Nanostructured surfaces for surface enhanced infrared absorption spectroscopy

Zhiqi Yao
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Nanostructured surfaces for surface enhanced infrared absorption spectroscopy

by

Zhiqi Yao

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Andrew Hillier, Major Professor
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Javier Vela
Meng Lu
Yue Wu

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

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<th>Abbreviation</th>
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<tr>
<td>SEIRA</td>
<td>Surface Enhanced Infrared Absorption</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface Plasmon Polariton</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized Surface Plasmon Resonance</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>LIL</td>
<td>Laser Interference Lithography</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>PED</td>
<td>Pulsed Electrodeposition</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>HDT</td>
<td>1-Hexadecanethiol</td>
</tr>
<tr>
<td>IRRAS</td>
<td>Infrared Reflection Absorption Spectroscopy</td>
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ABSTRACT

Surface enhanced infrared absorption (SEIRA) spectroscopy is a powerful analytical technique for enhancing vibrational signals of adsorbed analytes. This technique can be applied in many fields such as electrochemical dynamics, surface photochemistry and sensors in bio-spectroscopy. Metallic nanostructure surfaces are normally used as SEIRA active substrates. However, the controllability and reproducibility of most SEIRA active substrates are still on a poor level.

Chapter 1 provides the background of SEIRA spectroscopy. The discovery and development of surface enhanced spectroscopy is introduced, also including the development of SEIRA active substrates over past few decades. The enhancement mechanism of SEIRA is explained in terms of both electromagnetic and chemical mechanisms. Surface plasmon resonance (SPR) is also introduced here as both localized surface plasmon resonance (LSPR) and propagating SPR can be combined with SEIRA to improve its performance. The history, definitions and theory of SPR are discussed in detail. Also, the main platforms for exciting propagating SPR are illustrated.

Chapter 2 provides a novel method to prepare gradient metal films with sputter coating for applying as SEIRA active substrates. The gradient metal films have a changing morphology as a function of position along the substrate surface. With the increased film thickness, the surface morphology changed from isolated metal islands to interconnected metal clusters and became a continuous metal film finally. A maximum in SEIRA activity was observed at conditions where
the metal islands begin to merge into a continuous metal film, known as the percolation threshold. This location was able to be monitored with optical transmission spectroscopy and conductivity measurements. In the UV-Vis and near-IR transmission spectrum, the tail of the LSPR band would extended into near infrared region at the percolation threshold location. And this location is the area where the film changed from conductive to insulative. This fabrication technique provides a reproducible method to fabricate metal island SEIRA active substrates and the ability to understand the role of particle size and spacing on SEIRA activity.

Chapter 3 demonstrates the synthesis and immobilization of gold nanoparticles (AuNPs) on indium tin oxide (ITO) substrates by pulsed electrodeposition (PED) technique. The prepared substrates were used as SEIRA active substrates. We demonstrated that the size, density and gaps between adjacent AuNPs were able to be well controlled by adjusting the overpotential and deposition cycles using the PED technique. The maximum SEIRA enhancement could be achieved near percolation threshold of metal nanoparticle film and is able to be monitored via optical transmission spectroscopy. This protocol provides a cost effective and controllable approach to fabricate reproducible, highly sensitive and stable SEIRA active substrates.

Chapter 4 illustrates propagating SPR response is able to be tuned in infrared region via two grating platforms. One is compressive grating platform produced by fabricating a metallic grating on a flexible, PDMS substrate. The other is a spontaneously chirped Au/PDMS grating platform, fabricated through ordered buckling structures of thin stiff film on an elastomeric substrate with mechanical deformation. By mechanically compressing the substrates, the grating pitch could be controlled on both tunable grating platforms, which resulted in shifting of the SPR peak in the infrared spectra. The results demonstrate that these two substrates provide a highly tunable and flexible platform for controlling the SPR response. They are able to combine with
SEIRA spectroscopy to enhance vibrational signals of analytes adsorbed on the grating platforms.

This work aims to show the fabrication of novel SEIRA active substrates that can be applied in SEIRA technique to improve its performance. SEIRA activity is strongly correlated with the morphology of metal nanostructures on the substrate. The gradient metal film, AuNP substrates synthesized by PED and tunable grating platforms all show good tunability and reproducibility of their morphology. They can provide an especially controllable avenue for fabricating SEIRA active substrates and have great potential to be applied in routine SEIRA applications in the future.
CHAPTER 1

INTRODUCTION

1.1 Surface Enhanced Infrared Spectroscopy Development in Scientific Research

Surface enhanced spectroscopy is a practical analytical approach for sensitively and selectively detecting molecules adsorbed on noble metal nanostructured substrates. It has attracted considerable attention since 1970s. The most prominent technique in this area was surface enhanced Raman scattering (SERS). Fleischmann, M first observed SERS phenomenon in 1973 from a rough silver substrate prepared by electrochemical deposition with pyridine adsorbed on it.\(^1\) This work opened the field of surface enhanced spectroscopy. Since then, this technique has grown dramatically, over 5000 articles, 100 review papers and several books about SERS have appeared in scientific research. The enhancement factor of SERS can be as much as \(10^{10}\) to \(10^{11}\),\(^2\) which makes SERS more powerful than normal Raman spectroscopy and is able to detect single molecules adsorbed on a surface. This powerful analytical technique showed large impacts on various fields such as life sciences,\(^3\)-\(^6\) food science,\(^7\)-\(^9\) biology applications,\(^10\)-\(^12\) environment analysis,\(^13\)-\(^15\) sensors application\(^16\)-\(^19\) and material sciences.\(^20\)

Surface enhance infrared absorption (SEIRA) spectroscopy is another important aspect in surface enhanced spectroscopy. It has a similar origin to SERS, but occurs with a one photon process instead of two photon process.\(^21,22\) As SERS relies on inelastic scattering, also known as Raman scattering, of monochromatic light, one photon is absorbed and another photon is emitted simultaneously. But for SEIRA spectroscopy, it mainly explores that number of infrared photons absorbed by the molecule, only photon absorption process occurred during the measurement.

