distance of 300 nm and radius of around 100 nm (operated at electron energy of 20 KeV).

Fig. 2-6 SEM image of the hexagonal array of dots. The dots are composed of photoresist on a glass substrate. The surface has been coated with a thin film of silver to support the propagation of surface plasmon polaritons (SPPs). (from Ref.[95]).

2.3.1.3 Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample [96, 97]. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. It is based on the fundamental principle that each element has a unique atomic structure allowing

X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another. It is most commonly found on scanning electron microscope (SEM). Fig. 2-7 shows EDX spectra of Fe core-Au shell and unprotected Fe nanoparticles, and the excellent stability of the core-shell nanoparticles against core oxidation was verified by the EDX spectroscopy.

Fig. 2-7 Typical EDX patterns showing (a) Fe core–Au shell magnetic nanoparticles and (b) Fe nanoparticles stored in normal laboratory conditions for 2 weeks (from Ref.[97]).

2.3.2 Optical characterizations

2.3.2.1 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is a nondestructive, contactless optical technique measuring the changes in the polarization state of light reflected from a

substrate. In general, ellipsometry can obtain the complex reflection coefficient ratio of the sample from the ratio of the complex reflection coefficient for light polarized parallel and perpendicular to the plane of incidence. By analyzing the change of polarized light reflected from the substrate, ellipsometry is capable to reveal information about layers that are thinner than the wavelength of probing light, which gives access to investigate fundamental physical parameters like dielectric properties as well as structural properties, including morphology, crystal quality, chemical composition and electrical conductivity [47, 48, 50, 98-102].

The knowledge of the dielectric function and optical constants is not only important to the fundamental physics of metal nanoparticles, but also useful to applications of metal nanoparticles. SE provides a powerful tool for investigation of dielectric function of Au nanoparticle prepared by different synthesis methods. Over the last few decades, SE has been widely used to study the dielectric function as well as optical constants of Au nanoparticles. Hövel *et al.* has determined the dielectric properties of ultrathin metal films around the percolation threshold using variable-angle ellipsometer, as shown in Fig. 2-8(a) [45]. The real and imaginary part of the complex refractive indices (n and k) of Au nanoparticle thin film fabricated by layer-by-layer self-assembly can be evaluated from the fitting of ellipsometric angles (Fig. 2-8 (b)).

Fig. 2-8 (a) Dielectric constant of Au films with different thickness obtained at room temperature (from Ref.[45]). (b) Real (n) and imaginary (k) parts of the complex refractive indices of nanoparticle film fabricated by layer-by-layer self-assembly (from Ref.[103]).

2.3.2.2 Ultraviolet-visible spectrophotometry

In chemistry, spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. Spectrophotometry involves the use of a spectrophotometer, which is a photometer that can measure light intensity as a function of the light source wavelength. The most common spectrophotometers are used in the ultraviolet (UV) and visible regions of the spectrum.

The most fascinating feature of the noble metal nanoparticles, the SPR band, can be revealed as a strong optical absorption peak in the visible region of the spectrum [24, 63, 67, 81, 104]. Therefore, spectrophotometry provides a useful tool to investigate the properties of the SPR band, i.e., the dependence of the SPR band on the structural properties and influence of dielectric constant of the surrounding medium on

the SPR band. El-Sayed has demonstrated that for metallic nanorods, the plasmon resonance splits into low- and high-energy absorption bands due to the unevenly distributed polarization (as shown in Fig. 2-9) [105].

Fig. 2-9 Absorption spectrum of the nanorods (from Ref.[105]).

2.4 Study of optical properties of Au nanoparticles

Unlike the semiconductor nanoparticles where quantum confinement effect produces quantization of the electron and hole energy states to induce major modifications of their optical spectra, metallic nanoparticles exhibit major changes in their optical spectra derived from effects that can be explained using a classical dielectric picture [11]. As mentioned earlier, the light absorption by metallic nanoparticles is described by coherent oscillations of the confined conduction electrons, which is produced by the interaction with the external electromagnetic field. These oscillations produce surface plasmon waves, which are localized and dependent

on the specific wavelengths of light absorption. The localized surface plasmon wave can be revealed as a strong optical absorption peak in the visible range of the spectrum. Therefore, absorbance is considered to be an intuitive and powerful tool in investigating the optical properties of metal nanoparticles. Besides the experimental measurement, a number of theoretical models have been proposed to describe the optical properties of the metal nanoparticles.

2.4.1 Experimental measurement

A systemic study of the optical properties of metallic nanoparticles has been reported by Link *et al.*, which is based on the investigation of the absorption spectra [24]. The following conclusions have been discussed in [11]. For metallic nanoparticles significantly smaller than the wavelength of light, the light absorption is within a narrow wavelength range. The wavelength of the absorption peak maximum due to surface plasmon resonance (SPR) band is strongly dependent on the size and shape of the nanoparticles, as well as on the surrounding dielectric medium. For extremely small nanoparticles (<25 nm), the shift of the peak position of SPR band is much smaller. However, a broadening of the peak is observed. While, for larger nanoparticles (>25 nm), the SPR peak shows a distinct red-shift with the increase in the average size of the nanoparticles. Optical absorption spectra of Au nanoparticles with different sizes are shown in Fig. 2-10. For the nonspherical-shaped nanoparticles (i.e., nanorods), the SPR band splits into two bands corresponding to the oscillations of free electrons along (longitudinal) and perpendicular (transverse) to the long axis of the rod. Fig. 2-9 shows this splitting of SPR band for a Au nanorod. In addition, the

position of the transverse mode resonance is close to that observed for spherical nanoparticles, while the longitudinal mode is red-shifted, depending on the aspect ratio, which is the length divided by the width of the rod. Johnson *et al.* has reported that the strong longitudinal mode depends linearly on the length of the nanorod, which results from a mixture of orbital transitions [106]. The quantum confinement does affect the energy spacing of the various levels in the conduction band. However, this quantization mainly influence the conductive properties of the metal and is often used to describe the metal-to-insulator transition occurring as the particle size is shrunk from microscopic to nanoscopic size. When the dimensions of the metallic nanoparticles are large, the spacing of levels within the conduction band is significantly less than the thermal energy, kT (k is Boltzmann's constant and T is the temperature in Kelvin), and the particle exhibits a metallic behavior. When the nanoparticles approach a size at which the increased energy separation due to the quantum confinement effect is more than the thermal energy, an insulating behavior results because of these discrete levels. However, the energy level separations are still too small to affect the optical properties of metals in the UV to the IR range.

Fig. 2-10 Optical absorption spectra of Au nanoparticles of different sizes (from Ref.[67]).

Some studies on the dependence of optical properties on the size of metal nanoparticles have been reported [107, 108]. For nanoparticles with diameter less than 20 nm, the energy absorption is mainly through (1) the collective excitation of confined free electrons, referring as localized surface plasmon resonance; (2) interband transitions of bound electrons from occupied to empty bulk bands of different index; and (3) surface scattering of free or bound electrons, when the mean free path is comparable to the size of nanoparticles [108]. Besides, the scattering effects become significant only for nanoparticles of more than 30 nm in diameter, as the excited electrons are radiating energy in all directions [108]. Owing to the secondary radiation, the electrons lose energy through a damping effect. The corresponding spectrum was found to be less intense, wider and red-shifted with an increase in particle size [107]. Wokaun *et al.* suggested that this radiation damping limited the enhancement of plasmon resonance, and a depolarization field shifted the

spectrum towards longer wavelength [109]. Furthermore, the scattering effects dominate the optical response when the particles are larger than 100 nm in diameter [108].

Tunable shape of a metal structure at sub-wavelength dimensions exhibits interesting optical properties, especially the plasmon-based phenomena [43, 85, 105, 108, 110]. Widely varying the shapes of metal nanoparticles can be achieved with chemical methods, where the growth of gold or silver onto preferential crystalline facets of the nanoparticles is directed by the inclusion of surfactants and copolymers along with the chemical reduction of gold or silver acids [57]. Nehl *et al.* have reported the synthesis, structure, and optical properties of ca. 100 nm star-shaped Au nanoparticles, which have multiple plasmon resonances attributed to the different tips on the star-shaped structure [110]. The TEM image and corresponding extinction spectrum of the star-shaped Au nanoparticles are shown in Fig. 2-11. In addition, an interesting structure referred to as nanorice, has been designed and fabricated by Wang *et al.*, which are made up of dielectric core-metallic shell prolate spheroid nanoparticle [111]. It provides both great local field enhancement and high freedom in plasmon resonances tunability, as the hybridization between plasmon modes of a solid prolate spheroid and an ellipsoidal cavity inside a continuous metal. Fig. 2-12 shows the extinction spectra of nanorice with various thicknesses of the shell layer, and a representative SEM image of the nanorice with thickness of 13.1 ± 1.1 nm.

Fig. 2-11 (a) TEM image of star-shaped Au nanocrystals and (b) Extinction spectrum of nanostar solution exhibiting broad visible and NIR peaks (from Ref.[110]).

Fig. 2-12 (a) Extinction spectra of hematite-Au core-shell nanorice with different shell thicknesses. The samples measured are monolayers of isolated nanoshell immobilized on PVP-glass slides. (b) SEM image of monolayer of nanorice particles (shell thickness of 13.1 ± 1.1 nm) on a PVP-glass slide (from Ref.[111]).

2.4.2 Numerical determination

2.4.2.1 Mie theory

Among the various theoretical models in determining the optical properties of metal nanoparticles, the original classical model of Mie theory is often used, which is based on the assumption that particles and surrounding medium are homogenous and can be described by bulk dielectric function. Based on the Mie's calculation of the interaction between electromagnetic waves and smaller spheres, a series of multipole oscillation (dipole, quadrupole, etc.) as summation of both electric and magnetic components can be obtained [20, 112]. For particle much smaller than the wavelength of light ($\lambda \gg 2R$, where R is the nanoparticle radius), the dipole approximation is widely accepted since only dipole oscillation is concerned. The extinction coefficient k_{ex} (measure of absorption and scattering strengths under collective excitations) can be calculated using [11, 20]:

$$k_{ex} = \frac{18\pi NV\epsilon_h^{3/2}}{\lambda} \frac{\epsilon_2}{[\epsilon_1 + 2\epsilon_h]^2 + \epsilon_2^2} \quad (2.1)$$

where λ is the wavelength of light, N is the density of the nanoparticles, V denotes the volume of the nanoparticles, ϵ_h is the dielectric function of the surrounding medium, and ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant of metal, which are frequency dependent. The frequency of resonance condition occurs at $\epsilon_1 = -2\epsilon_h$, where the denominator takes its minimum, if ϵ_h is small or weakly dependent on frequency. The bandwidth and height is proportional to the ϵ_h , but the

size dependence of the SPR band is attributed to the size dependence of the dielectric function ϵ .

In the case of noble metals like gold and silver, the dielectric function is related to interband and intraband transitions, which are described as: (1) electrons from the inner d orbital to the conduction band; (2) free conduction electrons absorption, respectively [11]. The latter contribution, represented by Drude model, has the form [11, 20, 102]

$$\epsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2.2)$$

where $\omega_p = \hbar e \sqrt{N_e/m^* \epsilon_0}$ is the plasmon frequency of the bulk metal, N_e is the electron density, m^* is the effective mass and γ is the damping constant relating to the width of the plasmon resonance band. It depends on the lifetime associated with various electrons scattering processes [11]. In bulk metal, the major contributions to the scattering process are electron-electron scattering and electron-phonon scattering. However, in the case of smaller nanoparticles, scattering from the particle's boundaries becomes significant. This damping term γ associated with boundary scattering is inversely proportional to the size of nanoparticles. Therefore, this size dependence of γ will result in the size dependence in $\epsilon_D(\omega)$ and the SPR band accordingly.

Furthermore, in the case of noncontinuous conductive pathway, the plasmon resonance induced by oscillation of spatially confined free electrons under external excitation can be described by a Lorentz oscillator [102]

$$\varepsilon_L(\omega) = \varepsilon_\infty + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.3)$$

where ε_∞ is the plasmon resonance frequency, which is characteristic for specified size and material. For nonspherical nanoparticles, the split of plasmon resonance can be described by using two Lorentz oscillators, which model the lower and higher energy peaks, respectively [42, 47]. Nevertheless, in the condition of continuous metal film, the resonance frequency will be reduced to zero, and therefore, Lorentz oscillator is transformed into Drude model. This zero resonance frequency has been often used to determine the percolation threshold of the metal thin film [45, 98, 102].

However, there are some critical issues which restrict the further employment of Eq. (2.1): (1) for larger nanoparticles ($2R \geq 30$ nm), the extinction behavior is dominated by higher-order multipole absorption and scattering, and the full Mie equation is needed to represent the absorption spectrum. (2) In the case of non-spherical metal nanoparticles, i.e., cylindrical and needle-like nanoparticles, the original Mie theory has to be extended. (3) Mie theory is only applicable to non-interacting nanoparticles, in which nanoparticles are well separated from each other or with a low concentration in dispersion.

2.4.2.2 Discrete Dipole Approximation (DDA)

The discrete dipole approximation is one particular discretization method for solving Maxwell's equation in the presence of a particle with arbitrary shape [43, 113-115]. It has also taken the near-field interaction between neighboring nanoparticles into the calculation of total local field. In the DDA, the continuum particle is treated as

an array of polarizable N-point dipoles located on cubic lattice sites. Their positions are denoted as r_i , with polarizabilities α_i . The detailed elaboration on the DDA is presented below [43, 116]: the polarization induced in each dipole as a result of interaction with a monochromatic incident plane wave E_{loc} will be

$$P_i = \alpha_i \cdot E_{loc}(r_i) \quad (2.4)$$

E_{loc} , called local field at each dipole, is the sum of an incident field and a contribution radiated from all other dipoles in the same particle,

$$E_{loc}(r_i) = E_{loc,i} = E_{inc,i} + E_{self,i} = E_0 \exp(iK \cdot r_i) - \sum_{j \neq i} A_{ij} \cdot P_j \quad (2.5)$$

where P_j is the dipole moment of the j th element, and P_j and K are the amplitude and wave vector of the incident wave, respectively, and the interaction matrix A with 3×3 matrixes has the following form:

$$A_{ij} \cdot P_j = \frac{\exp(ikr_{ij})}{r_{ij}^3} \left\{ k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{(1 - ikr_{ij})}{r_{ij}^2} \times [r_{ij}^2 P_j - 3r_{ij}(r_{ij} \cdot P_j)] \right\} \quad (j \neq i) \quad (2.6)$$

where $k = \omega/c = 2\pi/\lambda$.

By solving these 3N complex linear equations, based on Eq. (2.4), each dipole moment is the dipole moment P_j can be determined. Therefore, the extinction and absorption cross section for a target, C_{ext} and C_{abs} , in terms of the dipole moments as

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^N \text{Im}(E_{inc,j}^* \cdot P_j) \quad (2.7)$$

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \left\{ \sum_{j=1}^N \text{Im}[P_j(\alpha_j^{-1})^* P_j^*] - \frac{2}{3} k^3 |P_j|^2 \right\} \quad (2.8)$$

where * indicates complex conjugate. The scattering cross section can be obtained using the following relation

$$C_{ext} = C_{sca} + C_{abs} \quad (2.9)$$

The only approximation of DDA is based on the replacement of the continuum target with an array of N-point dipoles, which is completely flexible regarding the geometry of the scatterer, being limited only by the need to use a dipole size d small compared to both any structural length in the scatterer and the wavelength λ [117]. However, abundant research work has been devoted to the study of its accuracy [118-120]. Besides, the large computational cost is another important limitation.

2.4.2.3 Finite-Difference Time-domain (FDTD)

The FDTD is one of the powerful computational electrodynamics modeling techniques. It is widely used to calculate the optical properties of nanostructures, as it can be used to study both the near and far field electromagnetic responses for heterogeneous materials of arbitrary geometry [121-123]. One major advantage of the FDTD method is that it can provide a full spectrum in a single simulation by propagating a short pulse in the time-domain [124]. Besides, FDTD simulation is fully

explicit, and has used up to 10^9 electromagnetic unknowns, which is much more than the typical linear algebra methods (limited to fewer than 10^6 electromagnetic unknowns) [125]. In addition, the sources of errors are well-known and bounded. Most importantly, the time marching aspect of the method allows direct observations of the time evolution of electromagnetic fields (both near and far field) during the simulation, which makes it possible to study the dynamics of the system [125].

The FDTD method belongs in the general class of grid-based differential time-domain numerical modeling methods. The time-dependent Maxwell's equations are discretized using central-difference approximations to the space and time partial derivatives. The resulting finite-difference equations are solved: the electric field vector components in a volume of space are solved at a given instant in time; then the magnetic field vector components in the same spatial volume are solved at the next instant in time; and the process is repeated over and over again until the desired transient or steady-state electromagnetic field behavior is fully evolved.