SEIRA was first observed by A. Hartstein etc. through attenuated total reflectance (ATR) geometry with adsorbing 4-nitrobenzoic acid on rough Ag islands in 1980.\(^23\) Since the discovery,
this phenomenon was observed in the external reflection and transmission geometries. However, SEIRA achieved much less attention than SERS as the enhancement factor of SEIRA is much lower. But SEIRA still has some unique advantages and is able to play an important role in many fields. In SERS, the Raman active molecules are the molecules that causes a change in polarizability. But in SEIRA spectroscopy, the IR active molecules are associated with the dipole moment change of the molecules. In addition, it is important to mention that Compared with SERS, SEIRA spectroscopy has different band selection rules in which only the vibrational modes give dipole change perpendicular to the metal surface are SEIRA active. Therefore, SEIRA can provide a complementary vibrational analytical technique of analyte molecules. In addition, the cost of instrumentation of SERS is high, but SEIRA spectroscopy is relatively cost effective. There has been a growing interest to study this phenomenon since 1990s and SEIRA has been developed into a promising analytical technique.

The enhancement factors in SEIRA can reach $10^3$, much less compared with SERS technique. In the SERS and SEIRA technique, the enhanced signal in spectra is due to the interaction between molecule and the enhanced electric field on the surface. The coupling between molecule and electric field could be described in classical electromagnetic theory. The description of the process is semi-classical and the interaction is known as the semi-classical theory of quantum transition. The probability of the absorption is proportional to the $E^2$. Since SERS is a two photon process, the signal magnitude of the molecule is proportional to $E^4$. As SEIRA is a one photon process, the absorption intensity is only proportional to $E^2$ which results a lower enhancement than SERS.

Even though SEIRA spectroscopy gives a smaller enhancement, it can still be applied for detection of monolayer films. A wide range of applications have already taken advantage of this
powerful analytical technique. SEIRA has been developed for monitoring surface photochemistry and catalytic reactions,\textsuperscript{30-32} characterizing monolayers on metal nanostructured substrates,\textsuperscript{33,34} studying electrochemical dynamics\textsuperscript{35-37} and applying as sensors in bio-spectroscopy.\textsuperscript{12,38}

1.2 Preparation of SEIRA Active Substrates

Coinage metals, such as Ag and Au, are the most widely employed metals for observing SEIRA effect as they show largest intensity enhancement.\textsuperscript{27,30} A few other metals have also been explored for SEIRA active substrates, including Pt\textsuperscript{39}, Sn\textsuperscript{40}, Cu\textsuperscript{41}, Pb\textsuperscript{42}, Fe\textsuperscript{43} and Ni\textsuperscript{44}. The supporting substrates commonly include IR transparent materials (CaF\textsubscript{2}, Si, MgO, BaF\textsubscript{2}, ZnS, KBr, Ge, sapphire) and non-transparent materials such as glassy carbon, metals and glass. Notably, low reflectivity materials are optically favorable in SEIRA measurements since their band shape in the corresponding IR spectrum has a reduced distortion. With high reflectivity materials, the bands appeared in the spectra would become slightly asymmetric since the rapid change of refractive index of the sample across the bands.

The SEIRA enhancement factor is strongly related to the characteristics of the metal morphology, including the size, coverage and shape of the metal nanostructures. Metal island films are the most widely used substrate in the SEIRA measurements. Normally, metal island film that serve as SEIRA active substrates should be discontinuous and consist of densely crowded small metal particles. The size of the islands needs to be smaller than the wavelength of light in the region of interest.\textsuperscript{24} SEIRA-active metal island substrates have most frequently been prepared on a supporting substrate by physical vapor deposition,\textsuperscript{45,46} electrochemical deposition,\textsuperscript{47} or electroless deposition.\textsuperscript{48,49} The enhancement factors are typically similar using these preparation methods, usually range from 10-1000 times,\textsuperscript{49} depend on the corresponding morphology of metal
island films. For largest enhancements, the morphology of the metal nanostructures needs to be densely crowded, but not in contact with each other.\textsuperscript{21}

Even though it is well known that controlling the metal morphology for SEIRA active substrates is necessary to achieve maximum enhancements, the controllability and reproducibility of SEIRA active substrates remains a challenge.\textsuperscript{48} For example, in the case of physical vapor deposition, many factors can affect the size, density and shape of the metal islands, including the deposition thickness, temperature of the substrate, and the deposition rate.\textsuperscript{45} Table 1 indicates the optimum reported metal thickness for maximum SEIRA enhancement factor from the chemicals adsorbed on metal island films. The optimum thickness of SEIRA active metal film varies from study to study, which makes the result hard to compare and reproduce.\textsuperscript{50}
Table 1.1 Optimum metal thickness for maximum SEIRA enhancement in literatures

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical adsorbed</th>
<th>Metal deposition method</th>
<th>Optimum metal thickness</th>
<th>Enhancement factor</th>
</tr>
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<tbody>
<tr>
<td>Ag$^{28}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Thermal evaporation</td>
<td>8nm</td>
<td>70</td>
</tr>
<tr>
<td>Ag$^{23}$</td>
<td>4-nitrobenzoic acid</td>
<td>Vacuum evaporation</td>
<td>6nm</td>
<td>20</td>
</tr>
<tr>
<td>Ag$^{24}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Thermal evaporation</td>
<td>5nm</td>
<td>50</td>
</tr>
<tr>
<td>Ag$^{45}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Thermal evaporation</td>
<td>20nm</td>
<td>1000</td>
</tr>
<tr>
<td>Ag$^{46}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Thermal evaporation</td>
<td>10nm</td>
<td>500-600</td>
</tr>
<tr>
<td>Au$^{49}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Electroless deposition</td>
<td>20nm</td>
<td>500</td>
</tr>
<tr>
<td>Ag$^{51}$</td>
<td>\textit{N}-\textit{(2-phenylethyl)perylenetetracarboxylic monoimide}</td>
<td>Vacuum evaporation</td>
<td>6nm</td>
<td>135</td>
</tr>
<tr>
<td>Ag$^{52}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Thermal evaporation</td>
<td>10nm</td>
<td>165</td>
</tr>
<tr>
<td>Ag$^{53}$</td>
<td>\textit{p}-nitrobenzoic acid</td>
<td>Sputter coating</td>
<td>7nm</td>
<td>40</td>
</tr>
</tbody>
</table>
Recently, engineered metallic nanostructures began to be explored as SEIRA-active substrates.\textsuperscript{33} Electron beam lithography (EBL)\textsuperscript{54,55} and focused ion beam lithography (FIBL)\textsuperscript{56} have been exploited to create SEIRA-active surfaces. In this way, ordered arrays of metallic nanostructures can be used to tune the plasmonic response directly by adjusting the periodicity or size of the nanostructures.\textsuperscript{34} Examples including nanoshells and nanoantenna substrates have been fabricated for SEIRA applications.\textsuperscript{31,32} By utilizing these approaches, the reproducibility of SEIRA active substrates can achieve a high level. However, fabricating these nanostructures are normally complicated and expensive. In addition, the fabrication area of these nanostructures is quite small as is limited by the serial nature of these fabrication methods.\textsuperscript{35} These factors limit the further application of engineered metallic nanostructures in SEIRA spectroscopy.