In more details, the methodology of Sullivan and Taflovie has been summarized by Oubre *et al.* as stated below [125-127]. The electric flux dependent form of Maxwell's equations is given by

$$\frac{\partial \vec{D}}{\partial t} = \nabla \times \vec{H} \quad (2.10)$$

$$D(\omega) = \epsilon(\omega)E(\omega) \quad (2.11)$$

$$\frac{\partial \vec{H}}{\partial t} = -\frac{1}{\mu_0} \nabla \times \vec{E} \quad (2.12)$$

These equations are solved on a discrete grid replacing all derivatives with finite differences. Following the Yee algorithm, both $\vec{D}$ and $\vec{H}$ are offset in both space and time [128]. This allows one to use central differences, making the algorithm second-order accurate. For instance, the discrete one-dimensional form of Eq. (2.10) is given by

$$\frac{D^{n+1/2}(k) - D^{n-1/2}(k)}{\Delta t} = \frac{H^n(k + 1/2) - H^n(k - 1/2)}{\Delta x} \quad (2.13)$$

where k is the spatial coordinate and then n superscript denotes time. It is then straightforward to solve for $D^{n+1/2}(k)$ in terms of $D^{n-1/2}(k)$, $H^n(k + 1/2)$, and $H^n(k - 1/2)$ which are already stored in memory [125].

2.4.2.4 Effective Medium Approximation (EMA)

Effective medium approximations (EMA) are physical models that describe the macroscopic properties of a medium based on the properties and the relative fractions of its components. They can be discrete models such as applied to resistor networks or continuum theories as applied to elasticity or viscosity but most of the current theories. There are many different effective medium approximations, each of them being more or less accurate in distinct conditions. However, they all assume that the macroscopic system is homogeneous.

Among the various EMA models, Maxwell-Garnett and Bruggemann EMAs are the two most common ones, and can be used to model numerous mixing effects such as multiphase medium and surface roughness. The Maxwell-Garnett EMA is

derived based on the assumption of spherical inclusions of one or two material(s) (denoted materials “2” and “3”) embedded in the host material (denoted material “1”):

$$\frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1} = f_2 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} + f_3 \frac{\varepsilon_3 - \varepsilon_1}{\varepsilon_3 + 2\varepsilon_1} \quad (2.14)$$

This equation must be interpolated for the effective complex dielectric function ε given the volume fractions of two of the constituents f_2 and f_3 (f_1 is equal to $1 - f_2 - f_3$) and the dielectric function of all the three materials. In the case of two constituent materials, the calculation can be carried out by fixing f_3 at zero.

The Bruggemann EMA makes the self-consistent choice of the host material complex dielectric function equaling the final effective complex dielectric function of the multi-constituent material [129]. It is capable of predicting the properties of a multiphase medium close to the percolation threshold. The Bruggemann EMA takes the form:

$$f_1 \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} + f_2 \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon} + f_3 \frac{\varepsilon_3 - \varepsilon}{\varepsilon_3 + 2\varepsilon} = 0 \quad (2.15)$$

This equation can also be used for three constituents as well as two component medium with f_3 fixed at zero. In practice, this equation can be more difficult to solve correctly due to a series of solutions generated from the complex equation, such that one must correctly choose the appropriate solution branch.

2.5 Device applications of Metal nanoparticles

As mentioned earlier, the main applications of metal nanoparticles can be classified into two groups: (1) sensing applications, utilizing the local field enhancement; (2) photonic devices, based on near-field coupling of localized SPR.

2.5.1 Overview of sensors and biosensors

The sensing applications of the metal nanoparticle are mainly derived from the local field enhancement under plasmon resonance condition [11]. The significant enhancement of electric field near the particle surface has been used for signal amplification in several optical techniques, i.e., surface-enhanced Raman spectroscopy (SERS) [109, 130, 131]. The enhancement factor can be as much as 10^{10} to 10^{11} , which means SERS is capable to detect single molecules [132-134]. Although the exact mechanism of the enhancement effects of SERS is still under debate, two primary theories offer possible explanations: the electromagnetic and chemical theories. The electromagnetic theory emphasizes the local field enhancement based on LSPR, while the chemical theory states the formation of charge-transfer complexes. However, the chemical theory is only applicable for the species with a chemical bond formed on the surface, which cannot explain the field enhancement observed in all cases. Meanwhile, the investigation of the chemical theory is beyond the scope of this study.

Electromagnetic theory explains the increase in intensity of the Raman signal in terms of the enhancement in the electric field near the surface. When the localized SPR are excited by the incident light, if the plasmon frequency is in resonance with the radiation, great field enhancement occurs. However, there is one important constraint on the oscillation direction - the plasmon oscillation must be perpendicular to the surface, otherwise, no scattering occurs. Thus, arrangements of nanoparticles are required in SERS experiments as localized collective oscillation can occur. In addition, as those progressively higher-order modes multipoles are non-radiative and not efficient in exciting Raman, only dipolar contribution is concerned in the interaction between nanoparticles and incident light, where the size of nanoparticle should be much smaller than the wavelength of light. The magnified Raman signal is realized based on the double enhanced local field. First, the intensity of incident light which will excite the Raman modes is amplified due to the field enhancement. The Raman signal is then further magnified by the LSPR, due to the same mechanism which excited the incident light, resulting in a greater increase in the total output. The maximum enhancement is achieved in the condition where the incident light and Raman signal are near resonance with the plasmon frequency. Therefore, the excitation of LSPR is the key in SERS, which is required to be controlled to maximize signal strength and ensure reproducibility. The principal factors influencing the LSPR include material, size, shape, interparticle spacing, and dielectric environment. Silver and gold are the common choices for SERS experiments, because their plasmon frequencies lie in the visible and near-infrared ranges, providing maximal enhancement within these ranges.

One of the most severe restrictions in the SERS applications is the tribology requirement of roughed or nanostructure surfaces. To overcome this limitation, one new technique, tip-enhanced Raman spectroscopy (TERS), has been proposed to achieve complete substrate generality for SERS [135-137]. TERS uses a scanning probe microscopy (SPM) tip as an external source to enhance Raman signals accessible for any adsorbate on any surface. When the LSPR is excited on a noble metal SPM tip, the strong electromagnetic field near the tip apex can magnify the Raman signals from the molecules in the vicinity of the tip through the long range of interaction between the molecules and the enhanced electromagnetic field. In addition, TERS combines the advantages of SERS and SPM, offering high sensitivity, rich chemical information content together with excellent spatial resolution [130]. Fig. 2-13 illustrates TERS spectra of a self-assembled monolayer (SAM) of benzenethiol adsorbed to an 8 nm Au island that is weakly SERS active at $\lambda_{\text{ex}} = 532$ nm. These spectra confirm the Raman signals are originated from the molecules on the Au island film, and the enhancement factor for each Raman mode is estimated to be $\sim 10^4$.

Fig. 2-13 TERS of a SAM of benzenethiol adsorbed to an 8 nm Au film on glass. (a) AFM tip engaged in contact mode. (b) AFM tip withdrawn by 100 μm . (c) AFM tip re-engaged in contact mode. (d) Laser focused solely on the AFM tip after has been removed (from Ref.[130]).

2.5.2 Overview of plasmon waveguides and nano-optics

Although the demand of huge amount of data zip across the Internet everyday is accomplished in the form of light waves conveyed by optical fibers, today's computing systems still rely on the electrical signals traveling through a dense network of metal lines linking together gigantic numbers of nanoscale devices on silicon chips, which have much lower bandwidth. Owing to the down scaling demand on the device structure, reduction in the pitch and cross-section of metal lines are

needed. However, this reduction gives rise to local heating and an increase in the RC delay of interconnected structures via the metal lines. Optical interconnects can overcome these limitations and have a much higher capacity due to much higher operating frequencies (optical frequency are about 100,000 times greater than the frequency of today's electronic microprocessors). However, conventional optical interconnect uses its boundaries to trap light, whose dimensions are limited by the diffraction limit of light. The minimum size of light confinement is of the order of $\lambda/2n$ where λ is the wavelength and n is the refractive index (in the order of a few 100 nm for visible light) [138]. Another limitation is the bend loss. For traditional metallic pipe waveguides can only transmit microwaves without losses and the dielectric guides, working in the infrared and visible range of the spectra, their radiation losses are strongly influenced by the curvature bends [28]. Therefore, novel waveguides using other mechanism of light confinement and guide are being investigated to realize an integrated and highly compacted photonic circuit. Using periodic array of closely-spaced metal nanoparticles like gold and silver, coupled plasmon modes induced from coupling between adjacent particles can give rise to coherent propagation along the array, with a transport velocity exceeding 10% of velocity of light and negligible transmission losses even around corners and tee structures [29, 139]. Schematic of the plasmon waveguide is shown in Fig. 2-14. Far-field spectroscopy and FDTD simulation on arrays of 50 nm diameter Au spheres with an interparticle distance of 75 nm both show a splitting of resonance energies in longitudinal and transverse plasmon-polarization modes [140]. Fig. 2-15 (a) shows a 60° corner structure fabricated using electron-beam lithography on indium tin oxide

(ITO) doped glass. The individual particles are 50 nm in diameter. Another synthesis method using dedicated AFM and manipulation software to assemble a straight line of 30 nm Au nanoparticles is demonstrated in Fig. 2-15 (b).

Fig. 2-14 Schematic of plasmonic guiding and its use to generate fluorescence excitation in a dye (from Ref.[29]).

Fig. 2-15 (a) SEM image of a 60° corner in a plasmon waveguide. The Au dots are ~ 50 nm in diameter and spaced by ~75 nm (center-to-center). (b) Straight waveguide made by 30 nm diameter colloidal Au nanoparticles (from Ref.[139]).

The principal mechanism of this nanoparticle waveguide is based on the near-field coupling, as the dipole field resulting from a plasmon oscillation in a single metal nanoparticle can induce a plasmon oscillation in a closely-spaced neighboring particle [141-143]. The propagation modes can be revealed from the dispersion relation via a polarization dependent interaction strength ω_1 derived from the electromagnetic interaction term and the plasmon dipole resonance ω_0 [139, 141]. Fig. 2-16 shows the dispersion relation for plasmon modes (longitudinal modes L and transverse modes T) in a linear chain of metal nanoparticles, showing the inclusion of five nearest neighbors has little effect but dominated by nearest neighbor coupling. An optimum efficiency nanoparticle waveguide with propagation distance as much as 150 μm constructed using one dimensional chain consisting of different particle size and interparticle distances in the illuminated and non-illuminated portions of the chain has been proposed [144]. The electric field contours for the chain with different structural properties in each portion of chain is represented in Fig. 2-17. In addition, the nanoparticles fabricated using electron-beam lithography is limited to the spatial resolution of ca. 50 nm, other bottom-up approaches like using template or interparticle coupling agents to self-assembly performed metal nanoparticle with 10 nm in diameter have been reported [142].

Fig. 2-16 Dispersion relation for plasmon modes (longitudinal modes L and transverse modes T) in a linear chain of metal nanoparticles (from Ref.[141]).

Fig. 2-17 Electric field contour plot for particles in the chain, showing particles close to the junction between illuminated and non-illuminated particles (from Ref.[144]).

2.6 Summary

In this chapter, a literature review of the research on Au nanoparticles has been presented. First of all, common synthesis techniques for Au nanoparticles have been reviewed, including direct-deposit self-assembly, chemical colloidal method,

electrodeposition, and electron-beam lithography. Among these potential techniques, direct-deposit self-assembly and electrodeposition methods have been chosen for this study, based on its compatibility with main stream CMOS technology and good control in particle size and distribution, respectively. Besides, the most common characterization techniques for the structural, material, and optical properties of Au nanoparticles have been reviewed. At last, the study of optical properties and applications of Au nanoparticles have been discussed in detail.

Chapter 3 Optical Properties of Au

Nanoparticles Synthesized on Silicon Substrate

using Direct-Deposit Self-Assembly Method

3.1 Introduction

The optical properties of Au nanoparticles have long been of interest as they are markedly different from their bulk counterparts. Unlike semiconductor nanoparticles where quantum confinement effects play a critical role in modifying their optical spectra, the major changes in the optical spectra of metallic nanoparticles can be explained using the classical dielectric theory [11]. There are different experimental ways to obtain the optical properties of metal nanoparticles, among which the extinction measurement has been widely used to study the absorption and scattering effects [110, 145]. For metallic nanoparticles with dimension much smaller than the wavelength of incident light, their optical properties including the dielectric functions are known to be dependent on their sizes, shapes and dielectric environment [40, 42, 43, 146]. However, few studies on the experimental determination of the dielectric functions of metal nanoparticles have been reported [146, 147]. The knowledge of the dielectric functions is not only important to the fundamental physics of metal nanoparticles, but also useful to the applications of metal nanoparticles. For example,

Au nanoparticles have shown several orders of signal enhancement on Raman spectroscopy [82, 148] and more than 1000 times enhancements on surface plasmon resonance spectroscopy [149], which depends on the dielectric functions of the Au nanoparticles. Furthermore, the knowledge of the dielectric properties of metal nanoparticles is also useful to the studies and applications of metamaterials consisting of metal nanoparticles [150, 151].

In this chapter, the effective dielectric function under collective excitations of Au nanoparticles on silicon substrate has been determined from spectroscopic ellipsometry (SE) measurement. The Au nanoparticles were fabricated using direct-deposit self-assembly method, as self-assembled nanoparticle arrays were obtained from the deposition of an ultrathin Au film followed by rapid thermal annealing treatment. This method provides high-throughput nanoparticles with good control in size, shape and distribution.

3.2 Ellipsometry

In this section, the basic principles of ellipsometry are introduced, together with its optical fundamentals, based on which we can describe the methodology that is employed in determining the dielectric function of Au nanoparticles in the following sections.

3.2.1 Basic principles

Ellipsometry is a nondestructive, contactless optical technique measuring the changes in the polarization state of light reflected from a substrate. Generally, light will be reduced in amplitude and shifted in phase if it is reflected from a single surface. For multilayer reflection regime, maxima and minima are obtained due to interaction of various reflecting beams. Ellipsometry can obtain the complex reflection coefficient ratio of the sample from the ratio of the complex reflection coefficient for light polarized parallel and perpendicular to the plane of incidence. The exact nature of the polarized modification is determined by the properties of the measured sample (i.e., thickness, dielectric function or complex refractive index). Besides, more fundamental physical parameters like morphology, crystal quality, chemical composition and electrical conductivity can be extracted from ellipsometric analysis.

The linearly polarized light is emitted from light source and polarization generator, reflected from the sample surface, becomes elliptically polarized and is collected by analyzer and detector. The incident polarized light is linear with both s- (perpendicular to the plane of incident) and p- (parallel to the plane of incident) components. The Fresnel reflection coefficient r is the ratio of the amplitude of the reflected wave to the amplitude of the incident wave for a single interface.

$$r_{12}^p = \frac{N_2 \cos \phi_1 - N_1 \cos \phi_2}{N_2 \cos \phi_1 + N_1 \cos \phi_2} \quad (3.1)$$

$$r_{12}^s = \frac{N_1 \cos \phi_1 - N_2 \cos \phi_2}{N_1 \cos \phi_1 + N_2 \cos \phi_2} \quad (3.2)$$

For multiple interfaces, the total reflection coefficients are defined as

$$R^p = \frac{r_{12}^p + r_{23}^p \exp(-j2\beta)}{1 + r_{12}^p r_{23}^p \exp(-j2\beta)} \quad (3.3)$$

$$R^s = \frac{r_{12}^s + r_{23}^s \exp(-j2\beta)}{1 + r_{12}^s r_{23}^s \exp(-j2\beta)} \quad (3.4)$$

Here, subscript “23” indicates that this Fresnel equation coefficient is for the interface between medium 2 and medium 3. β is the film phase thickness.

$$\beta = 2\pi \left(\frac{d}{\lambda} \right) N_2 \cos \phi_2 \quad (3.5)$$

The complex reflection ratio, ρ , defined in terms of the reflection coefficients R^p and R^s or the ellipsometric angles Ψ and Δ as

$$\rho = \frac{R^p}{R^s} = \tan(\Psi) e^{j\Delta} \quad (3.6)$$

where $\tan(\Psi)$ is the amplitude ratio upon reflection, and Δ is the phase difference.

In general, ellipsometry is an indirect method, since measured Ψ and Δ cannot be converted into optical constants directly. In practice, a layer model must be established, which considers the optical constants and thickness parameters of all individual layers of the sample including the correct layer sequence. The dielectric function and thickness parameters of the sample can be extracted based on an iterative procedure (using least-squares minimization). The calculated Ψ and Δ can be obtained using Fresnel equations by varying the unknown optical constants and/or thickness. The spectral fitting to the experimental ellipsometric angles (Ψ and Δ) was performed

by adjusting these parameters (i.e., optical constants and thickness) to minimize the mean-square error between the measured and calculated ellipsometric angles. The general idea of ellipsometric polarized light beam system is shown in Fig. 3-1.

Fig. 3-1 Schematic illustration of an ellipsometric experiment, showing the polarized light reflected from a plane surface.

Unlike single wavelength ellipsometry, using a monochromatic light source, spectroscopic ellipsometric measurement have extended the range of ellipsometry by using more than one wavelength. Furthermore, it is possible to vary not only the wavelength but also the angle of incidence, providing yet another freedom, which enables non-invasive, real-time process measurements [94]. In this study, spectroscopic ellipsometry will be used to study the dielectric function and optical constants of Au nanoparticles synthesized on Si substrate.

3.2.2 Dielectric functions and optical constants

Upon investigation of the dielectric function of Au nanoparticles, the understanding of optical function of material through the interaction of polarized light with the surface of a material is important. In general, the optical function describes the response of normal material to an external electromagnetic field. The polarization vector ($\vec{P}$) is related to the electric field ($\vec{E}$) described by the equation

$$\vec{P} = \chi \epsilon_0 \vec{E} \quad (3.7)$$

where χ is the electric susceptibility of the material and ϵ_0 is the dielectric constant of vacuum. The displacement field ($\vec{D}$) can be written as the sum of electric field ($\vec{E}$) and polarization field ($\vec{P}$) by

$$\vec{D} = (1 + \chi) \epsilon_0 \vec{E} \quad (3.8)$$

where the quantity $(1 + \chi)$ is referred to as its dielectric constant (ϵ) described by

$$\epsilon = 1 + \chi \quad (3.9)$$

As the dielectric constant is a complex quantity, it can be expressed as the sum of real and imaginary parts.

$$\epsilon = \epsilon_1 + i\epsilon_2 \quad (3.10)$$

ϵ can also be expressed in terms of its complex refractive index (N)

$$\varepsilon = N^2 = (n + ik)^2 \quad (3.11)$$

where n and k are defined as optical constants, in which n is the refractive index, and k is defined as extinction coefficient. Therefore, the real and imaginary parts of dielectric constant can be represented as

$$\varepsilon_1 = n^2 - k^2 \quad (3.12)$$

$$\varepsilon_2 = 2nk \quad (3.13)$$

For a particular material, the dielectric constant is usually a complicated function of frequency. This frequency dependence reflects the fact that a material's polarization does not respond instantaneously to an applied field, which can also be represented as a function of photon energy. Thus, the dielectric constant as a function of photon energy can be defined as dielectric function $\varepsilon(E)$. While, $n(E)$ and $k(E)$ represent the dispersion of refractive index and extinction coefficient, respectively. In this chapter, the real and imaginary part of the dielectric function can be obtained from Eq. (3.12) and (3.13).

3.3 Optical properties of Au nanoparticles

In this section, the effective dielectric functions of Au nanoparticles in the photon energy range of 1.1 - 4.1 eV were determined from spectroscopic ellipsometry (SE) measurement. The dielectric functions of the nanoparticles were best represented

by Lorentz-Drude model. The result suggests that the collective properties of the nanoparticles could be influenced by various factors such as the near-field interactions between adjacent nanoparticles, sizes and shapes of the nanoparticles, and the dielectric environment.

3.3.1 Sample fabrication

The sample fabrication began with the standard piranha clean of the *p*-type <100> Si substrates (resistivity is 9 – 12 Ω -cm), followed by a diluted hydrogen fluoride (HF) clean to remove the native oxide. A Au film with thickness of 3 nm was deposited on the Si substrate by electron-beam evaporation. During the deposition, the base pressure was below 5×10^{-6} mbar, and the deposition rate was 0.1 Å/s. After the deposition, these samples were annealed using rapid thermal annealing (RTA) at 550°C for 20 s in N₂ ambient.

3.3.2 AFM and SEM characterizations

In this study, an atomic force microscopy (AFM) with tapping mode and a scanning electron microscope (SEM) were used to characterize the structural properties of the Au nanoparticles formed on the silicon substrate. Both techniques provide essential information to understand the dependence of optical properties of Au nanoparticles on the structural morphology. Fig. 3-2(a) shows the top-view AFM image of the 3 nm Au thin films after RTA. The image confirms the formation of Au nanoparticles after RTA as a result of the stress relaxation, dispersion force, and

surface energy minimization during the annealing [16]. In more details, the difference in thermal expansion coefficient between the Au and the Si substrate leads to the formation of hillocks due to the relaxation of the thermal stress during the annealing process [59]. While, the thermal energy enhances the nucleation and growth of holes by surface diffusion, and those holes can even be coalesced into islands as a result of reducing the surface energy. The size of the nanoparticles varied from several nanometers to greater than 30 nm, as shown in Fig. 3-2(b). The mean diameter of the nanoparticles was 13.6 nm and the density of nanoparticle was $4.4 \times 10^{10} \text{ cm}^{-2}$.

3.3.3 Ellipsometry measurement

The SE measurements were performed using a variable angle spectroscopic ellipsometer (J. A. Wollam, Inc.). The ellipsometric angles (Ψ and Δ) were measured in the wavelength range of 300 – 1100 nm with the step of 5 nm at three different incident angles of 65°, 70°, and 75°, respectively. In addition, there are some critical optical components in this ellipsometry system that should be emphasized. Due to the long range of light irradiance in the UV and near IR region, Xe or Hg-Xe arc lamps are usually employed in ellipsometric measurement. In consequence, the light transport in the UV and IR region can be achieved by using specific optical fibers, which is also used in coupling the light beam from the monochromator to the polarizer. The modulated light intensity is controlled by a chopper. The most important optical component, which is used for converting light with any polarization into linearly polarized light, is the calcite Glan-Taylor polarizer. The Si and InGaAs photodetectors

are used as analyzers, owing to their insensitive nature to the polarization state and light intensity.

Fig. 3-2 (a) Top-view AFM image of the Au nanoparticle film and (b) size distribution of the Au nanoparticles obtained from SEM.

3.3.4 Methodology

A method is proposed to extract effective dielectric functions (including optical constants) of self-assembled Au nanoparticles from the spectroscopic ellipsometric analysis. Effective medium approximation (EMA) theory together with a proper optical dispersion relationship has been used to determine the dielectric functions of Au nanoparticles synthesized on Si substrate. The methodology and principles are presented as below.

3.3.4.1 Three-phase model

In this study, a three-phase model (i.e., air/Au nanoparticle layer/Si substrate) is used in the SE analysis. The Fresnel equations of obtaining the complex reflection coefficient can be found in Eq. (3.3) and (3.4), and the angles ϕ_1 and ϕ_2 between the directions of propagation of plane waves in phase 0 (i.e., air), phase 1 (i.e., Au nanoparticle layer) and phase 2 (i.e., Si substrate) are calculated by Snell's law:

$$N_0 \sin \phi_0 = N_1 \sin \phi_1 = N_2 \sin \phi_2 \quad (3.14)$$

where N_0 , N_1 and N_2 are the complex refractive index of each phase, which is defined as $N_0 = n_0 + ik_0$ (n and k are the refractive index and extinction coefficient, respectively).

To determine the dielectric function, the Au nanoparticle layer is treated as a composite layer consisting of the Au nanoparticles and voids [152]. The effective

dielectric function ε_i of this layer can be calculated with the Maxwell-Garnett EMA [153]

$$\frac{\varepsilon_i - \varepsilon_{nc-Au}}{\varepsilon_i + 2\varepsilon_{nc-Au}} = v_i \frac{\varepsilon_{void} - \varepsilon_{nc-Au}}{\varepsilon_{void} + 2\varepsilon_{nc-Au}} \quad (3.15)$$

where v_i is the volume fraction of the voids, ε_{void} is equal to unity for the dielectric function of the voids, and ε_{nc-Au} is the dielectric function of the Au nanoparticles under collective excitations. In Eq. (3.15), it is assumed that the volume fraction of the voids is small as compared to that of the metal (the voids are embedded in the metal layer). There is also another choice, i.e., the metal particles are embedded in empty space. With the first choice, all spectral features can be fitted excellently for the three angles of incidence. In contrast, the second choice yielded a poorer quality of the spectral fittings. The volume fractions of the voids and Au nanoparticles yielded from the first choice were 16% and 84%, respectively. However, the volume fractions of voids yielded from the second choice is only $\sim 2\%$. A comparison to the AFM and SEM images suggests that the result of the first choice is more reasonable. Therefore, the first choice is used in the present study.

3.3.4.2 Dispersion model

In the spectral fitting, an appropriate optical dispersion model is needed to represent the functional dependent dielectric functions and optical constants of the Au nanoparticles. In the study, the Lorentz-Drude model is used to perform the spectral fitting.

The optical properties of Au nanoparticles are related to free and bound electron transitions, which can be described by the Drude term and Lorentz oscillators, and the corresponding energy-dependent complex dielectric function is described by [102]

$$\varepsilon(E) = \varepsilon_{\infty} + \sum_{i=1}^n \frac{A_i}{E_i^2 - E^2 - i\Gamma_i E} - \frac{E_p^2}{E^2 + i\hbar \frac{E}{\tau_D}} \quad (3.16)$$

where ε_{∞} is a background constant or an offset, A_i is the amplitude of the oscillator with the unit of $(eV)^2$, E_i is the resonance energy with the unit of eV , Γ_i is the damping factor of the oscillator with the unit of eV , E_p is the unscreened plasma energy with the unit of eV , and τ_D is the electron relaxation time with the unit of fs . The number (n) of Lorentz oscillators is to be determined. For example, as will be discussed later, one oscillator is good enough to describe the dielectric function of a Au thin film, while three oscillators are required to describe the dielectric function of the Au nanoparticles of this work.

3.3.4.3 Spectral fitting

The spectral fitting to the experimental ellipsometric angles (Ψ and Δ) was performed by adjusting the parameters in Eq. (3.16) together with the Au nanoparticle layer thickness and void volume fraction to minimize the mean-square error (MSE) between the measured and calculated ellipsometric angles [154].

$$MSE = \frac{1}{2N-M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{cal} - \psi_i^{exp}}{\sigma \psi_i^{exp}} \right)^2 + \left(\frac{\Delta_i^{cal} - \Delta_i^{exp}}{\sigma \Delta_i^{exp}} \right)^2 \right] \quad (3.17)$$

Where N is the number of data points in the spectra, M is the number of variable parameters in the model, σ is the standard deviations on the experimental data points, and ψ^{exp} and Δ^{exp} are the measured values of the ellipsometric angles while ψ^{cal} and Δ^{cal} are the corresponding calculated data.

3.3.5 Results and discussions

The spectral fitting based on Eq. (3.15), Eq. (3.16) and Eq. (3.17) with $n = 3$ for the Au nanoparticle sample is shown in Fig. 3-3. All spectral features can be fitted excellently. All model parameters of Au nanoparticles yielded from the spectral fitting are listed in TABLE 3.1. The Lorentz-Drude dispersion (i.e., Eq. (3.16)) with one Lorentz oscillator describing the interband transitions represented the dielectric function of the Au thin film [155], and the model parameters of the Au thin film are listed in TABLE 3.1, also for comparison.

Fig. 3-3 Spectral fittings to the experimental ellipsometric data at different incident angles.

TABLE 3.1 Values of the Lorentz-Drude parameters of Eq. (3.16) yielded from the fittings.

	Au nanoparticles	Au thin film [155]
Lorentz oscillators		
A_1 (eV ²)	53.99	65.53
E_1 (eV)	3.65	4.03
Γ_1 (eV)	0.80	1.98
A_2 (eV ²)	31.61	
E_2 (eV)	1.26	
Γ_2 (eV)	0.47	
A_3 (eV ²)	3.81	
E_3 (eV)	2.22	
Γ_3 (eV)	0.73	
Drude term		
E_p (eV)	8.8	8.8
τ_D (fs)	0.15	72.27

The dielectric function ϵ of the Au nanoparticles is shown in Fig. 3-4, and the counterpart of the Au thin film [155] is also included in the figure for comparison. For the Au nanoparticles, there are two distinct peaks at ~ 1.2 and ~ 3.7 eV and a small peak at ~ 2.2 eV in the imaginary part ϵ_2 . The real part ϵ_1 of the dielectric function is no longer negative over the entire photon energy range of our measurement (1.1 - 4.1 eV), which is consistent with previous measurements on discrete metal islands [100, 102]. The refractive index n and the extinction coefficient k as a function of photon energy are shown in Fig. 3-5. The refractive index of the Au nanoparticles is larger

than that of the Au thin film over the entire photon energy range. In addition, the Au nanoparticles have two distinct peaks in the extinction spectrum, which are close to the peak positions observed in ϵ_2 . The calculated absorption coefficient of the Au nanoparticles is illustrated in Fig. 3-6. In addition to the two prominent absorption peaks corresponding to the two distinct peaks observed in the ϵ_2 and extinction spectra, a clear absorption structure at ~ 2.2 eV can be identified.

Fig. 3-4 Real part (ϵ_1) and imaginary part (ϵ_2) of the dielectric function ϵ of the Au nanoparticles. The dielectric function of the Au thin film [155] is also included in the figure for comparison.

Fig. 3-5 Refractive index n and extinction coefficient k of the Au nanoparticles.

Fig. 3-6 Absorption coefficient ($= 4\pi k/\lambda$), where λ is the wavelength.

The peak structures described above are actually due to the three Lorentz oscillators with resonance energy E_i ($i = 1, 2$, and 3) at 3.65, 1.26, and 2.22 eV, respectively. The first oscillator is due to the $3d$ energy band-to-Fermi level interband transitions centered at $E_i = 3.65$ eV with an effective broadening or bandwidth determined by $\Gamma_1 = 0.80$ eV. The value of E_1 of the Au nanoparticles is about the same as that of the void-free Au thin film [156], and it is also close to the value of the Au thin film listed in TABLE 3.1. However, the broadening (i.e., 0.80 eV) of this transition in the Au nanoparticles is much smaller than the value of 1.9 eV in the Au thin films (see [156] and TABLE 3.1), which is probably due to a confinement effect [157]. As the sizes of the Au nanoparticles are in the nanometer range, some of the free electrons inside the Au nanoparticles are spatially limited due to the morphology-dependent restoring force [102]. These limited free electrons experience localized surface plasmon resonance under electromagnetic excitation. Therefore, additional Lorentz oscillators are required to model these confined free electron transitions. A single Lorentz oscillator was used to represent the light absorption of Au nanoparticles associated with surface plasmons [103, 158]. However, for an imperfectly spherical shape, two Lorentz oscillators are required to describe the plasmon resonance in the ellipsometric fittings, showing a splitting of the plasmon resonance with the energy separation of ~ 1 eV. Two plasmon resonance peaks are also reported for the electrodeposited Au nanoparticles [40]. The mechanisms for the two plasmon resonance peaks are not clear yet. They could be related to the imperfectly spherical shapes with a high aspect ratio of the fabricated nanoparticles [40]. The splitting of the plasmon resonance could also be due to the lateral near-field interaction between

neighboring nanoparticles and the image charge effect of the substrate. When both the lateral interaction of the nanocrystals and the image charge effect were taken into account, a splitting of the plasmon resonance parallel and perpendicular to the interface was predicted [47]. The splitting of the plasmon resonance could also be explained by the interaction between neighboring nanoparticles in terms of the concept of plasmon chemistry [151]. As can be seen in TABLE 3.1, the plasmon resonance at the lower energy (1.26 eV) is much stronger than the plasmon resonance at higher energy (2.22 eV). The much lower intensity of high energy plasmon resonance hinders the distribution of the separate features, although the peak splitting (~ 1 eV) is quite large, as shown in the ϵ_2 spectrum (see Fig. 3-4).

The plasmon energy E_p is another important parameter, which is directly influenced by free electron transitions. It is given by [20]

$$E_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}} \quad (3.18)$$

where N is the conduction electron density, e is the electron charge, ϵ_0 is the permittivity of free space, and m^* is the electron effective mass. A change in plasma energy would imply a change in the conduction electron density or the effective electron mass for small particles. It is possible that there is no change in the plasma energy for particles larger than 5 nm in diameter [99]. Thus, our plasma energy E_p is fixed at the bulk value [42] of 8.8 eV in the spectral fitting. The relaxation time τ_D of conduction electrons yielded from the fitting is 0.15 fs. The much smaller relaxation time could be due to the increased grain boundaries or defect density caused by the

nanoparticle fabrication [102]. Nevertheless, the result indicates that the contribution from the Drude term to the dielectric function of the Au nanoparticles is less significant as compared to those from the Lorentz oscillators.

3.3.6 Conclusion

In conclusion, the dielectric function of the Au nanoparticles is best represented by a Drude term and three Lorentz oscillators with the resonance energies at 1.26, 2.22 and 3.65 eV, respectively. The contribution from the Drude term is less significant as compared to those from the Lorentz oscillators. The Lorentz oscillator at 3.65 eV is due to the interband transitions, while the other two oscillators are attributed to the surface plasmon resonance. The mechanisms for the two plasmon resonance peaks are not clear yet. To understand the origin of the splitting of the plasmon resonance, a further study is required to examine the influence of various factors such as the lateral near-field interactions between adjacent nanoparticles, image charge effect of the substrate, distribution of nanoparticle sizes, shape of nanoparticles, and etc.