Currently, the fabrication of sensitive, economical and reproducible SEIRA active substrates remains challenging, which limits the routine application of SEIRA spectroscopy. It is therefore critical to identify methods to manipulate the morphology of metal nanostructured surfaces by optimizing preparation parameters during the fabrication process. The controllability and reproducibility of creating SEIRA active substrates is a main focus of this research.

1.3 Electromagnetic Enhancement Mechanism

Electromagnetic enhancement is believed to contribute to the SERIA effect.\textsuperscript{36} In case of metal island substrates, the nanostructures can be simplified as prolate ellipsoids with uniform size and shape (Figure 1.1) in theoretical studies of SEIRA.\textsuperscript{21,28} The major radius of metal island is in parallel with the surface and defined as $a$. The minor radius, in perpendicular with the metal surface, is defined as $b$. The aspect ratio of islands can be described as $\eta=a/b$. The adsorbed molecules are assumed to be a monolayer covering around the metal islands uniformly. The dielectric function of metal islands and adsorbed molecules are characterized by $\varepsilon_m$ and $\varepsilon_d$. The electric field of
incident infrared radiation is perpendicular to the major radius $a$ of ellipsoids in the transmission measurement. When the IR light source incident on the metal island films, the metal islands will be polarized, which induced a point dipole $p$ via collective electron resonance excitation, which is known as localized surface plasmon resonance (LSPR). The LSPR occurs when the frequency of incident light is in resonance with the collective oscillation of valence electrons in a coinage metal nanoparticle. The electromagnetic enhancement mechanism in SEIRA measurement via metal island substrates.

Figure 1.1. The electromagnetic enhancement mechanism in SEIRA measurement via metal island substrates.
The enhanced electric field around metal islands is much stronger than the incident electric field, but it is not uniform. The strongest field is at the tip of islands where the radius of curvature is greatest, and the weaker where curvature is less. The magnitude of the enhanced local electric field decreases rapidly at locations away from the substrate. It has been demonstrated that the enhanced electric field is related with the signal enhancement of adsorbed molecules in SERS. In the SEIRA spectroscopy, the enhanced local electric field is also believed to contribute to the enhancement of vibrational signals of adsorbed molecules. The mechanism of enhancement in SEIRA can be seen as similar with interpretation accepted for SERS.

The vibrational signal magnitude in the IR spectra is associated with the change of the molecule’s dipole moment. The dipole moment is a vector with three components, \( \mu = \mu_x + \mu_y + \mu_z \). Each component can be described by:

\[
\mu = \mu_0 + \left( \frac{\partial \mu}{\partial q} \right)_0 q + \frac{1}{2} \left( \frac{\partial^2 \mu}{\partial q^2} \right)_0 q^2 + \ldots
\]

where \( \mu_0 \) represents the dipole moment equilibrium value and \( q \) represents the displacement. The first partial derivative \( \left( \frac{\partial \mu}{\partial q} \right)_0 \) is determined part of fundamental vibrational frequencies in the infrared spectrum. For an IR active molecule, one of these three components should have some displacement in their direction. The interaction between the electric vector of the electric field and the vibrational modes of molecule can enhance infrared absorption in the infrared spectra. The interaction is known as the semi-classical theory of quantum transitions. The magnitude of infrared absorption is proportional to \( (E \cdot \mu)^2 \), where \( E \) is the local electric field and \( \mu \) is the dipole moment change in the plane of electric field. Since an amplified electric field is generated around the metal islands, the enhancement of infrared absorption signals can be achieved in infrared spectra. The
corresponding intensity of enhanced infrared absorption signals is proportional to the square of enhanced local electric field. Therefore, electromagnetic enhancement mechanism is believed to be contributed to SEIRA performance. Notably, the SEIRA active molecules are the vibrational modes that possess dipole moments oriented perpendicular to the surface only. Thus, SEIRA enhancement follows the surface dipole selection rule. Since the enhanced electric field is perpendicular to the entire surface around the circumference of metal islands, this selection rule holds for any molecule bound to the surface with that orientation.

The metal island morphology has important impacts on the SEIRA enhancement. Connected metal islands or well separated metal islands will both significantly reduce the enhancement factor. The largest SEIRA enhancement appeared from densely crowded, but discontinuous islands. When the metal islands are densely placed, the dipole inside the metal island, induced by the incident electric field, would interact between islands. These nanogaps between the noble metal islands are assumed as “hot spots” that harvest extremely high electromagnetic field which owning to the interaction among the surface plasmon resonances through dipole-dipole electromagnetic interactions. Therefore, the narrow gap region between adjacent metal islands were believed to serve as the strong SEIRA active absorption sites. Figure 1.2 showed the UV-Vis and near infrared transmission spectrum of Ag film sputter coated on glass substrates with different thickness. The spectra were collected at different locations on the gradient Ag film illustrated in Chapter 2. The localized surface plasmon resonance (LSPR) band of isolated Ag islands can be observed around 500nm in spectra. As LSPR is able to maximize its optical absorption at the plasmon resonant frequency, a sharp and narrow dip appears in the transmission spectra of isolated metal island morphology. With increasing the Ag thickness, the Ag islands become densely packed and dipole coupling occurs between the islands, which shifts the absorption band to longer
wavelengths. It is important to note that the tail of the LSPR band extends into the mid-IR region.\textsuperscript{57} With increasing Ag thickness (continuous film), the LSPR band disappears and the transmission spectra exhibits a similar shape to a continuous metal film. These results indicates that nature of the metal nanoisland film can have a big impact on the nature of the localized surface plasmon resonance that is exhibited, and the wavelength range where it appears.

Figure 1.2. UV-Vis and near infrared transmission spectra of Ag film sputter coated on glass substrate with different thickness. The top curve illustrates that the transmission spectra of thin Ag film thickness with isolated islands. The middle curve illustrates the transmission spectra of increased Ag mass thickness with dense islands. The bottom curve illustrates the transmission spectra of increased Ag thickness with continuous film morphology.