3.4 Split of surface plasmon resonance of Au nanoparticles on Si substrate

3.4.1 Introduction

For metallic nanoparticles, whose sizes are significantly smaller than the wavelength of light, a strong optical absorption peak in the visible range of the spectrum can be identified; and this phenomenon is related to the localized surface plasmon resonance (LSPR). The localized surface plasmon resonance (LSPR) is a collective oscillation of conduction electrons inside nanoparticles, whose frequency is strongly dependent on the size and shape of the particles, the interparticle distance, and the refractive index of surrounding medium [24-26]. For anisotropic nanoparticles, more than one plasmon excitation bands (longitudinal or transverse waves) may be simultaneously observable according to the symmetric axes of excitation [24, 46, 159]. For instance, multipolar surface plasmon peaks have been observed on Au nanotriangles [85]. Moreover, some researchers reported that near-field coupling between neighboring nanoparticles may give rise to the plasmon band splitting [47, 48]. The collective effects have been described by many authors, especially the work by Kooij *et al.* gives an indication of the extent of peak splitting [42]. Besides the coupling effect, the influence of the substrate can also be significant [47]. However, the effective dielectric function study on the effects of near-field coupling and image dipole is so far limited.

3.4.2 Sample fabrication and experimental details

3.4.2.1 Sample fabrication

The self-assembled Au NPs were fabricated by the deposition of an ultrathin Au film with electron-beam (e-beam) evaporation followed by rapid thermal annealing (RTA). The substrates were prepared from single crystalline Si wafers with (100) orientation polished on one side. Prior to the Au film deposition, the substrates were chemically cleaned using an aqueous mixture of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, followed by buffered hydrofluoric acid and rinsing with deionized water. The Si wafer with its native oxide removed by diluted HF solution was used as substrate. Au films of 3, 5 and 8 nm thick were deposited on the silicon wafer by electron-beam evaporation. After the deposition, these samples were annealed using RTA at 400°C for 30 sec in N_2 ambient. The deposition processes were carried out in a vacuum chamber with a base pressure of 5×10^{-6} mbar, equipped with an electron gun where Au deposition was controlled with the use of quartz crystal monitor.

3.4.2.2 SEM Characterization

Fig. 3-7 shows the SEM images of Au thin film of various thicknesses after RTA. It was observed that the Au thin films break into particles due to surface tension and compressive stress associated with the mismatch of the thermal expansion coefficients of Si and Au [160]. Although the fabricated nanoparticles have a large size distribution, their mean particle size varies proportionately to the initial Au layer

thickness. The thicker the Au film was deposited, the more inter-links between particles can be observed, which gradually turned into irregular interlocked islands [16]. In more details, for the 3 nm thick Au thin film (sample 1), the mean size of Au nanoparticles obtained was 24.5 nm, with density of $9.88 \times 10^{11} \text{ cm}^{-2}$ and average particle-particle distance (assume a square distribution) of approximately 14.2 nm. For the 5 nm (sample 2) and 8 nm (sample 3) thick Au thin films, the mean sizes of nanoparticles were 31.7 and 53.9 nm, with densities of 4.94×10^{11} and $1.61 \times 10^{11} \text{ cm}^{-2}$, and average separations of approximately 20.1 and 35.2 nm, respectively.

3.4.2.3 SE measurement

The SE measurements were performed using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc). The ellipsometric angles (Δ and Ψ) were measured in the wavelength range of 300 - 1100 nm with the step of 5 nm at three different incident angles (i.e., 65°, 70° and 75°). The detailed methodology in determining the optical properties of the Au nanoparticles from the spectral fitting of ellipsometric angles using optical dispersion model (Lorentz-Drude) and effective medium approximation (Maxwell-Garnett EMA) has been presented in section 3.3.4.

Fig. 3-7 Size distribution of the Au nanoparticles: (a) sample 1 (mean size: 24.5 nm; average separation: 14.2 nm), (b) sample 2 (mean size: 31.7 nm; average separation: 20.1 nm) and (c) sample 3 (mean size: 53.9 nm; average separation: 35.2 nm). The inserts show the SEM micrographs of the samples.

3.4.3 Size effect on the dielectric function

In this section, the effective dielectric functions of the self-assembled Au nanoparticles on silicon substrate under collective excitations were well presented by a Drude term and three Lorentz oscillators: one Lorentz oscillator and Drude term modeled the interband and free electron transitions, respectively; while the other two Lorentz oscillators each modeled the polarization parallel and perpendicular to the

substrate. The results revealed that the responses of the Au nanoparticles are more related to the image charge effect of the Si substrate.

3.4.3.1 Split of surface plasmon resonance band

Fig. 3-8 shows the spectral fitting for sample 1 (as shown in Fig. 3-7). All spectral features can be fitted excellently. However, it shows that although the contribution of the Drude term increases with the nanoparticle size, it is much smaller as compared to that of the Lorentz oscillators for all the samples. As such, the report will focus on the Lorentz oscillators only in the discussions below.

Fig. 3-8 Spectral fittings to the experimental ellipsometric data at different angles of incidence for sample 1.

Fig. 3-9 shows the effective dielectric functions of Au nanoparticles with different mean sizes and interparticle spacing, and the dielectric function of Au film with thickness of 80 nm considered as bulk Au is also included for comparison. It was observed that the effective dielectric functions of Au nanoparticles become more

similar to that of bulk Au as their mean size and interparticle distance increase. As shown in Fig 3-9(a), the real part (ϵ_1) of dielectric function is partially positive for samples 1 and 2, while it becomes fully negative over the entire spectral range like bulk Au for sample 3. Similar observation has been reported for discrete metal island films [100]. In addition, a prominent increase in ϵ_1 for sample 1 can be observed when the photon energy decreases below ~ 1.3 eV and a positive value of ϵ_1 is achieved at the photon energy of ~ 1.1 eV. On the other hand, some peak structures in the imaginary part ϵ_2 at ~ 3.6 , ~ 2 and ~ 1 eV can be also observed from Fig. 3-9(b). Fig. 3-10 shows the absorption coefficients of the Au nanoparticles of samples 1, 2 and 3, and the bulk Au film is also included for comparison. The absorption peaks corresponding to the interband transition and the surface plasmon resonances can be observed. Note that due to the limited spectral range of the SE measurement, the plasmon resonance at ~ 1 eV (~ 1240 nm) cannot be fully displayed in the spectra of both ϵ_2 and the absorption coefficient.

Fig. 3-9 (a) Real part (ϵ_1) and (b) imaginary part (ϵ_2) of the effective function ϵ of the Au nanoparticles. The dielectric function of bulk Au film is also included in the figure for comparison.

Fig. 3-10 Absorption coefficient α ($=4\pi k/\lambda$ where k is the extinction coefficient and λ is the wavelength) of the Au nanoparticles. The absorption coefficient of bulk Au film is also included in the figure for comparison.

3.4.3.2 Image charge effect of the silicon substrate

The inhomogeneous polarizations parallel and perpendicular to the substrate can cause splitting of the plasmon band. One of the possible reasons for the inhomogeneous polarizations is the non-sphericity of the nanoparticles [24, 98]. However, the dielectric functions obtained from the spectral fittings to the experimental ellipsometric angles at three different angles of incidence are found to be independent of the angles of incidence. Therefore, the non-sphericity of the

nanoparticles should not be the major reason for the plasmon resonance splitting observed in this work.

The near-field coupling between the neighboring nanoparticles and/or the image charge effect of the Si substrate could be the main factors responsible for the inhomogeneous polarizations. Such argument is supported by the dependence of the Lorentz oscillators on the structural properties of the nanoparticles. Fig. 3-11 shows the imaginary part of the three Lorentz oscillators as a function of photon energy for different samples. As shown in Fig. 3-11(a), the resonance energy of Lorentz 1 corresponding to the interband transitions is about the same for different samples (i.e., samples 1 to 3), indicating that the interband transitions are not largely affected by the structural properties of the nanoparticles. However, Fig. 3-11(b) and (c) demonstrate a clear structural dependence of the two other Lorentz oscillators which represent the two plasmon resonance bands. It has been pointed out that the low energy band corresponding to the resonance parallel to the substrate is a dominant one, while the perpendicular resonance is less significant [101]. Therefore, Lorentz 2 at ~ 2 eV and Lorentz 3 at ~ 1 eV are attributed to the polarizations perpendicular and parallel to the substrate, respectively.

It can be seen from Fig. 3-11(b) and (c) that both perpendicular and parallel resonances are red-shifted when both the nanoparticle size and separation increase. It has been reported that interparticle coupling could split the plasmon resonance band into a blue-shifted perpendicular resonance and a red-shifted parallel resonance [161]. If a nanoparticle is regarded as a harmonic oscillator, in the perpendicular direction, the near-field coupling effect between neighboring nanoparticles can increase the

effective restoring force, resulting in a blue shift in the resonance energy; but in the parallel direction, the coupling effect can reduce the effective restoring force, leading to a red shift [161]. Therefore, with increasing the interparticle separation, a weaker coupling effect is expected, and thus a red shift in the perpendicular resonance and a blue shift in the parallel resonance should be observed. However, as shown in Fig. 3-11(b) and (c), when the average interparticle separation increases from 14.2 to 35.2 nm, both the perpendicular and parallel resonances show a red shift. This could suggest that the coupling effect is not the dominant factor responsible for the splitting of the plasmon band as a result of the relatively large interparticle separations. On the other hand, the plasmon resonances are also sensitive to the image charge effect of the Si substrate. Assuming the nanoparticle acts like a point dipole, the interaction between the induced image point dipole in the substrate and the nanoparticle itself should modify the polarizations, and thus lead to changes in the plasmon resonance bands. The induced image charge in the substrate reduces the net effective restoring forces in both directions as the induced point dipole offsets the restoring forces of the nanoparticle [161]. Therefore, although the strength of the image dipole contribution is dependent on the dielectric functions of the substrate as well as the separation between the image and the nanoparticle [162], red shifts in both resonances are expected. An enlarged contact area is achieved as the particles become flatter when the film thickness (or nanoparticle size) grows [163], and this can lead to a more prominent substrate effect. In addition, as the size of the nanoparticles increases, the image charge in the substrate will be increased also [101]. Therefore, the red shifts in both resonances with increasing nanoparticle size shown in Fig. 3-11(b) and (c) could

be explained by the image charge effect of the Si substrate. A similar observation of red-shifts of the plasmon resonance bands as a result of growing silver islands has been reported also [98].

Fig. 3-11 Influence of structural properties on the three Lorentz oscillators: (a) Lorentz 1; (b) Lorentz 2; (c) Lorentz 3.

3.4.4 Conclusion

In summary, the split of surface plasmon resonance of self-assembled Au nanoparticles on Si substrate has been observed from the dielectric functions of the nanoparticles. The split is attributed to the inhomogeneous polarizations parallel and perpendicular to the substrate. Both parallel and perpendicular resonances are red-shifted when the nanoparticle size increases. The split and the red shifts in both resonances could be explained by the image charge effect of the Si substrate.

3.5 A comparative study of the dielectric function of Au nanoparticles self-assembled on Si substrate without and with a SiO₂ layer

The substrate effect on the manipulation of the SPR band is normally considered as an additional mirror image of the nanoparticle inside the substrate [51, 161]. The modified polarization in both parallel and perpendicular directions along the major particle axis can be calculated in order to estimate the strength of particle-substrate interaction [161, 164]. This image charge effect was reported to be dependent on the size of the nanoparticle, the separation between the nanoparticle and its image in the substrate, and the dielectric constant of the substrate [47, 51, 161, 164]. Previous discussion on the image charge effect is mainly focused on the varied polarization, and

its contribution to the interband transition of the metallic nanoparticles is still under debate. On the other hand, SiO₂ layer is generally considered as a barrier to isolate the influence from the substrate [102]. However, the isolation effect of a SiO₂ supporting layer as a function of its layer thickness has been less covered. To better understand these issues, we have examined the influence of SiO₂ supporting layers with various thicknesses on both the SPR band and the interband transitions based on the dielectric function study.

The effective dielectric functions of the self-assembled Au nanoparticles (Au NPs) on Si substrate and SiO₂ layers with different film thicknesses, which are well modeled by a Drude term and three (or four) Lorentz oscillators, have been determined from the SE measurement. Together with the structural properties of Au nanoparticles obtained from AFM measurement, influence of the Si substrate and SiO₂ layers on the Lorentz oscillators has been investigated.

3.5.1 Experiment

Direct-deposit self-assembly method is employed in the synthesis of Au nanoparticles. After gone through the standard chemical cleaning procedures, a SiO₂ layer with various thicknesses (3, 10 and 30 nm) was thermally grown on Si substrate with dry thermal oxidation. In addition, a Si substrate without a SiO₂ layer was prepared also by removing its native oxide with diluted HF solution. Then, all samples were transferred into a vacuum chamber with a base pressure of 5×10^{-6} mbar, equipped with an electron gun where the deposition was controlled with the use of

quartz crystal monitor. The thickness of the deposited Au film was 3 nm. After that, the Au film was heat-treated in nitrogen ambient by rapid thermal annealing at 550°C for 30 sec. An atomic force microscopy (AFM) with tapping mode was employed to investigate the structural properties of the Au nanoparticles formed on the substrates with and without a SiO₂ layer. The SE measurements were performed using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc). The ellipsometric angles (Ψ and Δ) were measured in the wavelength range of 300-1100 nm with the step of 5 nm at three different incident angles (i.e., 65°, 70° and 75°).

Fig. 3-12 shows the plane-view AFM images of the Au nanoparticles formed on the Si substrate and the SiO₂ supporting layers with different thicknesses. As shown in Fig. 3-12, the nanoparticle formed on the Si substrate has a larger size distribution as compared to those synthesized on the SiO₂ supporting layers; and the nanoparticles on the SiO₂ supporting layers also have a more perfect spherical shape. Based on previous study on the movement of the SPR band due to the structural modification of the Au nanoparticles [63], the size variation observed in Fig. 3-12 should have little influence on the variation of the SPR band, although larger size distribution may result in a larger band-width. Thus, we believed that the evolution of the SPR band is mainly due to the presence of the SiO₂ supporting layers.

Fig. 3-12 Plane-view AFM images of the Au nanoparticles self-assembled on Si substrates without and with a SiO₂ layer.

3.5.2 Modeling and results

Similar methodology in determining the dielectric function of Au nanoparticles has been employed in this section. However, owing to the presence of the SiO₂ supporting layer, a four-phase model (i.e., air/Au-nanoparticle layer/SiO₂ film/Si substrate) is used in this SE analysis. Note that for the case of Au NPs on Si substrate,

a three-phase model (i.e., air/Au-nanoparticle layer/Si substrate) should be used. The number (n) of Lorentz oscillators (Eq. 3.16) was determined to be 4 for Au NPs synthesized on Si substrate, where two oscillators are due to the interband transitions, while the other two Lorentz oscillators are required to describe the SPR band splitting. However, for Au nanoparticles formed on a thicker SiO₂ film (e.g., 10nm), the split of the SPR band cannot be observed, thus only three Lorentz oscillators are used to describe the typical SPR band and the two interband transitions. Spectral fittings to the SE measurements at various angles of incidence were carried out based on Eq. 3.16 and the SE models (i.e., either the three- or four-phase models). The spectral fittings to the measured Tan(Ψ) and Cos(Δ) (Ψ and Δ are the ellipsometric angles) are shown in Fig. 3-13 and 3-14, respectively. As shown in the figures, all spectral features can be fitted excellently for all the three angles (i.e., 65°, 70° and 75°) of incidence. The values of the model parameters and the effective thickness of the Au-nanoparticle layer yielded from the fittings are given in TABLE 3.2.

Fig. 3-13 Spectral fittings of $\tan(\Psi)$ at three different incident angles.

Fig. 3-14 Spectral fittings of $\text{Cos}(\Delta)$ at three different incident angles.

TABLE 3.2 Values of the parameters of the Lorentz oscillators and the effective thickness of the Au-nanoparticle layer yielded from the spectral fittings.

Process	Lorentz parameters	Au NPs on Si substrate	Au NPs on 3 nm SiO ₂	Au NPs on 10 nm SiO ₂	Au NPs on 30 nm SiO ₂
Image charge effect	A1 (eV ²)	20.60	0.18	N.A.	N.A.
	E1 (eV)	1.15	1.11	N.A.	N.A.
	Γ 1 (eV)	0.31	0.86	N.A.	N.A.
SPR band	A2 (eV ²)	2.98	3.05	0.52	0.69
	E2 (eV)	2.16	2.27	2.48	2.12
	Γ 2 (eV)	0.75	0.36	0.32	0.34
Interband transition 1	A3 (eV ²)	21.22	3.86	2.67	3.46
	E3 (eV)	3.28	3.28	3.06	3.26
	Γ 3 (eV)	0.80	1.26	1.25	1.80
Interband transition 2	A4 (eV ²)	12.21	1.21	1.12	1.27
	E4 (eV)	3.92	4.12	4.11	4.13
	Γ 4 (eV)	0.66	0.20	0.89	0.53
Drude term	E _p (eV)	8.8	8.8	8.8	8.8
	τ_D (fs)	0.034	0.016	0.005	0.006
	Thickness of Au NP layer (nm)	11.15	15.81	18.36	16.15

3.5.3 Substrate effect on the dielectric function

The effective dielectric functions of the Au nanoparticles on Si substrate and SiO₂ layers with different thicknesses are shown in Fig. 3-15. Both real and imaginary parts (ϵ_1 and ϵ_2 , respectively) of the dielectric functions are strongly dependent on the supporting substrate/SiO₂ layers. The magnitudes of ϵ_1 and ϵ_2 of the Au NP formed on Si substrate are much larger than that of the Au NPs on SiO₂ supporting layers, and the amplitudes of ϵ_1 and ϵ_2 are inversely proportional to the thickness of the SiO₂

supporting layer. In addition, some characteristic features of ε_1 become less pronounced and gradually vanished with a thicker SiO_2 supporting layer. A peak at ~ 2 eV can be identified in the ε_2 spectra for all samples, and it is not largely affected by the presence of a SiO_2 layer. However, the prominent peak at ~ 1 eV can only be observed from the Au NP formed on Si substrate.

Fig. 3-15 Effective dielectric function ε of the Au nanoparticles formed on different substrates: (a) real part, ε_1 and (b) imaginary part, ε_2 . For a better visibility, the insets show the ε_1 and ε_2 of the Au nanoparticles formed on the SiO_2 supporting layers with various thicknesses.

3.5.4 Image charge effect

It has been reported that Au NP formed on Si substrate shows splitting in the SPR band with a strong resonance peak located at ~ 1 eV besides the typical SPR band at ~ 2 eV in the imaginary part ϵ_2 due to the image charge effect. Fig. 3-16 shows the dielectric functions of the Lorentz oscillator (Lorentz oscillator 1) modeling the resonance peak located at ~ 1 eV which could be due to the image charge effect as a function of photon energy for the Au NPs deposited on either the Si substrate or the 3 nm SiO₂ supporting layer. As can be observed from Fig. 3-16, the oscillator has a similar pattern in the dielectric function for the two samples; however, the inclusion of the 3 nm SiO₂ supporting layer has greatly suppressed this resonance peak (the amplitude of the oscillator is reduced from 20.60 eV² for the Au NP on Si substrate to 0.18 eV² for the Au NP on the 3 nm SiO₂ supporting layer, as shown in TABLE 3.2). For Au NP on a thicker SiO₂ supporting layer (10 and 30 nm), this resonance peak disappears. The disappearance of the splitting in the SPR band of silver particles on thermally oxidized substrate has been reported [101]. As proposed by Wormeester *et al.*, the image charge contribution from the Si substrate is inversely proportional to the height of the nanoparticles above the substrate [47]. Therefore, a SiO₂ supporting layer enlarges the separation between the nanoparticles and the Si substrate, and thus reduces the image charge contribution. With a sufficiently thick SiO₂ supporting layer (e.g., 10 nm), the image charge effect is insignificant, leading to the disappearance of the splitting in the SPR band. On the other hand, it may be also possible that disappearance of the Lorentz oscillator is related to the formation of a continuous Au layer (i.e., the Au film has percolated and formed a continuous conductive pathway on

the SiO₂ layers). The growth of the Au NP formed on the SiO₂ layer is considered to be in Stranski-Krastanov mode, where a continuous film is followed by island growth. The image charge effect of the Au NP can be suppressed as a result of the formation of the percolated conductive Au layer on the SiO₂ layer.

Fig. 3-16 Dielectric function of Lorentz oscillator 1 for Au NPs on Si substrate. The inset shows the dielectric function for Au NP on the 3 nm SiO₂ supporting layer. The solid and dotted curves represent the Lorentz oscillator in the measurement range and beyond the measurement range, respectively.

Unlike the resonance peak located at ~ 1 eV, the typical SPR band (at ~ 2 eV) is relatively less influenced by the presence of the SiO_2 layer. The dielectric functions of the Lorentz oscillator (Lorentz oscillator 2) modeling the typical SPR band as a function of photon energy are shown in Fig. 3-17 for all the samples. The amplitude and peak position of the Lorentz oscillator show a random or weak dependence on the thickness of the SiO_2 supporting layer. Nevertheless, the movement of the peak position can be attributed to the change in the average size of the nanoparticles, i.e., an increase in the Au NP size will lead to a red-shift in the SPR peak [63].

Fig. 3-17 Dielectric function of Lorentz oscillator 2 for Au NPs on the Si substrate and on the SiO_2 supporting layers with various thicknesses.

The interband transition in the near-edge region (2-6 eV) of Au has been reported many times before [165, 166]. As shown in TABLE 3.2, the interband transitions of the Au nanoparticles can be modeled using two Lorentz oscillators: one oscillator (Lorentz oscillator 3) at ~ 3 eV corresponds to the transitions from the uppermost d state (band 5) to states in the s, p band (band 6) just above the Fermi level; while the other (Lorentz oscillator 4) at ~ 4 eV represents a composite structure involving transitions from the lower-lying d bands (band 3 and 4) to band 6 and transitions from s, p states in band 6 across the $L_6^- \rightarrow L_6^+$ gap to s, p -like states in band 7 [91, 165, 166]. Fig. 3-18 shows the dielectric functions of Lorentz oscillator 3 for all the samples. It can be concluded from TABLE 3.2 and Fig. 3-18 that the Si substrate greatly enhances the interband transition and the interband transition decreases with increasing the SiO₂ supporting layer thickness. Although the mechanism responsible for the substrate influence on the interband transition is still not clear, one may suspect that the influence could be related to the image charge effect from the Si substrate. In addition, the interband transitions could be also affected by the change in the structural properties of Au nanoparticles as the introduction of a SiO₂ supporting layer can significantly modify the structural morphologies of the Au nanoparticle.

Fig. 3-18 Dielectric function of Lorentz oscillator 3 for Au NPs on the Si substrate and on the SiO_2 supporting layers with various thicknesses.

3.5.5 Conclusion

In summary, a strong splitting in the SPR is observed for Au NP on Si substrate; however, it is greatly suppressed for the 3 nm SiO_2 layer and disappears for the 10 nm

and 30 nm SiO₂ layer. Besides, a SiO₂ layer also has a significant influence on the interband transitions of Au NP. These observations are discussed in terms of the image charge effect and/or the formation of percolated conductive Au layer on the SiO₂ layer.

3.6 Summary of this chapter

In this chapter, the optical properties of Au nanoparticles synthesized on Si substrate using direct-deposit self-assembly method have been determined based on spectroscopic ellipsometric (SE) measurement. The structural morphology of the nanoparticles can be controlled by various synthesis conditions, i.e., the size, shape and distribution of the Au nanoparticles are related to the thickness of the Au wetting layer and the temperature and duration of the annealing process. The effective dielectric function of the nanoparticles can be modeled with three Lorentz oscillators together with a Drude term, which represent the surface plasmon resonance (SPR) band, interband transitions and intraband transition (i.e., free conduction electrons absorption), respectively. The contribution from the Drude term is less significant as compared to those from the Lorentz oscillators. The Lorentz oscillator at 3.65 eV is due to the interband transitions, while the other two oscillators (at 1.26 and 2.22 eV) are attributed to the surface plasmon resonance.

In addition, the split of surface plasmon resonance of self-assembled Au nanoparticles on Si substrate is observed from the dielectric functions of the nanoparticles. The split plasmon resonances are modeled with two Lorentz oscillators

located at ~ 1 and ~ 2 eV, respectively, to represent the polarization in different directions. The positions of both Lorentz oscillators are red-shifted when the nanoparticle size increases. The red shifts in both resonances are explained by the image charge effect of the Si substrate. To further verify the substrate effect on the band transitions of Au nanoparticles, a comparative study of the dielectric function of Au nanoparticles self-assembled on Si substrate without and with a SiO₂ layer has been carried out. Based on the dielectric functions of Au nanoparticles on different substrates (Si substrate, SiO₂ layer with thickness of 3, 10 and 30 nm), a splitting in SPR band in the imaginary part of the dielectric function ϵ_2 is only observed on Si substrate. As it is greatly suppressed for the 3 nm SiO₂ layer and disappears for the 10 nm and 30 nm SiO₂ layers. In addition, the interband transitions of Au nanoparticles are affected by the presence of a SiO₂ layer. These observations can be explained in terms of the image charge effect and the formation of the percolated conductive Au layer on the SiO₂ layer.

Chapter 4 Absorbance of Au Nanoparticles on Silica Substrate

4.1 Introduction

The most fascinating phenomenon associated with metal nanoparticles, is the surface plasmon resonance (SPR), which is interpreted as the collective oscillation of the confined free electrons in the nanoparticle under external electromagnetic excitation. The SPR can be revealed as a strong optical absorption peak in the visible range of the spectrum [24, 167]. Therefore, absorbance measurement has been considered as an intuitive and powerful tool in investigating the optical properties of the metal nanoparticles. On the other hand, the bandwidth, the peak height, and the position of the absorbance maximum depend on the size, size distribution, shape, surface coverage, and surrounding environment of the given nanoparticles [24, 25, 167]. For example, the size effects on the optical properties of the Au nanoparticles have been reported extensively, through both experimental measurements and numerical simulations [24, 42, 43, 67]. Many applications based on SPR have been proposed, ranging from nano-scale optical and photonic devices [139, 168, 169] to sensors and biosensors [33, 170, 171].

In this chapter, the tunable surface plasmon resonance of Au nanoparticles self-assembled on fused silica substrate can be achieved by controlling the synthesis conditions and or changing the dielectric environments. The detailed mechanism has been elaborated in this chapter. Furthermore, by modeling the absorbance of Au nanoparticles using optical dispersion model (Lorentz-Drude) together with effective medium approximation (EMA), a comprehensive optical study on the size and dielectric medium dependence of the SPR band and interband transitions has been carried out.

4.2 Sample fabrication and experimental details

4.2.1 Sample fabrication

The fused silica wafer was purchased from Bonda Technology, with the thickness of $500 \pm 25 \mu\text{m}$, two sides polished. The fused silica wafer was cleaned by sequential sonication for 10 min at room temperature in each of the following liquids (1) acetone, (2) isopropyl alcohol, and (3) deionized water. Ultra-thin Au films with different thicknesses (from 3 to 10 nm) were deposited onto the fused silica wafer using electron-beam evaporation. The deposition was performed at a base pressure of 3×10^{-6} mbar and the wafer was held at room temperature during the Au film deposition. The deposition rate was controlled at about 0.1 Å/sec. The as-deposited samples without annealing treatment were used to study the effect of the thickness of Au ultra-thin film on the evolution of the SPR band. After the deposition, the samples

were annealed using RTA at different temperatures (from 100 to 400°C) for 30 sec in N₂ ambient. A SiO₂ capping layer with the thickness of 30 nm was deposited by plasma-enhanced chemical vapor deposition (PECVD) using the low temperature (50°C) recipe. The absorption measurements were performed using a UV/VIS/NIR spectrophotometer (PerkinElmer Lambda 950) in the wavelength range of 350-900 nm with the step of 1 nm. All measurements were conducted in room temperature environment.

4.2.2 AFM characterization

An atomic force microscopy (AFM) with tapping mode was used to characterize the structural properties of the Au nanoparticles. The AFM images of the Au nanoparticle films synthesized under different conditions are shown in Fig. 4-1, Fig. 4-2 and Fig. 4-3. The formation of Au nanoparticles can be explained by the stress relaxation, dispersion force and surface energy minimization during the annealing process [16]. The variation in structural features can be attributed to the Ostwald ripening and coalescence, which are the two major mechanisms of nanoparticle growth [172, 173]. Fig. 4-1 illustrates the structural changes of the Au nanoparticles as a result of increasing the average size of the Au nanoparticles. The thicker the Au film was deposited, the larger sizes of Au nanoparticles can be observed. For the as-deposited samples, the difference in thermal expansion coefficient between metal and the substrate leads to the formation of hillocks, as the elastic energy associated with film stress induced during the deposition process can be reduced by breaking the film into islands along the initial perturbation [59]. As the thickness of the deposited ultra-

thin film increases, the islands gradually turn into a continuous Au thin film, which is shown in Fig. 4-2. The effect of increasing post-annealing temperature on the structural properties of the nanoparticles can be observed from the AFM images shown in Fig. 4-3. The details of the effect can be revealed from the measurements of the surface roughness and the heights of the nanoparticles. As shown in Fig. 4-3, the low temperature annealing at 100 °C reduces both the surface roughness and the height of the nanoparticles as compared to the situation before the annealing; however, as the annealing temperature increases further (e.g., from 200 to 400°C), both the surface roughness and the height increase. The mechanism responsible for annealing temperature influence on the structural properties is still under study.

Fig. 4-1 AFM images of the Au-nanoparticle films of samples S1a, S1b, S1c and S1d

with the initial film thickness of 3, 5, 8 and 10 nm, respectively.

Fig. 4-2 Plain-view AFM images of the Au islands thin film with thickness of (a) 3 nm; (b) 5 nm; (c) 8 nm; and (d) 10 nm.

Fig. 4-3 AFM images and surface roughness/height measurements of the Au-nanoparticle films of the following samples: S3a, as-deposited (i.e., without annealing); S3b, annealed at 100°C; S3c, annealed at 200°C; S3d, annealed at 300°C; and S3e, annealed at 400°C. All the samples have the initial film thickness of 5 nm. The annealing duration is fixed at 30 s.

4.3 Structural influence on the surface plasmon resonance

In this section, the dependence of surface plasmon resonance (SPR) band on the structural properties has been revealed from the variation of the absorption maxima as a result of modified morphology of Au nanoparticles, including the thickness of the initial ultrathin Au film, the thickness of the Au islands thin film, annealing temperature and the deposition of SiO₂ capping layer.

4.3.1 Influence of the average size of the Au nanoparticles

Fig. 4-4 shows the absorbance spectra of the Au-nanoparticle films of Fig. 4-1. For each spectrum, the SPR wavelength is the wavelength at which the absorption maximum occurs [24, 167]. As shown in Fig. 4-4, the SPR wavelength is shifted from 529 to 565 nm, as the average size of the nanoparticles increases from 10.9 to 37.1 nm. Based on the Mie's calculation of the interaction between electromagnetic waves and small spheres, a series of multipole oscillations (dipole, quadrupole etc.) can be obtained [24]. For particles much smaller than the wavelength of light, the dipole approximation is widely used since only the dipole oscillation is concerned. However, for larger nanoparticles, they cannot be polarized homogeneously, thus higher-order-mode oscillations become important. These higher-order modes peak at lower energies, and therefore the overall plasmon resonance band red shifts with increasing particle size [24].

Fig. 4-4 Absorbance spectra of the Au-nanoparticle films of the samples shown in Fig. 4-1.

4.3.2 Influence of the thickness of Au islands thin film

The absorbance spectra of the Au islands thin films of Fig. 4-2 are presented in Fig. 4-5. As shown in Fig. 4-5, the SPR wavelength is red-shifted as a result of the increasing thickness of Au islands thin films. Fig. 4-6 shows the evolution of the SPR wavelength as a function of the thickness of the Au islands thin films. A quasi-linear relationship can be observed from Fig. 4-6, which implies that the SPR wavelength is determined by the film thickness. The red-shifts of the SPR wavelength can be attributed to the growing size of the Au islands, where higher-order mode resonance

oscillations have to be taken into account. Besides the size effect, the formation of a continuous Au thin film may play a determinate role in the evolution of the SPR wavelength. In general, when the islands thin film turns into a continuous layer, the phenomenon of localized SPR associated with Au nanoparticles will disappear. The absorption peak associated with SPR band will be gradually transformed into the free electron absorption band, which is normally located at longer wavelength region. This interpretation is consistent with the varied absorbance spectra observed at longer wavelength as a result of the increase in the film thickness (as shown in Fig. 4-5). On the other hand, the formation of a continuous Au thin film can be confirmed from the measurement of surface roughness, which is shown in Fig. 4-7. Owing to the growing size of the nanoparticles, the surface roughness increases proportionally. However, the reduction in the surface roughness for the 10 nm thick Au islands film should be observed together with a reduction in the nanoparticle size, which is not consistent with the results shown in Fig. 4-7. The smaller surface roughness associated with 10 nm thick Au island film may be due to the formation of a continuous film, where similar results have been reported by Hövel *et al.* [45]. In addition, the measured larger average size from 10 nm thick Au islands film can be related to the grain boundaries on top of the Au film, which differentiate the neighboring islands during the measurement, but does not separate the islands physically.

Fig. 4-5 Absorbance spectra of the Au islands thin films shown in Fig. 4-2.

Fig. 4-6 Evolution of the SPR wavelength as a function of the thickness of the Au islands thin films.

Fig. 4-7 Average size of the Au nanoparticles and surface roughness as a function of thickness of the Au islands thin films.