In addition, it is important to mention that strong inelastic scattered light would be emitted from metal islands in a SERS measurement. This is due to the metal islands that are polarized by the Raman scattered light and dipoles are induced in the metal islands. Similar situation can also be considered in the SEIRA measurement. When molecules are absorbed around the metal islands,
additional dipoles can be induced and oscillate the metal islands.\textsuperscript{59} The spectrum generated from the oscillation of metal particles should be the same with adsorbed molecules, but giving stronger signals at the frequency of the molecular vibration than at other frequencies. Also, considering of the absorption coefficients of metal particles in the infrared region, even though they have smaller values than those corresponding continuous metals, they are still much larger than adsorbed molecules, according to infrared spectroscopic ellipsometric measurements.\textsuperscript{60} The mass of metal islands will also be much larger than adsorbed monolayer molecules. Therefore, the IR spectrum collected from metal island substrates will show much stronger vibrational signals of adsorbed molecules than the conventional measurement without metal. The metal islands can be identified as an amplifier in SEIRA.

1.4 Chemical Enhancement Mechanism

In previous studies, it was found that the molecules chemisorbed on the metal surface would have a stronger signal than physical adsorbed molecules.\textsuperscript{61} For example, Osswa \textit{etc} found that the signals of p-nitrobenzoic acid (PNBA) chemisorbed on isolated Ag island film could still be enhanced with no coupling of collective electron resonance was observed in infrared region,\textsuperscript{46} suggesting the enhancement was not related with electromagnetic enhancement mechanism, but some chemical mechanism existing in the SEIRA spectroscopy.

From previous studies, the absorption coefficients of chemisorbed molecules have been found to be larger than the physical adsorbed molecules.\textsuperscript{61} It is assumed that the absorption coefficient of chemisorbed molecule can be increased from the charge oscillations between molecule orbitals and metal surface, which results in a larger vibrational signal.\textsuperscript{62} With specified chemical effect, an interaction would occur between the atoms adsorbed around the metal surface and the adsorbed molecules. With incident electric field excitation, the electron that filled metal
level in the metal surface would transfer to the excited molecular orbital of the adsorbed molecules. The electrons can also transfer from occupied molecular orbital to the unfilled metal level. When the energy of incident photons is equal to the energy gap of electron transfer between the adsorbed molecules and the metal surface, resonance will be reached and results an increase of oscillating dipole of the adsorbed molecules. As a result, the infrared signal can be enhanced. In addition, the interaction between molecules can also affect the signal amplitude.

Chemical enhancement mechanism is related with the charge transfer from metal states below the Fermi level to unoccupied molecular orbital. Many factors could affect it, such as binding effect between the molecule and the substrate, molecular structure and electronic structure. However, the details of chemical enhancement mechanism is still not clear. In order to clearly interpret the chemical enhancement mechanism, additional efforts for chemical enhancement mechanism in theoretical and experimental aspects are necessary.

1.5 Surface Plasmon Resonance

Surface plasmon resonance (SPR) is the resonant oscillation of electrons excited via an incident electric field at an interface between two medium with positive and negative permittivity, normally between a metal film and a dielectric substrate. SPR is excited by incident photon field under specific matching conditions. When the conditions are matched, surface bound electromagnetic waves, which are known s surface plasma polaritons (SPPs), can be excited at the interface. SPPs are a transversal magnetic wave, known as TM- or p-polarized wave. Its electric field is perpendicular to the direction of propagation and its magnetic field is parallel with the interface plane (Figure 1.3). Its field amplitude will be maximum at the interface and decay exponentially into both medium. When SPR is excited, the energy from incident photons will be transferred to surface plasmons that oscillate around the interface.
The SPR phenomenon was first described by Wood in 1900s. In the late 1960s, Kretschmann and Otto proved the optical excitation of SPR by the prism based attenuated total reflection method. Since then, both theoretical and experimental studies of SPR are intensively investigated and are applied in diverse aspects. Since it has the advantages of sensitivity, label free and versatility, it is a promising analytical technique to be applied in biosensors, environment analysis, food science and clinical diagnosis.

1.6 Localized Surface Plasmon Resonance

In traditional SPR excitation, a continuous metal film is used. However, SPR can also be excited around metal nanoparticles, typically Au or Ag, which is known as localized surface plasmon resonance (LSPR). LSPR is a particular type of SPR as light interacts with metal particles.
In order for LSPR to be observed, the size of metal nanoparticles needs to be much smaller than the wavelength of incident light. An enhanced electric field can be generated around metal particle’s surface when the collective oscillation of the valence electrons in the metal nanoparticle is in resonance with the frequency of light. In addition, the incident light absorbed is a maximum absorbed at the plasmon resonant frequency. LSPR is sensitive to the changes of the surrounding local dielectric environment, which has been explored by researchers as a sensing platform in many applications.

1.7 Surface Plasmon Resonance Combined with SEIRA

SPR can be combined with several spectroscopy methods, such as SERS and SEIRA, to improve its performance or extend its application in more fields. Researchers have demonstrated that SPR can be combined with SEIRA to characterize ultrathin films, detect specific fingerprints of biological analytes, and couple with molecular vibrational resonance.

Most SEIRA active substrates take advantage of LSPR to enhance vibrational signals in IR spectra, which have already been mentioned in previous sections. In the case of SEIRA active substrate by utilizing LSPR, they normally consist of nano-scaled metal structures on the surface, such as islands, nanospheres or nanoantennas. Besides LSPR, propagating surface plasmons excited from continuous metal films can also be utilized in SEIRA. Previous studies have demonstrated an angle tunable grating platform could be utilized for enhancing the vibrational modes of polymer films. However, only a few experimental examples have explored this area which signifies this technique still have more space to be improved and can provide more flexibility in SEIRA applications. Compared with LSPR, propagating SPR is able to tune the enhanced electric field directly in infrared region by adjusting coupling conditions, which makes SEIRA active substrates more controllable and more reproducible.
1.8 Theory of Propagating SPR

Considering an interface between a metal and dielectric with dielectric functions $\varepsilon_m$ and $\varepsilon_d$ respectively, the resulting electromagnetic waves can only be excited when the incident electric field is perpendicular to the surface (z direction). Otherwise the incident electric field is not able to couple with the electric field at the interface. For s-polarized light, its electric field is parallel with the surface (y direction) when it is propagating along the x-direction, so it is unable to excite SPPs. P-polarized light possesses the electric field in x and z plane which is able to coupling with this mode and excite SPPs. Figure 1.4 represents the schematic view of resulting electromagnetic waves from propagating SPR.