4.3.3 Influence of annealing temperature

Fig. 4-8 shows the absorbance spectra of the Au nanoparticles of Fig. 4-3. As shown in this figure, the SPR wavelength is red-shifted after the annealing at 100°C as compared to the initial Au film; however, a continuous blue-shift with increasing annealing temperature (from 200 to 400°C) is observed. Fig. 4-3 clearly shows that the increase in the annealing temperature leads to increases in both the surface roughness and the average height of the Au nanoparticles. Therefore, the blue-shifts of the SPR wavelength with the increase of the annealing temperature could be related to the increase in the surface roughness and/or the height. It was proposed that increase of

the surface roughness can result in a red-shift in the SPR wavelength based on the argument that a larger surface roughness means larger sizes of the nanoparticles (note that as mentioned early, the SPR wavelength red shifts with the increase of the particle size) [63]. However, this is contrary to the result of Fig. 4-3 and Fig. 4-8 which show that as the annealing temperature increases, the SPR wavelength blue shifts while the surface roughness increases. Therefore, the surface roughness effect should not be the dominant factor responsible for the blue shifts of the SPR wavelength. On the other hand, the blue shifts shown in Fig. 4-8 are larger than the particle size-related red shifts shown in Fig. 4-4. Here the blue shifts shown in Fig. 4-8 are attributed to the increase of the heights of the nanoparticles due to the increase of the annealing temperature. As pointed out by Jensen *et al.*, the height sensitivity factor (i.e., SPR wavelength shift due to 1 nm variation in nanoparticle height) is larger than the size sensitivity factor (i.e., SPR wavelength shift due to 1 nm variation in nanoparticle size) [113]. This means that a more pronounced shift of the SPR wavelength can be achieved by manipulating the height of nanoparticles. A red-shift of SPR wavelength can be obtained by reducing the height of nanoparticle, while increasing the height can result in a blue-shift [63, 113]. This is related to the height effect on the polarizations of the nanoparticles, although the detailed mechanisms are not known yet. Indeed, if the SPR wavelength is presented as a function of the average height of the nanoparticles based on the results of Fig. 4-3 and Fig. 4-8, a continuous blue-shift with increasing height is observed, as shown in Fig. 4-9.

Fig. 4-8 Absorbance spectra of the Au-nanoparticle films of the samples shown in Fig. 4-3.

Fig. 4-9 SPR wavelengths of the samples without and with the SiO_2 capping layer as a function of the average height of the Au nanoparticles.

4.3.4 Influence of the SiO₂ capping layer

Another important way to manipulate the SPR wavelength is to modify the dielectric medium around the nanoparticles [25, 167, 174]. After the deposition of a 30 nm SiO₂ capping layer onto the samples of Fig. 4-3 with PECVD, the Au nanoparticles are now embedded in a SiO₂ matrix, leading to a change in the dielectric environment of the Au nanoparticles. The low temperature (50°C) recipe was employed in order to minimize the temperature effect on the morphology of the nanoparticles during the SiO₂ deposition. Fig. 4-10 shows the changes of the absorption spectra of samples S2a and S2e of Fig. 4-3 after the deposition of the SiO₂ capping layer. The capping layer causes a large red shift in the SPR wavelength, although the spectrum shape is not changed significantly. A comparison between the SPR wavelengths with the capping layer and those without the capping layer for the samples of Fig. 4-3 are shown in Fig. 4-9. A large red shift in the SPR wavelength caused by the capping layer is observed in Fig. 4-9 for all the samples. The red shifts can be qualitatively explained in the following. Based on the Mie's theory, the extinction coefficient k_{ex} (measure of absorption and scattering strengths under collective excitations) can be calculated using the equation [20, 24]:

$$k_{ex} = \frac{18\pi NV\epsilon_h^{3/2}}{\lambda} \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_h]^2 + \epsilon_2(\omega)^2} \quad (4.1)$$

where λ is the wavelength of light, N is the density of the nanoparticles, V denotes the volume of the nanoparticle, ϵ_h is the dielectric function of the surrounding medium, and ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant of the metal,

which are frequency dependent. The frequency of the resonance condition occurs at $\epsilon_1 = -2\epsilon_h$ where denominator takes its minimum, if ϵ_2 is small [24]. The frequency of the resonance position can be calculated as [20, 174]

$$\omega_1 = \omega_p / \sqrt{1 + 2\epsilon_h} \quad (4.2)$$

where ω_p is the plasmon frequency of the bulk metal. Therefore, an increase in ϵ_h due to the introduction of the SiO₂ capping layer leads to a decrease in the resonance frequency ω_1 , and thus a red-shift in the SPR wavelength will be observed.

Fig. 4-10 Influence of the SiO₂ capping layer on the absorbance spectra for samples S3a (a) and S3e (b).

4.3.5 Conclusion

In summary, tunable surface plasmon resonance bands can be achieved by controlling the synthesis conditions and or changing the dielectric environments. The red-shift SPR wavelength is obtained by increasing the size of the Au nanoparticles, as higher-order mode oscillations have to be taken into account and thus the overall SPR band is red-shifted. In addition, the thickness of the Au islands thin film may play a significant role in the evolution of the SPR band. Either red-shifts or blue-shifts of the SPR wavelength could be observed depending on the annealing temperature, which can be explained in terms of the change of the height of the nanoparticles due to the annealing. The introduction of the SiO₂ capping layer causes a red shift in the SPR wavelength as a result of the change in the dielectric environment of the Au nanoparticles.

4.4 Modeling of absorbance of Au nanoparticles self-assembled on fused silica substrate

In this section, modeling of absorbance of Au nanoparticles self-assembled on the fused silica substrate has been performed based on the Beer-Lambert law [175], Lorentz-Drude model [102] and Maxwell-Garnett effective medium approximation (EMA) [153]. Three Lorentz oscillators were used to model the SPR band and the two interband transitions of the Au nanoparticles, respectively. It has been revealed that

both the SPR band and the two interband transitions are strongly dependent on the average size of the nanoparticles.

4.4.1 Modeling methodology

Based on our earlier study, the dielectric function of self-assembled Au nanoparticle can be represented by the Lorentz-Drude model, which is attributed to the bound and free electron transitions, respectively. The corresponding energy-dependent dielectric function is described as

$$\varepsilon(E) = \varepsilon_{\infty} + \sum_{i=1}^n \frac{A_i}{E_i^2 - E^2 - i\Gamma_i E} - \frac{E_p^2}{E^2 + i\hbar \frac{E}{\tau_D}} \quad (4.3)$$

where ε_{∞} is a background constant or an offset, A_i is the amplitude of the i^{th} oscillator with the unit of $(eV)^2$, E_i is the resonance energy with the unit of eV , Γ_i is the damping factor of the oscillator with the unit of eV , E_p is the unscreened plasma energy with the unit of eV and τ_D is electron relaxation time with unit of fs . The number of Lorentz oscillators (n) is three (i.e., $n = 3$), as two oscillators model the interband transitions and the other oscillator models the surface plasmon resonance. On the other hand, the Au nanoparticle layer is considered as a composite layer consisting of the Au nanoparticles and voids, whose effective dielectric function can be calculated using the Maxwell-Garnett effective medium approximation (EMA) [153]

$$\frac{\varepsilon_i - \varepsilon_{nc-Au}}{\varepsilon_i + 2\varepsilon_{nc-Au}} = v_i \frac{\varepsilon_{void} - \varepsilon_{nc-Au}}{\varepsilon_{void} + 2\varepsilon_{nc-Au}} \quad (4.4)$$

where v_i is the volume fraction of the voids, ε_{void} is equal to unity for the dielectric function of the voids, and ε_{nc-Au} is the dielectric function of the Au nanoparticles under collective excitations.

In Eq. (4.4), it is assumed that the volume fraction of the voids is smaller as compared to that of the Au nanoparticles (the voids are embedded in the Au layer). This assumption has been verified from the absorbance modeling, as the yielded volume fraction of the Au nanoparticles is much larger. In addition, as shown in Fig. 4-1, the AFM images reveal that there is a high density of nanoparticles with a surface coverage larger than 50%. Thus, the volume fraction of the Au nanoparticles is believed to be larger than that of the voids. Therefore, the Au nanoparticles should be considered as the host material, while the voids are treated as inclusions in the EMA.

Therefore, the dielectric function ε of the Au nanoparticle is first calculated with Eq. (4.3), and then the effective dielectric function ε_i of the Au nanoparticle layer can be obtained from the Maxwell-Garnett EMA calculation (i.e., Eq. (4.4)). The effective extinction coefficient k (imaginary part of the effective refractive index) of the Au nanoparticle layer can be obtained from,

$$k = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}} \quad (4.5)$$

where ε_1 and ε_2 are the real and imaginary part of the effective dielectric function ε_i of the Au nanoparticle layer, respectively. The effective absorption coefficient of the Au nanoparticle layer can be calculated with

$$\alpha = 4\pi k/\lambda \quad (4.6)$$

where λ is the wavelength of light. Therefore, the absorbance (A) of the Au nanoparticle layer as a function of wavelength can be determined using the derived Beer-Lambert equation [175]

$$A = \frac{\alpha d}{\ln 10} \quad (4.7)$$

where d is the effective thickness of the Au nanoparticle layer. The modeling of the absorbance can be performed by adjusting the parameters in Eq. (4.3) and the d value together with the volume fraction of the voids to minimize the mean-square error between the measured and calculated absorbance spectra. However, in this absorbance modeling, the reflection of Au nanoparticle layer has been ignored or considered to be insignificant. This assumption is based on the conclusion that the scattering effect is negligible for metal nanoparticles with size smaller than 30 nm [20, 107]. Fig. 4-11 shows the modeling of absorbance for the Au nanoparticle samples with different average sizes. All the spectral features can be fitted excellently. However, the modeling becomes deteriorated as the average size of nanoparticle increases to 34.9 nm. This is because the scattering effect becomes significant, and thus, the modeling is less accurate. The values of the Lorentz oscillator parameters yielded from the absorbance modeling are listed in TABLE 4.1.

Fig. 4-11 Modeling of absorbance of Au nanoparticle self-assembled on fused silica substrate with different average sizes. The insets show the plain-view AFM images of the samples.

TABLE 4.1 Values of the Lorentz oscillator parameters yielded from the absorbance modeling.

Process	Lorentz parameters	S1a, average size: 10.9 nm	S1b, average size: 21.0 nm	S1c, average size: 34.9 nm
SPR band	A_1 (eV ²)	11.69	9.47	2.75
	E₁ (eV)	2.24	2.14	2.11
	Γ_1 (eV)	0.30	0.38	0.48
Interband transition 1	A_2 (eV ²)	8.86	7.98	1.34
	E₂ (eV)	3.12	3.19	3.28
	Γ_2 (eV)	1.06	1.19	1.13
Interband transition 2	A_3 (eV ²)	5.90	4.91	4.16
	E₃ (eV)	3.91	4.01	4.37
	Γ_3 (eV)	0.93	0.79	1.60

4.4.2 Size effect

Fig. 4-12 shows the imaginary part of the three Lorentz oscillators as a function of photon energy for different samples. The evolution of the SPR band with the average size of the nanoparticle is shown in Fig. 4-12(a). The red-shift of the SPR band with the increase in the average size of the nanoparticles can be attributed to the inhomogeneous polarization of the nanoparticles, which enhances the higher-order-mode oscillations at lower energy [24]. While the amplitude of the SPR band decreases as the nanoparticle grows, it is possible that the suppressed collective effect is related to the reduced density of the nanoparticles. As shown in Fig. 4-12(b) and (c), the resonance energies of both interband transitions are blue-shifted with increasing particle size. The blue-shifts of the interband transitions can be explained in terms of the varying gap between the discrete energy levels [176]. Based on the quantum size

effects, a reduction in the gap can result in a shift of the first unoccupied discrete level away from the d bands [177, 178]. The narrower d band in larger nanoparticles can be due to the reduction in the discreteness of the electronic levels [177]. Therefore, an increase in the interband transition energy is expected.

Fig. 4-12 Imaginary part of the three Lorentz oscillators as a function of photon energy for different samples: (a) SPR band; (b) interband transition 1; and (c) interband transition 2.

Fig. 4-13(a) shows the dielectric function of the Au nanoparticles described by the Lorentz-Drude model extracted from the absorbance modeling. For comparison, the dielectric function of the Au nanoparticle synthesized on 30 nm SiO₂ layer thermally grown on Si substrate obtained from the spectroscopic ellipsometric (SE) analysis is shown in Fig. 4-13(b). For both cases, the self-assembled Au nanoparticles were synthesized using the same method (i.e., direct-deposit self-assembly) and under the same conditions. However, the structural properties of the nanoparticles synthesized on the two different substrates are similar, but not exactly the same, as revealed by AFM images shown in the insets of Fig. 4-13. In the SE analysis, Eq. (3.16) is employed to describe the dielectric responses of the Au nanoparticles, and the Maxwell-Garnett EMA is used to represent the effective dielectric function of the Au nanoparticle layer. The detailed methodology of determining the dielectric function of the Au nanoparticles using the SE analysis has been discussed in section 3.3.4. As shown in Fig. 4-13, the contribution of each Lorentz oscillator can be clearly identified in both cases. As can be observed in Fig. 4-13, the absorbance modeling and the SE analysis show similar features of the dielectric functions and similar behaviors (in particular, the resonance energies) of the Lorentz oscillators. However, the values of the dielectric functions yielded from the two methods are different (shown in Fig. 4-13). This could be due to the difference in the structural properties between the samples used in the absorbance and SE measurements.

Fig. 4-13 Imaginary part of the dielectric function of Au nanoparticles and the contribution of each Lorentz oscillator obtained from the absorbance modeling of the Au nanoparticle on fused silica substrate (a) and the SE analysis of the Au nanoparticle on 30 nm SiO_2 layer thermally grown on Si substrate (b). The insets show the plain-view AFM images of the samples.

4.4.3 A study on the influence of dielectric environment

As mentioned in section 4.3.4, the influence of SiO₂ capping layer on the SPR band has been quantitatively investigated based on the absorbance spectra measurement and Mie theory calculation. The relationship between the frequency of the resonance position and the dielectric function of the surrounding medium has been revealed in Eq. (4.2). Owing to the increase in the refractive index of dielectric medium (i.e., from air to SiO₂), a red-shifted SPR will be observed (as shown in Fig. 4-10). In this section, based on the modeling of absorbance spectra of Au-nanoparticle films with and without SiO₂ capping layer, the effect of dielectric environment on different band transitions, including both SPR band and interband transitions, has been studied.

4.4.3.1 Experimental details

Ultra-thin Au films with thickness of 5 nm were deposited onto the fused silica wafers using electron-beam evaporation. The rapid thermal annealing treatments were carried out at 400°C for 30 seconds in the N₂ ambient. The change of the dielectric environment can be achieved by deposition of a SiO₂ layer with thickness of 30 nm on top of the Au-nanoparticle films using plasma-enhanced chemical vapor deposition (PECVD). The absorption measurements were performed using a spectrophotometer (Perkin Elmer Lambda 950) in the wavelength of 300 – 900 nm with the step of 5 nm. The measurement was conducted in room temperature environment.

4.4.3.2 Modeling methodology

The detailed methodology in modeling the absorbance spectra has been presented in section 4.4.1, the Lorentz-Drude dispersion model together with Beer-Lambert law have been employed to determine the absorbance as a function of wavelength. However, due to the inclusion of the SiO₂ capping layer, the Au nanoparticles are now embedded in a SiO₂ matrix. Thus, the effective medium approximation (EMA) model has to be modified, in order to obtain the effective dielectric function of the composite layer. As the thickness of the SiO₂ capping layer (~ 30 nm) is much larger as compared to that of the Au nanoparticle film (i.e., ~ 5 nm), the Au nanoparticles are considered as inclusions, while the SiO₂ layer is treated as host material (i.e., Au nanoparticles embedded in the SiO₂ layer). Therefore, the effective dielectric function ϵ_i of the SiO₂ layer with Au nanoparticles embedded can be calculated using the Maxwell-Garnett EMA model given as

$$\frac{\epsilon_i - \epsilon_{SiO_2}}{\epsilon_i + 2\epsilon_{SiO_2}} = v_i \frac{\epsilon_{nc-au} - \epsilon_{SiO_2}}{\epsilon_{nc-au} + 2\epsilon_{SiO_2}} \quad (4.8)$$

where v_i is the volume fraction of the Au nanoparticles, ϵ_{SiO_2} is the dielectric function of the SiO₂, and ϵ_{nc-au} is the dielectric function of the Au nanoparticles. The choice that Au nanoparticles are embedded in the SiO₂ layer has been verified from the yielded volume fractions of Au nanoparticle, which is ~ 4.3 %.

Fig. 4-14 shows the modeling of absorbance spectra for the Au nanoparticle film without and with a SiO₂ capping layer. Excellent fitting can be achieved from both samples. All Lorentz oscillator parameters of the Au nanoparticles yielded from

the spectral fitting are listed in TABLE 4.2. The number of Lorentz oscillators is determined to be $n = 3$, as one oscillator describing the SPR band and two oscillators modeling the interband transitions.