**Figure 1.4.** Schematic of electric field intensity at the interface between metal and dielectric medium. Z direction is normal to surface plane and x direction is the propagation direction. The surface plasmon polaritons propagates along the x direction and decay exponentially in the z direction.
The electric and magnetic fields of SPPs, which excited by p-polarized light, travelling in x, y plane along the metal/dielectric interface can be described by

\[ \mathbf{E}_d = \begin{pmatrix} E_{dx0} \\ 0 \\ E_{dz0} \end{pmatrix} \exp[i(k_{dx}x + k_{dz}z - wt)] \quad z > 0 \]  

(1.1)

\[ \mathbf{H}_d = \begin{pmatrix} 0 \\ H_{dy0} \\ 0 \end{pmatrix} \exp[i(k_{dx}x + k_{dz}z - wt)] \quad z > 0 \]  

(1.2)

\[ \mathbf{E}_m = \begin{pmatrix} E_{mx0} \\ 0 \\ E_{mz0} \end{pmatrix} \exp[i(k_{mx}x - k_{mz}z - wt)] \quad z < 0 \]  

(1.3)

\[ \mathbf{H}_m = \begin{pmatrix} 0 \\ H_{my0} \\ 0 \end{pmatrix} \exp[i(k_{mx}x - k_{mz}z - wt)] \quad z < 0 \]  

(1.4)

Where \( \mathbf{E} \) represents the electric field, \( E \) represents the magnitude of electric field, \( \mathbf{H} \) represents the magnetic field, \( H \) represents the magnitude of magnetic field, \( k_{dx} \) and \( k_{mx} \) are the wave vectors of both media in x direction, \( k_{dz} \) and \( k_{mz} \) are the wave vectors of both media in z direction, \( w \) represents the angular frequency and \( t \) represents time. The two fields of \( \mathbf{E} \) and \( \mathbf{H} \) should obey Maxwell’s equations:

\[ \nabla \cdot \mathbf{H} = 0 \]  

(1.5)

\[ \nabla \cdot \mathbf{E} = 0 \]  

(1.6)

\[ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} = 0 \]  

(1.7)

\[ \nabla \times \mathbf{H} - \frac{\varepsilon}{c} \frac{\partial \mathbf{E}}{\partial t} = 0 \]  

(1.8)
Where \( \varepsilon \) is the dielectric function of the relative permittivity of the material and \( c \) is the speed of light in vacuum. The tangential components of \( E \) and \( H \) need to be equal at the interface. Therefore, the equations need to be satisfied with following boundary conditions:\(^{87}\)

\[
E_{dx} = E_{mx} \quad (1.9)
\]

and

\[
H_{dy} = H_{my} \quad (1.10)
\]

From equation 1.9, it follows that \( k_{dx} = k_{mx} = k_x \) \((1.11)\)

In addition, by putting the equations 1.1-1.4 into equation 1.8, it is able to get that

\[
k_{dz}H_{dy} = \frac{w}{c}\varepsilon_d E_{dx} \quad (1.12)
\]

\[
k_{mx}H_{my} = -\frac{w}{c}\varepsilon_m E_{mx} \quad (1.13)
\]

By combining equations 1.9, 1.10, 1.12 and 1.13, it leads to:

\[
k_{dz}\varepsilon_m = -k_{mx}\varepsilon_d \quad (1.14)
\]

This above equation 1.14 indicates that the relative permittivity of the two media need to be opposite in order to excite surface plasma polaritons. The relative permittivity of most dielectric material is positive in the UV-Vis and IR regions. Therefore, the other media’s relative permittivity needs to be negative. Silver, gold and aluminum are the most common choice as they are able to fulfill the condition at optical wavelength.\(^{88}\) This is the reason why noble metal normally will be chosen as another media.

From equations 1.7, 1.8, 1.11, 1.12 and 1.13, it is able to obtain
\[ k_x^2 + k_{iz}^2 = \left( \frac{\omega}{c} \right)^2 \varepsilon_i \] (1.15)

or

\[ k_{iz} = \sqrt{\varepsilon_i \left( \frac{\omega}{c} \right)^2 - k_x^2} \] (1.16)

Based on equation 1.14, the dispersion relationship of surface plasmons at the metal/dielectric interface can be solved from equations 1.15 or 1.16:

\[ k_{sp} = k_x = \frac{w}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} = \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \] (1.17)

Where \( \lambda \) represents the light wavelength and \( \varepsilon_m, \varepsilon_d \) are referred to the relative permittivities of metal and dielectric material at that wavelength. The momentum of surface plasmons can also be derived from equation 1.17. As the relative permittivities of metal and dielectric medium would be opposite sign, the above equation indicates that the values of relative permittivity of the two media must be \( \varepsilon_m < -\varepsilon_d \) for exciting surface plasmon polaritons.

In addition, it has been mentioned before that the electromagnetic waves of surface plasmon achieved the maximum field amplitude at the interface, but will decay sharply into the both media, which indicated by equation 1.1 and 1.3. Therefore, it exhibits a finite propagation length \( L_x \) and a finite penetration length \( L_c \) (Figure 1.5). Since the relative permittivity of materials are complex (\( \varepsilon = \varepsilon' + i\varepsilon'' \)), the propagation constant \( k_{sp} \) is also complex. The propagation length \( L_x \), defined as the distance at which the plasmon energy was attenuated to 1/e of its original value in the x direction, can be described by:

\[ L_x = \frac{1}{2k_{sp}^{\varepsilon''}} \] (1.18)
Where $k_s'\text{p}$ is the imaginary part of propagation constant $k_{sp}$. Table 1.2 showed the propagation length along the metal/water interface.

The penetration length $L_c$ is defined as the length that the fields decayed to $1/e$ of the interface magnitude. It can be defined as:

$$L_c = \text{Re}\left(\frac{\lambda\sqrt{\varepsilon_m+\varepsilon_d}}{i\cdot2\pi j}\right)$$

(1.19)

Where $j$ stands for the medium, either metal or dielectric material. Table 1.2 also shows the penetration length for gold, silver and dielectric. The penetration length into metal is limited to several tens of nm only indicates the high loss in the metal. However, the penetration length into dielectric is found to be a few hundred nanometers. Therefore, the majority of fields are concentrated in the dielectric medium instead of metal medium.
**Figure 1.5.** Schematic of light impinging on at the metal dielectric interface and exciting propagating surface plasmon modes. The surface plasmon mode propagates as a damped oscillatory wave in the $x$-direction and decays evanescently along the $z$-direction. The propagation length and penetration length are illustrated in the figure, which should be $1/e$ of its original energy at that direction.