Fig. 4-14 Modeling of absorbance of Au nanoparticle films (a) without SiO₂ capping layer; (b) with 30 nm SiO₂ capping layer.

TABLE 4.2 Values of the Lorentz oscillator parameters yielded from the fittings

Process	Lorentz parameters	Au nanoparticles film without SiO ₂ capping layer	Au nanoparticles film with SiO ₂ capping layer
SPR band	A ₁ (eV ²)	17.07	3.86
	E₁ (eV)	2.24	2.05
	Γ ₁ (eV)	0.45	0.48
Interband transition 1	A ₂ (eV ²)	8.82	0.45
	E₂ (eV)	3.07	3.04
	Γ ₂ (eV)	1.02	0.48
Interband transition 2	A ₃ (eV ²)	35.95	5.73
	E₃ (eV)	4.19	4.05
	Γ ₃ (eV)	1.94	2.10

4.4.3.3 Influence of the dielectric medium on the dielectric function

The imaginary part of the dielectric functions of the Au nanoparticles as a function of photon energy for samples without and with SiO₂ capping layer is shown in Fig. 4-15. A pronounced peak at ~ 2 eV can be identified from both samples, while two minor peaks at ~ 3 and ~ 4 eV are less prominent. All peak positions are consistent with the resonance energies of the Lorentz oscillators yielded from the spectral fitting (see TABLE 4.2), as well as our earlier results obtained from spectroscopic ellipsometric analysis (see Chapter 3).

The relative contributions of the three Lorentz oscillators to the imaginary part of the dielectric function ϵ_2 are also included in Fig. 4-15. The prominent peak at ~ 2 eV is associated with the surface plasmon resonance (SPR) of the Au nanoparticles. This collective oscillation of confined free electrons under external excitation is found

to be dependent on the size, shape and dielectric medium of the metallic nanoparticles [24]. In this case, the presence of the SiO₂ capping layer makes the position of SPR band red-shifted, although the shape of the SPR band stays relatively unchanged (see Fig. 4-15). In more details, the increase in the refractive index of the surrounding medium (from air of ~ 1.0 to SiO₂ of ~ 1.54 at 600 nm) of the nanoparticles reduces the frequency of the resonance band, which makes the SPR band red-shifted. However, the modified dielectric environment has little influence on the shape of the SPR band. In addition, the presence of the SiO₂ capping layer has greatly suppressed the intensity of the SPR band. On the other hand, for the interband transitions, the influence of the SiO₂ capping layer is limited. As shown in Fig. 4-15 and TABLE 4.2, both the position and shape of the two Lorentz oscillators remain unchanged, which suggests that the effect of dielectric environment on the interband transitions is insignificant. The less influenced interband transitions can be related to the rarely modified structural properties of the Au nanoparticles. As the deposition of the SiO₂ capping layer was carried out with PECVD using low temperature recipe (at $\sim 50^\circ\text{C}$), the structural properties of the Au nanoparticles are expected to stay the same. Thus, the merely unchanged nanoparticles in both size and shape keep the interband transitions less affected by the change in the dielectric environment. Furthermore, the intensity of the interband transitions has also been reduced due to the inclusion of the SiO₂ capping layer. Although further studies are required in order to determine the mechanism of the reduced intensity in both SPR band and interband transitions, we believe that the presence of the SiO₂ capping layer plays an important role here. It is

possible that the SiO₂ capping layer is acting as a barrier to isolate the Au nanoparticles from the influence of external electromagnetic field [102].

Fig. 4-15 Imaginary part of the dielectric function of Au nanoparticles and the contribution of each Lorentz oscillator obtained from the absorbance modeling of the Au nanoparticle films (a) without SiO₂ capping layer; (b) with 30 nm SiO₂ capping layer.

4.4.4 Conclusion

In conclusion, modeling of absorbance of Au nanoparticle self-assembled on fused silica substrate has been successfully carried out based on the Beer-Lambert law, Lorentz-Drude model and Maxwell-Garnett EMA. The contributions of the SPR band and the two interband transitions to the absorbance are well modeled with three Lorentz oscillators, respectively. The SPR and interband transitions are found to be largely affected by the structural properties of the Au nanoparticles. The dielectric function of the Au nanoparticles can be extracted from the absorbance modeling, and the features of the dielectric function yielded from the absorbance modeling are generally similar to that obtained from the SE analysis. Furthermore, the influence of the dielectric environment on both the SPR band and interband transitions has been investigated based on the modeling of absorbance spectra.

4.5 Summary of this chapter

In this chapter, the absorbance spectra of Au nanoparticles synthesized by deposition of an ultrathin Au film on fused silica substrate with electron-beam evaporation followed by rapid thermal annealing have been obtained from spectrophotometry measurement. The tunable surface plasmon resonance (SPR) band can be achieved by controlling the synthesis conditions, including the thickness of initial ultrathin Au film, the thickness of the ultrathin Au films, the annealing temperature, and deposition of a SiO₂ capping layer. Either blueshifts or redshifts of

the SPR wavelength could be observed depending on the actual size of the nanoparticle (in both horizontal and vertical dimensions) as well as an increase in the refractive index of the surrounding environment. Furthermore, the modeling of absorbance of the Au nanoparticles has been performed based on optical dispersion model (Lorentz-Drude), Maxwell-Garnett effective medium approximation (EMA), and Beer-Lambert law. The contributions of the SPR band and the two interband transitions to the absorbance are well modeled with three Lorentz oscillators, respectively. Influence of the structural properties on the SPR and interband transitions has been examined. In addition, the dielectric function of the Au nanoparticles has been extracted from the absorbance modeling, and it is found to be consistent with the result yield from the spectroscopic ellipsometric analysis. The effect of dielectric environment of the Au nanoparticles on the SPR band as well as interband transitions has also been determined.

Chapter 5 Optical Properties of Au

Nanoparticles Synthesized by Electrodeposition

5.1 Optical properties of Au nanoparticles

Besides the direct-deposit self-assembly method, electrodeposition is an alternative technique to synthesize metallic nanoparticles on conductive substrate [40, 74, 75]. As mentioned earlier, the particle coverage can be controlled by the applied voltage, while the mean particle diameter can be adjusted by deposition time, concentration and temperature of the solution [78, 79]. Owing to its low resistivity, a heavily-doped Si substrate can be used as an electrode in the electrodeposition process. The obtained nanoparticles are directly adhered to the Si substrate with good control of coverage and aggregation. For example, in the application of surface-enhanced Raman spectroscopy (SERS), the silicon substrate exhibits a strong and easily recognized phonon band at $\sim 520\text{ cm}^{-1}$, offering a useful internal reference or standard. In addition, unlike glass, there is no interfering fluorescence background from the silicon substrate.

In this chapter, the effective dielectric function of the Au nanoparticles obtained from the SE analysis shows that the SPR band is red-shifted due to a larger average

diameter of the nanoparticles, while the amplitudes of the two bands of interband transition are greatly reduced owing to the changes in the lattice structure.

5.1.1 Sample fabrication

The electrodeposition synthesis of Au nanoparticles was carried out by using a two-electrode cell [40]. A $2 \times 2 \text{ cm}^2$ platinum mesh was used as the anode. A piece of heavily-doped *p*-type silicon wafer (size: $\sim 2 \times 2 \text{ cm}^2$; resistivity: $0.001 \sim 0.006 \text{ ohm-cm}$), whose native oxide was removed by diluted HF solution, was used as the cathode. The distance between the two electrodes was fixed at 5 cm. All chemicals used in this experiment were of analytic grade and were used without further purification. The electrolytic solutions used in the synthesis of the Au nanoparticles consisted of $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$, and $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ HAuCl}_4$. A constant current was applied (via a Keithley 2400 source meter) to the electrolysis at room temperature.

5.1.2 SEM and EDX characterization

Scanning electron microscope (SEM) was used to characterize the structural properties of the Au nanoparticles formed on the silicon substrate. Energy-dispersive X-ray spectroscopy (EDX) analysis data of the Au nanoparticle film was recorded by an Oxford Link Isis installed at the SEM (JEOL, JSM-5600LV) system. Fig. 5-1(a) shows the representative plane-view SEM image of the Au nanoparticles. It is observed that there are many large particles (tens of nanometers in size) randomly distributed on the substrate surface. In addition, there are also many tiny nanoparticles

between the large particles. It is believed that the large particles were formed as a result of the aggregation of the tiny nanoparticles. The surface morphology, size and size distribution of these Au nanoparticles on the Si substrate are strongly dependent on the distance between the anode and cathode electrodes, as well as the duration of deposition. For example, the nanoparticles could be more monodisperse for a short duration of deposition [40]. The particle size distribution is shown in Fig. 5-1(b). A Gaussian profile was used to fit to the size distribution of the nanoparticles. It is found that the mean particle size and standard deviation are of 61.3 and 21.0 nm respectively. The EDX analysis shown in Fig. 5-2 confirms that the nanoparticles are indeed Au nanoparticles.

To fabricate Au nanoparticles with different morphology, electrodeposition experiments were performed with variable distance between two electrodes, and same applied current and deposition time. Fig. 5-3 shows the SEM images collected after electrodeposition for two different distances between two electrodes, 3 and 5 cm, respectively. It was observed that there was no much difference between the nanoparticles synthesized under different electrodes separation. This conclusion has been confirmed by a detailed analysis of the fabricated nanoparticles. The mean diameter of the Au nanoparticles obtained was 50.3 and 49.5 nm, with density of 4.43×10^9 and $4.52 \times 10^9 \text{ cm}^{-2}$, respectively. Thus, we believe that the effect of variable distance between two electrodes may not play an important role in determining the morphology of the Au nanoparticle, or its effect is limited in this range of separation. On the other hand, the duration of electrodeposition process is another critical

parameter, which can influence the distribution of Au nanoparticles. A detailed analysis will be presented in the following section.

Fig. 5-1(a) Plane-view SEM image of the Au nanoparticles electrochemically synthesized on a heavily-doped Si substrate. (b) Size distribution of the Au nanoparticles.

Fig. 5-2 EDX analysis of the sample of Au nanoparticles on Si substrate.

5.1.3 Methodology

The SE measurements were performed using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc). The ellipsometric angles (Ψ and Δ) were measured in the wavelength range of 300-1100 nm with a step of 5 nm at three different incident angles (i.e., 65°, 70° and 75°).

Fig. 5-3 Plain-view SEM images of the Au nanoparticles synthesized with different distance between two electrodes (a) 3 cm, and (b) 5 cm. Other processing parameters were kept on the same.

In this section, similar technique has been employed to determine the effective dielectric function of the Au nanoparticles synthesized on Si substrate using SE analysis. However, a few modifications have been made to the methodology: (1) the

number of Lorentz oscillator is determined to be three, as two oscillators model the interband transitions and the other oscillator models the surface plasmon resonance; (2) as shown in Fig. 5-1(a), the surface coverage of the Au nanoparticles is less than 30%, thus, the volume fraction of the voids should be larger than the volume of the Au nanoparticles. In fact, the volume fractions of Au nanoparticles and voids yielded from the SE spectral fitting are ~ 20 and $\sim 80\%$, respectively. Therefore, the Au nanoparticles should be treated as an inclusion in the EMA. Fig. 5-4 shows the spectral fittings to the experimental data at different incident angles. The Lorentz model parameters obtained from the fittings are listed in TABLE 5.1.

TABLE 5.1 Values of the Lorentz oscillator parameters of Eq. (3.16) yielded from the SE fittings.

	Lorentz 1	Lorentz 2	Lorentz 3
A_i (eV ²)	4.48	1.29	4.70
E_i (eV)	1.73	3.07	4.32
Γ_i (eV)	0.87	1.20	2.70

Fig. 5-4 Spectral fittings to the experimental ellipsometric data at different incident angles.

5.1.4 Results and discussions

Fig. 5-5 shows the effective dielectric function ϵ of the Au nanoparticles as a function of photon energy. A prominent peak at ~ 1.7 eV can be identified in the

imaginary part ε_2 , while two minor peaks at ~ 3.1 and ~ 4.2 eV can be barely observed. All these peak positions are consistent with the resonance energies of the Lorentz oscillators yielded from the spectral fittings (see TABLE 5.1). The real part ε_1 of the effective dielectric function is positive over the entire spectral range of the ellipsometric measurement, which is consistent with previous study on discrete metal islands [100, 102].

The contributions of the three Lorentz oscillators to the dielectric function are also shown in Fig. 5-5. The first oscillator with the resonance energy of ~ 1.7 eV is associated with the surface plasmon resonance (SPR) of the Au nanoparticles. In general, the SPR band is determined by the size and shape of the nanoparticles, as well as the surrounding dielectric medium. In our study, the SPR band is located at ~ 1.7 eV. This energy is lower than the commonly proposed characteristic band position of Au nanoparticles (~ 2.3 eV), which is associated with average particle size of 48 nm [42]. The red-shifted SPR band observed here can be explained by the large average diameter of the nanoparticles [63]. As mentioned earlier, it can be explained by the phase retardation and multipole contributions due to the unevenly distributed polarization over the nanoparticles [24, 42]. Image charge effect from Si substrate was also proposed for a red-shifted SPR band [47, 101]. However, the image charge effect might not play an important role here, because the Si substrate could have been oxidized during the electrodeposition process as a clear O signal was observed in the EDX analysis (see Fig. 5-2). It is also possible that the O signal is related to the NO_3^- in the solution. On the other hand, the Lorentz oscillators with the resonance energies of ~ 3.1 and ~ 4.2 eV are attributed to the interband transitions. Based on the early

discussion on the nonrelativistic band structure of Au, the oscillator of 3.1 eV corresponds to the transitions from the uppermost d states (band 5) to states in the s, p band (band 6) just above the Fermi level; while the oscillator of 4.2 eV represents a composite structure involving transitions from the lower-lying d bands (band 3 and 4) to band 6 and from s, p states in band 6 across the $L_6^- \rightarrow L_6^+$ gap to $s-, p$ -like states in band 7 [91, 165, 166]. These transitions would be affected by the structural properties of Au nanoparticles. As can be concluded from Fig. 5-5, the amplitudes of the two bands of interband transitions are very small. This should be related to the structures of the Au nanoparticles, but the detail is not known yet.

The refractive index n and the extinction coefficient k of the Au nanoparticles can be obtained from the calculation using the dielectric function shown in Fig. 5-5 with the following equations,

$$n = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}} \quad (5.1)$$

$$k = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}} \quad (5.2)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function, respectively. The refractive index and extinction coefficient of the Au nanoparticles as a function of photon energy obtained from the above calculation are shown in Fig. 5-6. As can be observed in the figure, the refractive index and extinction coefficient of the Au nanoparticles are very different from that of a Au film [155]. The difference is due to the large contribution of the surface plasmon resonance of the Au nanoparticles and

the significant changes in the interband transitions associated with the structures (e.g., size and shape) of the nanoparticles, as discussed above.

Fig. 5-5 Effective dielectric function of the Au nanoparticles: (a) real part ϵ_1 and (b) imaginary part ϵ_2 . The contributions of the three Lorentz oscillators are shown in the figure also.

Fig. 5-6 Refractive index n and extinction coefficient k of the Au nanoparticles. The optical constants of a Au film [155] are also shown in the figure for comparison.

5.1.5 Conclusion

In conclusion, Au nanoparticles have been synthesized on a heavily-doped Si substrate using electrodeposition approach. The morphology of the nanoparticles can

be manipulated by adjusting the distance between the anode and cathode of the electrochemical cell as well as the process time. The effective dielectric function of the Au nanoparticles can be modeled with three Lorentz oscillators together with a Drude term. A prominent peak in the imaginary part ϵ_2 , which is attributed to the surface plasmon resonance of the Au nanoparticles, is observed. Besides, two minor Lorentz bands due to the interband transitions are also identified.

5.2 Comparison of the optical properties of Au nanoparticles synthesized with the two techniques

The optical properties of Au nanoparticles synthesized by direct-deposit self-assembly and electrodeposition techniques have been quantitatively investigated in section 3.3 and 5.1, based on the ellipsometric analysis. In both cases, the effective dielectric functions of Au nanoparticles can be modeled by a Drude term and three Lorentz oscillators. However, the obtained results are rather different from each other. In this section, a comprehensive study on the comparison of the optical properties of Au nanoparticles synthesized by the two techniques will be presented.

5.2.1 Comparison of the structural properties

As shown in Fig. 3-2 (a) and 5-1 (a), the surface morphologies of nanoparticles fabricated using the two techniques are distinct from one another. The difference in the structural properties of the obtained nanoparticles can be explained in terms of the disparate types of nanoparticle growth. For Au nanoparticles formed on Si substrate using direct-deposit self-assembly method, the difference in thermal expansion coefficient between Au and Si leads to the formation of hillocks. As to reduce the elastic energy with film stress induced during the deposition process, the Au thin film breaks into islands along the initial perturbation [59]. In the situation before percolation occurs, the nanoparticles gain the thermal energy during the annealing treatment will go through nucleation and growth of holes by surface diffusion even coalesce into islands as a result of reducing the surface energy.