**Table 1.2**

Propagation length and penetration length into both media of surface plasmon waves at the metal water interface$^{65}$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Silver</th>
<th>Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>630nm</td>
<td>850nm</td>
</tr>
<tr>
<td>Propagation length($L_x$) ($\mu$m)</td>
<td>19</td>
<td>57</td>
</tr>
<tr>
<td>Penetration length($L_c$) into metal (nm)</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>Penetration length($L_c$) into dielectric (nm)</td>
<td>219</td>
<td>443</td>
</tr>
</tbody>
</table>
1.9 The platforms to excite SPR

The propagation constant of SPs was derived in the previous section. In order to excite SPR, the momentum of surface plasmon needs to be matched with that of the incident light. The momentum of light wave travelling in one dielectric media can be described by

\[ k_{ph} = \frac{w}{c} \sqrt{\varepsilon_d} \]  

(1.20)

Compared with the momentum of surface plasmon mode \(k_{sp}\), the value of \(k_{ph}\) in air is always smaller than \(k_{sp}\) at the same wavelength. Therefore, additional momentum needs to be added into incident light in order to excite SPR. Three coupling devices are most widely used for exciting SPR: prism based couplers, metal grating based couplers and optical waveguide based couplers. The details of the three couplers will be described in the following section.

Prism based couplers (Figure 1.6a) was developed independently by Kretschmann and Otto in 1960\(^7\)\(^0\)\(^,\)\(^7\)\(^1\). Following equation described the matching condition

\[ \frac{2\pi}{\lambda} n_p \sin \theta = Re\{k_{sp}\} \]  

(1.21)

Where \(n_p\) represents the refractive index of prism and \(\theta\) represents the light incidence angle. As the refractive index of prism is larger than dielectric media, the light will be totally internally reflected at the bottom of prism. An evanescent wave would then be generated, which penetrates through a thin metal film. The propagation constant of the evanescent wave from incident electric field along the interface can be larger than normal dielectric-metal interface. It can be matched with the propagation constant of surface plasmon via manipulating light incident angle. Therefore, surface plasmon resonance can be excited via this prism based coupler. Notably, the metal film thickness needs to be precisely controlled in this configuration.
Grating based coupler (Figure 1.6b) is another configuration to excite surface plasmon. A metallic diffraction grating is used as the platform. When the light incident on the grating, the light can be diffracted and additional momentum is able to be added in the incident light, which is then able to couple with surface plasmons. The matching condition can be described by

$$\frac{2\pi}{\lambda} n_d \sin \theta + m \frac{2\pi}{\Lambda} = \pm Re \{k_{sp}\}$$

(1.22)

Where $n_d$ represents the refractive index of dielectric medium, $\theta$ represents the incident angle of light, $m$ represents the diffracted orders ($0, \pm 1, \pm 2...$) and $\Lambda$ represents the grating pitch. By controlling the light incident angle or grating periodicity, the propagation constant of incident light
can be matched with the propagation constant of surface plasmons. And the SPR excitation can be accomplished at different wavelength. In addition, multiple diffracted orders excite surface plasmons makes this method more multiplex and information rich.

The third coupler method is optical waveguide based couplers (Figure 1.6c). Light propagates in a waveguide in the form of guided modes. In a guided mode, most of the electromagnetic field is in the waveguiding layer. But a small portion of the field would propagate into the medium with low refractive index around the waveguiding medium as an evanescent wave. When light incident the waveguide region consists a metal film, the evanescent wave is coupled to the surface plasmons. Therefore, the surface plasmons can be excited on the outer border of metal film. The following equation describe the matching condition\(^67\)

\[
k_{mode} = Re\{k_{sp}\} \tag{1.23}
\]

When the propagation constant of optical waveguide mode is consistent with real part of surface plasmon propagation constant, surface plasmons coupling via this configuration can be achieved.

1.10 References:


(2) Blackie, E. J.; Ru, E. C. L.; Etchegoin, P. G. Journal of the American Chemical Society 2009, 131, 14466-14472.


CHAPTER 2
TUNING SURFACE ENHANCED INFRARED SPECTROSCOPY
USING GRADIENT METAL NANO-ISLAND FILMS

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2.1 Abstract

Surface enhanced infrared absorption (SEIRA) spectroscopy is an analytical technique that exploits surface plasmon resonance to enhance absorption signals associated with thin films and bound analytes in infrared spectroscopy. Metal island films represent the most widely used substrate for SEIRA due to the simplicity in preparation and broad applicability. However, fabricating metal island films with a large and reproducible enhancement remains challenging. In this report, we describe results involving the fabrication of silver and gold nano-island films that possess a spatial gradient in surface properties. We exploit off-axis, metal sputtering to create a film thickness gradient, which is accompanied by a variation in film properties along the sample surface, including nanoparticle morphology, size, connectivity, and coverage. These variations in nanoparticle properties lead to a spatially varying plasmonic response as well as a changing and reproducible magnitude in the infrared enhancement. We use a combination of atomic force microscopy, optical spectroscopy, and electrical conductivity measurements to show changes in film properties as a function of position. SEIRA measurements are performed on a 1-hexadecanethiol (HDT) monolayer. Notably, the magnitude of infrared enhancement is strongly dependent on the location along the metal film and the largest enhancement occurs at the transition
between isolated nano-islands and a continuous, conductive film. This transition region is identified in terms of the onset of a percolating film morphology, a broadening of the plasmon response into the infrared, and just prior to the appearance of electrical conductivity, indicating contact between neighboring metal islands. Notably, this sample design allows for a facile, reproducible route to fabricate metal island substrates that can be used to find the maximum surface enhancement in infrared spectroscopy measurements.

2.2 Introduction

Surface enhanced infrared absorption (SEIRA) spectroscopy\(^1,2\) is a powerful analytical tool for probing thin films and analytes bound to surfaces. This method is based upon the enhancement of infrared signals associated with plasmonic substrates.\(^3\) Initially reported by Hartstein \emph{etc.} in 1980\(^4\) using the attenuated total reflectance (ATR) geometry, SEIRA has subsequently been observed in various other configurations and geometries.\(^5,6\) It has been applied in various applications, including the in situ characterization of species on metal electrode surfaces,\(^7-11\) sensor applications in bio-spectroscopy,\(^12-15\) and characterization of ultrathin films.\(^16-18\)

A variety of substrates have been used for SEIRA. Periodic metallic nanostructures, for examples, such as nanoparticle arrays\(^19,20\) and optical nanoantennas,\(^21,22\) have been used for SEIRA. Periodic surfaces allow the surface plasmon response to be tuned across the infrared spectrum by manipulating the size or shape of the structures. In addition, the reproducibility of these substrates is well controlled. However, fabricating periodic structures is complicated and expensive, and is typically limited to small areas (mm\(^2\)),\(^23-25\) which limits their application.

Metal island films, particularly those made of coinage metals (Ag, Au) represent the most frequently used substrates for SEIRA measurements. These metal films are typically prepared by thermal evaporation, sputtering,\(^6,26-29\) or electroless reduction.\(^7,30-32\) Metal island films that show
strong SEIRA enhancement tend to be discontinuous and consisting of small metal islands. These metal island films generate localized surface plasmons, which create an enhanced surface electric field. This enhanced electric field strongly affects surface enhanced Raman scattering (SERS) and is also likely a significant contributor to SEIRA.

Prior work has shown that SEIRA enhancement is strongly dependent on metal film morphology. The size, shape, density and inter-particle spacing of the metal islands are important factors that affect SEIRA enhancement. Notably, the presence of connectivity in metal films can significantly reduce SEIRA enhancement. Therefore the presence of discontinuity between the particle grains of a metal film is critical to strong SEIRA enhancement. It has been observed that maximum SEIRA enhancement typically occurs just below the percolation threshold, or just prior to the appearance of connectivity between the grains, of metal island films. Notably, the metal island morphology is strongly related with the film mass thickness, the deposition conditions, and the chemical nature of substrates. The controllability and reproducibility of SEIRA active metal island films remains poor, thus limiting its widespread application. In order to achieve maximum SEIRA enhancement, it is of critical importance to monitor and control the metal film morphology and improve its reproducibility. Optical spectroscopy can be a useful tool to monitor metal island morphology as the spectral features of the plasmonic response react strongly to slight changes of metal morphology. As a result, proper metal film preparation must be well controlled to achieve high SEIRA activity.

In this work, we exploited a gradient silver film consisting of metal nanoparticles with variable size, coverage, and morphology in order to understand the role of film properties on SEIRA enhancement. Silver or gold films exhibiting a linear thickness gradient were fabricated on glass substrates via off-axis sputter coating. The optical and electrical properties of the films were
measured at different locations along the film surface. Infrared transmission spectra were measured along the gradient metal films in the presence of a 1-hexadecanethiol (HDT) monolayer. Results show enhanced infrared signals of the C-H vibrational mode from HDT, with enhancement factors that varied significantly as a function of position along the surface. SEIRA enhancement was observed at the thinnest film regions and the enhancement increased in magnitude with increasing film thickness. A maximum in SEIRA enhancement was observed at the location just prior to the formation of a continuous, conductive film. This also corresponded to the region where the substrate’s plasmonic response extended furthest into the infrared region, but prior to the appearance of metallic reflectivity. Similar results were observed in other silver and gold gradient films.

2.3 Experimental

Materials and Reagents. Glass microscope slides and ethanol were obtained from Fisher Scientific (Waltham, MA). Silver (99.99% purity) and gold (99.99% purity) sputtering targets were purchased from AJA Intentional, Inc. (North Scituate, MA). 1-Hexadecanethiol (HDT, 99%) was purchased from Sigma Aldrich (St. Louis, MO). Deionized water with electrical resistivity of more than 18 MΩ (NANOPure, Barnstead, Dubuque, IA) was used to rinse and clean the substrates.

Gradient Metal Film Fabrication. Glass microscope slides were used as substrates for gradient metal films. Before metal deposition, the slides were cleaned with soap solution and rinsed with ethanol and DI water and then dried with nitrogen gas. The slides were then baked at 150°C for 1 min to remove any residual moisture. A multi-gun sputter coating system (ATC 1800-F, AJA Intentional, Inc., North Scituate, MA) was utilized for fabricating gradient metal films. Details of the target and sample geometry are depicted in Figure 2.1. The sputtering target was
tilted at an angle of 27° with respect to the substrate normal and the substrate was mounted 12.8 cm away from the target. A quartz crystal thickness monitor was mounted near the edge of the substrate closest to the target. Typical deposition conditions included an argon gas flow of 10 SCCM, yielding a chamber pressure around 15 mTorr, a sputter power of 9 W, and a deposition rate, as measured by the thickness monitor, of 0.02 nm/s. During deposition, the sample stage was fixed without rotation. The resulting deposition produced a nonuniform film thickness along the length of the sample, with the largest deposition rate occurring nearest to the target and an approximately linear decrease in deposition when moving away from the target. Deposition continued until the desired thickness was achieved, typically between 20 and 40 nm at the thickest portion of the sample.

![Schematic of sputter chamber configuration](image)

**Figure 2.1** Schematic of sputter chamber configuration used for creation of gradient metal island films.

**UV-Vis and Near Infrared Transmission Spectroscopy.** Optical transmission spectra were measured with a custom-built optical bench (Figure S2.1, Supporting Information). White light from a tungsten-halogen light source (Model OSL1, Thorlabs, Inc., Newton, NJ) was collimated using a parabolic mirror and then directed through a 2 mm diameter aperture before illuminating
the sample, which was mounted on a manual translation stage. Transmitted light was collected with a 600 µm bifurcated optical fiber, which allowed the light to be directed into two different spectrometers. The first was a UV-VIS spectrometer (200-1100 nm, HR4000CG-UV-NIR, Ocean Optics, Inc., Dunedin, FL) while the second covered the near-infrared range (900-2500 nm, NIRQUEST512-2.5, Ocean Optics, Inc., Dunedin, FL). Spectra collected from the two spectrometers were combined to create transmission spectra covering 200-2500 nm. Transmission spectra were recorded at multiple locations along the 7.5 cm length of the glass slide sample, at nominal spacings of ~1 cm.

**Film Thickness Measurements.** A P-7 stylus profiler (KLA Tencor, Milpitas, CA) was used to measure the metal film thickness along the length of the gradient film. Thickness measurements were performed at the same locations where transmission spectra were collected. Film thicknesses were measured by scratching the metal film with a razor blade to remove material down to the substrate. The sample was then scanned over the scratch to determine the height of the metal film with respect to the substrate (Figure S2.2, Supporting Information). During each measurement, the applied force was set to 2 mN with a scan length of 2 µm. The step heights determined from the profiler indicated the actual silver thickness at each location along the gradient film.