On the other hand, for the electrodeposition technique, the growth mechanism of nanoparticles is explained by the three-dimensional island growth (Volmer-Weber mode), including instantaneous and progressive nucleation [76, 77]. In the early stage of synthesis, instantaneous nucleation is the dominant one, which results in a narrow size distribution of nanoparticles [76-78]. As shown in Fig. 5-1(a), the formation of larger nanoparticles could be as a result of the aggregation of the tiny nanoparticles, and it could also be separate nucleation sites followed by growth [40]. For example, by increasing the duration of deposition (from 15 to 90 mins), both size and density of the nanoparticles are magnified (as shown in Fig. 5-7).

Fig. 5-7 Plain-view SEM images of the Au nanoparticles synthesized at different duration of deposition (a) 15 mins, and (b) 90 mins. Other processing parameters were kept on the same.

As mentioned in the previous sections, the strong dependence of the optical properties on the structural morphology of Au nanoparticles has been well discussed.

It is possible that the variation in the optical properties of the Au nanoparticles can be attributed to the two different growth modes of nanoparticles. In addition, the difference in the chemical state of the substrate may also lead to the variation in the optical properties. Based on the EDX analysis shown in section 5.1.2, the Si substrate may be oxidized during the electrodeposition process.

5.2.2 Comparison of the dielectric functions

Fig. 5-8 shows the dielectric functions of Au nanoparticles synthesized by the two techniques. The intensity of both real and imaginary parts of the dielectric function of the Au nanoparticles fabricated by direct-deposit self-assembly method is much larger as compared to those of nanoparticles obtained from electrodeposition technique. The much lower intensity of the dielectric function hinders the distinction of the separate features as shown in Fig. 5-5. As discussed in section 5.2.1, it is possible that the significant differences in the optical properties of Au nanoparticles synthesized by the two different techniques are related to the variation in the structural properties, as the nanoparticles are grown in different modes. However, the effect of size and shape of the nanoparticles on its optical properties is found to be important, but not as significant as shown in Fig. 5-8. Thus, the greatly restrained intensity of dielectric function of the Au nanoparticles obtained from electrodeposition process should be also related to other factors. As shown in Fig. 5-2, a pronounced O signal observed in the EDX analysis can be used to confirm the oxidation of the Si substrate during the electrodeposition process. Therefore, it is possible that the Au nanoparticles synthesized by this technique may be directly adhered to a thin SiO₂ layer instead of

Si substrate. As a result, the image charge effect from the Si substrate could be isolated by the thin SiO₂ barrier, as it cannot be identified in Fig. 5-5 and TABLE 5.1. Furthermore, the isolation effect of SiO₂ layer on the greatly reduced amplitude of the dielectric function of the Au nanoparticles has been discussed in section 3.5.3. On the other hand, the interparticle separation has been enlarged in the case of electrodeposition, which may weaken the near-field coupling between neighboring nanoparticles. Together with the suppressed image charge effect, they may attribute to the lower intensity of dielectric function of the nanoparticles synthesized by electrodeposition technique. In addition, due to the disappearance of the image charge effect or the weakened near-field coupling, one of the Lorentz oscillators becomes to model the interband transitions instead of splitting of the SPR band. After all, there are two Lorentz oscillators modeling the interband transitions and one oscillator representing the SPR band. Moreover, using single Lorentz oscillator modeling the interband transition can be equivalent to that modeling with two Lorentz oscillators, as the position of the single Lorentz oscillator is located between the two Lorentz oscillators.

Fig. 5-8 Effective dielectric functions of Au nanoparticles synthesized with two different techniques.

5.2.3 Conclusion

By comparing the optical properties of Au nanoparticle synthesized with the two techniques (i.e., direct-deposit self-assembly and electrodeposition), it is found that the prominent difference in the dielectric function are not only dependent on the variation

in the structural properties of the nanoparticles, but also related to the oxidized Si substrate during the electrodeposition process, which greatly suppresses the image charge effect of the Si substrate and weakens the near-field coupling between neighboring nanoparticles.

5.3 Summary of this chapter

The structural properties Au nanoparticles synthesized on a heavily-doped Si substrate using electrodeposition approach can be controlled by adjusting the distance between anode and cathode electrodes of the electrochemical cell, as well as the duration of process. The effective dielectric function can be modeled with three Lorentz oscillators and a Drude term. A prominent and two minor peaks in the imaginary part ϵ_2 , which are attributed to the surface plasmon resonance and interband transitions of the Au nanoparticles, are observed.

In addition, a detailed comparison of the optical properties of Au nanoparticles synthesized by the two approaches (i.e., direct-deposit self-assembly and electrodeposition techniques) has been presented. It reveals that the obtained optical properties are different, which can be attributed to the unlike surface chemical states and structural morphologies obtained from these two synthesis methods. In more details, a split of SPR band can only be observed in the samples fabricated by direct-deposit self-assembly technique, where various factors (i.e., imperfectly spherical shape, inter-particle interaction, image charge effect, and etc.) can influence its

emergence. In addition, the common proposed characteristic SPR band can be identified in both cases, and it is found to be closely related to size of the nanoparticles. Interband transitions can be represented by either a single Lorentz oscillator or two oscillators, which constitute the important contribution to the dielectric function.

Chapter 6 Conclusion and Future Work

6.1 Conclusion

The significance of the study of optical properties of metallic nanoparticles is not only in the understanding of fundamental physics of the nanoparticles, but also in the various potential applications utilizing metallic nanoparticles. Over the past decades, experimental determination and numerical simulation of the optical properties of metal nanoparticles has been developed tremendously, driven by the distinct differences as compared to their bulk counterparts. However, few studies on the experimental determination of the dielectric functions of metal nanoparticles have been reported. In addition, the emergence of multiple SPR band can be attributed to several factors: anisotropic shape of nanoparticles, near-field coupling between neighboring nanoparticles, image charge effect of the substrate and etc. Nevertheless, the dielectric function study on the effects of near-field coupling and image charge effect is so far limited. In this thesis, the synthesis of Au nanoparticles has been successfully demonstrated using direct-deposition self-assembly method (deposition of an ultrathin metal layer followed by rapid thermal annealing) and electrodeposition technique, which have the advantage of being able to control the size, size distribution, and shape of the nanoparticles by adjusting the synthesis conditions. The optical properties of the Au nanoparticles have been investigated in detail based on the

spectroscopic ellipsometric analysis and absorbance measurement. The results presented in this thesis enrich our understanding of the optical properties of the Au nanoparticles (in particular, surface plasmon resonance). This section briefly summarizes the overall work presented in this thesis.

6.1.1 Optical properties of Au nanoparticles synthesized with direct-deposit self-assembly method

The optical properties of Au nanoparticles on Si substrate synthesized by direct-deposit self-assembly method have been determined using spectroscopic ellipsometric analysis. The optical dispersion model (Lorentz-Drude) together with effective medium approximation (Maxwell-Garnett EMA) has been employed to represent the dielectric function of the Au nanoparticles. It has shown that two SPR band located at ~ 1 and ~ 2 eV and interband transition band at ~ 3.6 eV can be clearly identified in the imaginary part of the dielectric function ϵ_2 and the extinction coefficient k . The emergence of the two plasmon resonance peaks can be due to the influence of various factors: lateral near-field interaction between adjacent nanoparticles, image charge effect of the Si substrate, distribution of nanoparticle sizes, shape of nanoparticles, and etc. To better understand the mechanism of the split of the SPR band, a study of the dielectric function of the self-assembled Au nanoparticles has been carried out. The emergence of two SPR bands represented by two Lorentz oscillators is due to the inhomogeneous polarizations parallel and perpendicular to the substrate. By examining the variation of the two SPR band as a result of increased nanoparticle sizes, the mechanism of the split of SPR band can be explained in terms of the image charge

effect of the Si substrate. Furthermore, a comparative study of the dielectric function of Au nanoparticles self-assembled on Si substrate without and with a SiO₂ layer has been carried out. The splitting in the SPR band is greatly suppressed for the 3 nm SiO₂ layer and disappears for the 10 nm and 30 nm SiO₂ layers. Therefore, the image charge effect is believed to be the major contribution to the splitting of SPR band. On the other hand, the SiO₂ layer underneath the Au nanoparticles is found to have significant influence on the interband transitions of Au nanoparticle, which has been discussed in terms of the image charge effect and the formation of the percolation conductive Au film on the SiO₂ layer.

6.1.2 Absorbance measurement and modeling

Tunable SPR band of Au nanoparticles self-assembled on fused silica substrate has been observed from spectrophotometry measurement. The movement of the SPR wavelength can be obtained by controlling the synthesis conditions and/or changing the dielectric environment. Either redshifts or blueshifts of the SPR band is dependent on the actual size, size distribution and refractive index of the surrounding environment of the nanoparticles. In addition, modeling of the absorbance of Au nanoparticles has been achieved based on Beer-Lambert Law, Lorentz-Drude dispersion function and Maxwell-Garnett effective medium approximation. The contributions of the SPR band and the two interband transitions to the absorbance are well modeled with three Lorentz oscillators, respectively. Furthermore, influence of the structural properties on the SPR and interband transitions has been examined. In addition, the dielectric function of the Au nanoparticles has been obtained from the

absorbance modeling, and it is found to be consistent with the result yielded from the spectroscopic ellipsometric analysis. At last, the influence of dielectric medium on the SPR band as well as interband transitions has been investigated based on the modeling of the absorbance of Au nanoparticles.

6.1.3 Optical properties of Au nanoparticles synthesized by electrodeposition technique

The Au nanoparticles deposited on a heavily-doped Si substrate can be synthesized through direct electroreduction of bulk AuCl_4^- ions, whose morphology can be manipulated by adjusting the distance between the anode and cathode electrodes of the electrochemical cell as well as the process time. The effective dielectric function of the Au nanoparticles can be modeled with three Lorentz oscillators together with a Drude term. However, the splitting of SPR band cannot be observed from Au nanoparticles synthesized electrochemically, only the characteristic SPR located at ~ 2 eV has been identified, which can be related to the oxidized Si substrate during the electrodeposition process. In addition, two greatly suppressed interband transitions located at ~ 3.1 and ~ 4.2 eV could be due to the modified lattice structures of the nanoparticles. Furthermore, a detailed comparison of the optical properties of Au nanoparticles synthesized by the two techniques (i.e., direct-deposit self-assembly and electrodeposition) has been presented.

6.2 Future Work

The work presented in this thesis has added more understanding about the optical properties of the Au nanoparticles, and opens up new possibilities for their applications in nanophotonics, nano-optics, sensors and biosensors. In more details, with better understanding about the optical properties of Au nanoparticles, especially the SPR properties, we can facilitate the development of plasmonic waveguide, which is considered to be the prominent candidate for the next generation on-chip optical interconnect due to the down scaling demand on the device structure. It has been demonstrated that this plasmon waveguide can overcome the issues like size limitation and bend loss of traditional waveguide. In addition, the study of the structural influence (e.g, size, shape, dielectric medium, interparticle space, and SiO₂ capping layer on the substrate) on the SPR can be used to manipulate the position of SPR band in the ultraviolet and visible regime, which has been employed to detect biopolymers such DNA or proteins. Furthermore, the investigation of significant increase in the absorption can be extended to the light absorption in photovoltaic cells by depositing Au nanoparticles on the solar cell surface. To make the research more complete, the following research could be done.

6.2.1 Synthesis of Au nanoparticles using other techniques

Besides the direct-deposit self-assembly and electrodeposition methods, other techniques such as solution-based (i.e., chemical colloidal), co-sputtering and electron-beam lithography can also be used to prepare the Au nanoparticles. Although

both techniques provide good control in size, size distribution, shape and reproducibility, in particular, the direct-deposit self-assembly technique can be compatible with mainstream CMOS technology, other techniques have their own advantages. Some unique properties could be exclusively associated with a particular synthesis technique. The future work should include the synthesis of Au nanoparticles using techniques other than the two employed in this thesis. The structural and optical properties of samples synthesized by different techniques can be compared, and the results can enrich the understanding about the relationship between the synthesis technique and the structural and optical properties.

6.2.2 Simulation of optical properties using other theoretical models

In this thesis, the optical properties (i.e., dielectric function) of the Au nanoparticles have been obtained from spectroscopic ellipsometric analysis based on the optical dispersion function (Lorentz-Drude model) and effective medium approximation (Maxwell-Garnett EMA). This experimental determination provides an important approach to understand the fundamental physics of metal nanoparticles. Nevertheless, to complete the study on the optical properties, theoretical simulations are needed, not only to verify the accuracy of the experimental determination, but also to investigate the optical properties from another point of view. Recently, a number of theoretical models have been proposed, including Mie theory, discrete dipole approximation (DDA), finite-difference time-domain (FDTD) and etc. The first two methods have been discussed in section 2.4.2, which will not be repeated here. FDTD method is another popular computational electrodynamics modeling technique, which

can cover a wide frequency range. In particular, the FDTD techniques have emerged as primary means to computationally model many scientific and engineering problems dealing with electromagnetic wave interactions with material structures, which is widely used to solve the time-dependent Maxwell's equations. Thus, the employment of these theoretical models in studying the optical properties of Au nanoparticles can lead to the proper understanding about fundamental physics of metallic nanoparticles.

6.2.3 Development of plasmonic waveguide

One of the promising applications using SPR is the plasmon waveguide, which uses a closely-packed array of metallic nanoparticles to guide an electromagnetic wave in the dimension much smaller than the wavelength of light. Noble metal nanoparticles with size smaller than ~ 100 nm exhibit fascinating remarkable optical phenomenon since the localized surface plasmon resonance can be excited by light, and the resulting huge enhancement of the local electromagnetic field can be used in various applications. The strong interaction between individual metal nanoparticles with light can be used to build waveguides where the energy transfer can be realized between nanoparticles. The dipole field resulting from a plasmon oscillation in a metal nanoparticle can induce a plasmon oscillation in a closely-spaced neighboring particle due to near-field electrodynamics interaction. When the separation between neighboring nanoparticles is only a few tens of nanometers, the electric dipole interaction is dominated by the near-field term, which is strongly dependent on the separation. The interaction strength and the relative phase of the electric field in neighboring particles both depend on polarization and frequency. This interaction

leads to coherent modes with a wave vector k along the nanoparticle array. In the future work, to realize practical nanoscale optical interconnects based on near-field coupling between surface plasmon-polariton modes of neighboring particles, some critical issues have to be addressed: (1) a good understanding on the processes and physics of the near-field coupling and the energy transfer; (2) suitable metal nanostructures that maximize coupling efficiency, lowest energy loss and compatible with Si technology are required.

6.2.4 Development of solar cell based on Au nanoparticles

The photovoltaic industry has achieved extraordinary annual growth rate of over 30% over the last few years, driven by the improvement in the efficiency and demand for renewable energy resource. Recently, the demonstration of absorption and emission enhancement from Si solar cells by making use of nano-scale properties of metals has been reported [81, 179, 180]. Near the condition of surface plasmon resonance, light may interact with the particle over a cross-sectional area larger than the geometric cross section of the particle as the polarizability of the particle becomes very high in frequency range [81, 181]. In addition, tuning of surface plasmons can be realized by a range of ways, including changing the size, shape, particle material, and refractive index of the surrounding medium. As a result, the desired spectral range can optimize the local dielectric environment. On the other hand, scattering and absorption of metal nanoparticles depend on the actual size. Nanoparticles whose sizes are much smaller than the wavelength of light, the extinction are dominated by the absorption in the metal particles, which is dissipated through heat. However, for nanoparticles with

larger size, extinction is dominated by scattering, and this property can be used for application of light trapping in solar cells. Beyond certain limit, this scattering effect can be deteriorated by increasing the particle size, due to the increased retardation effects and higher order multipole excitation modes [24, 81]. Therefore, more sophisticated fabrication techniques are needed to optimize both high efficiency scattering and plasmon resonance. The future work should also include the understanding the effects of high efficiency scattering and plasmon resonance on the improvement of solar cell efficiency.

List of Publications

Journals:

- [1] **S. Zhu**, T. P. Chen, Z. H. Cen, Y. C. Liu, and Y. Liu, "Collective Excitations and Dielectric Function of Self-Assembled Gold Nanoparticles on a Silicon Substrate," *Electrochemical and Solid State Letters*, vol. 13, pp. K39-K42, 2010.
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- [5] **S. Zhu**, T. P. Chen, Y. C. Liu, Y. Liu, and S. F. Yu, "Influence of SiO₂ Layer on the Dielectric Function of Gold Nanoparticles on Si Substrate," *Electrochemical and Solid-State Letters*, vol. 15, pp. K5-K9, 2012.
- [6] **S. Zhu**, T. P. Chen, Y. C. Liu, Y. Liu, and S. Fung, "A quantitative modeling of the contributions of localized surface plasmon resonance and interband

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- [1] **S. Zhu**, T. P. Chen, Y. C. Liu, "A study of surface plasmon resonance of gold islands films on fused silica substrate with the film thickness", *International Conference on Materials for Advanced Technologies 2009*, June 26 – July 1, 2011, Singapore.

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