**Formation of Monolayer Films.** Monolayers of 1-Hexadecanethiol (HDT) were formed on the metal films by immersing the metal-coated glass into a 0.1 M HDT solution in ethanol for 30 min. A chemisorbed HDT monolayer was generated on the metal surface. The samples were subsequently rinsed with ethanol and dried with a stream of nitrogen gas.

**Infrared Transmission Spectroscopy.** Infrared transmission spectra were collected using a Fourier transform infrared spectrometer (FTIR) (Nicolet iS50, Thermo Scientific, Waltham, MA) equipped with a custom transmission accessory and a liquid nitrogen cooled mercury cadmium
telluride (MCT) detector (Figure S2.3, Supporting Information). Incident light was directed through an 8 mm diameter aperture and then through the sample, which was mounted on a manual translation stage. The translation stage allowed infrared transmission measurements to be performed as a function of position along the sample. The measured locations on each substrate were consistent with the locations used for film thickness and UV=VIS/Near-IR transmission spectroscopy measurements. The reference spectra in all cases were obtained from HDT-free substrates with similar metal thicknesses. All the spectra were collected at a resolution of 4 cm$^{-1}$ with 64 scans, and have been background subtracted over the selected measurement region.

**Method for Determining SEIRA Enhancement Factors.** The SEIRA enhancement factors were estimated by comparing the SEIRA FTIR absorbance peak of the HDT monolayer relative to the equivalent peak for a HDT monolayer film on a bare glass substrate. This was achieved by creating a thin film of HDT on glass by spin coating. A spun film was prepared by taking a 10 mM HDT solution dissolved in ethanol and spinning it on a bare glass slide at 3000 rpm for 1 min (Model WS-650MZ-23NPP spin coater, Laurell Technology Corp., North Wales, PA). Prior to coating, the glass slides were cleaned with soap solution, rinsed vigorously with ethanol and acetone, and dried with nitrogen gas. The HDT film thickness was measured using spectroscopic ellipsometry (Model Alpha-SE spectroscopic ellipsometer, J.A. Woollam Co., Inc., Lincoln, NE) operating at a wavelength between 380 and 900 nm at 65°, 70°, and 75° incident angles. The measured values of delta ($\Delta$) and psi ($\Psi$) for the film were translated into equivalent optical thickness by fitting a dielectric film model on glass using the CompleteEase™ software package.

According to the ellipsometry results, the thickness of the spun HDT film was estimated to be 39 nm. This compares to an approximate monolayer thickness of 2.43 nm, as determined by the
length of a single HDT molecule consisting of 15 C-C bonds and 1 C-S bond with bond lengths of C-C = 0.15 nm, C-S = 0.18 nm. Therefore, the spun HDT film was equivalent to ~16 HDT monolayers. The FTIR transmission peaks for the spun HDT film (Figure S2.4, Supporting Information) was converted to an equivalent monolayer value by the following relation:

\[
\text{absorbance of HDT monolayer on glass} = \frac{\text{absorbance of HDT thin film on glass}}{\text{HDT layers on glass}}
\]  \hspace{1cm} (1)

The enhancement factor (EF) for the SEIRA measurements was then estimated according to:

\[
\text{Enhancement Factor (EF)} = \frac{\text{absorbance of HDT monolayer on SEIRA active substrate}}{\text{absorbance of HDT monolayer on glass}}
\]  \hspace{1cm} (2)

**Atomic Force Microscope (AFM) Imaging.** A dimension 3100 scanning probe microscope with Nanoscope IV controller (Veeco Metrology, LLC, Santa Barbara, CA) was utilized to collect topographical images of the metal films. Imaging was conducted in tapping mode using silicon TESP7 AFM tips (Vecco metrology, LLC, Santa Barbara, CA) with a spring constant of ~79 N/m and a resonance frequency of ~280 kHz. Imaging locations were the same as those as noted earlier.

**Conductivity Measurements.** Conductivity of the metal films was measured by collecting electrical impedance spectra using an electrochemical workstation (Model 760B, CH Instruments Inc., Austin, TX). A two-electrode configuration was used to collect electrical impedance spectra across the width of the sample at various locations (Figure S2.5, Supporting Information). In all cases, the electrodes were placed on opposing sides of the sample with a gap of 1 cm. The electrical impedance spectrum was measured over the frequency range from 1 Hz to 10 kHz.

### 2.4 Results and Discussion

Figure 2.2A depicts an optical image of a gradient silver film on a glass slide fabricated by off-axis, sputter coating. The top edge of the sample (position 1) was located closest to the silver sputtering target while the bottom edge (position 7) was the furthest away. The change in film
thickness along the sample is indicated by the variation in color from the very top to the bottom of the sample. The thickest part of the sample (position 1) appears gray and reflective, much like a silver mirror, while the thinnest region (position 7) displays a pink hue. The colors displayed by the film are a function of the film thickness, as well as the changing metal island morphology (size, shape, coverage, etc.). The metal thickness along the sample, as measured by contact profilometry, is shown in Figure 2.2B. Each measurement location, as noted in Figure 2.2A and 2.2B, is equally spaced along the sample with a 1 cm gap between each measurement. The thickness results show a near-linear decrease in metal thickness ranging from 22 nm at position 1 down to 4 nm at position 7.
Figure 2.2 (A) Optical image of silver gradient film on glass slide. Locations 1 to 7 are noted. (B) Thickness of silver film as a function of location as measured by contact profilometry.

Atomic force microscopy (AFM) was used to measure the morphology of the metal film along the sample surface. Figure 2.3 depicts a series of AFM height images at locations 1 to 6 over a 200 x 200 nm$^2$ area. These images show the typical surface morphology, and illustrate an evolution in that morphology with increasing film thickness. In all cases, an island-like morphology is observed. At the thinnest sample region (~region 7), the surface is covered by
spherically-shaped islands or nanoparticles. This is consistent with the typical morphology of metals sputtered on inert substrates in which small metal islands form during the initial nucleation stage.\textsuperscript{45} This morphology is the result of the low interaction energy between the metal and substrate, leading to the formation of isolated nuclei and the characteristic three-dimensional, Volmer-Weber growth mechanism.\textsuperscript{46} Overall, this growth mechanism results in increasing particle sizes and an evolution in the film morphology from isolated islands to interconnected clusters and then finally to a continuous film with increasing film thickness.

**Figure 2.3** Atomic force microscope (AFM) height images of Ag gradient film at locations 1 to 6.

At the initial stages of deposition, silver favors formation of individual, isolated nuclei on the glass slide. The shape of the metal nuclei appears nearly spherical in the AFM images, although they likely have a more hemispherical form as they deposit on the substrate surface. At the thinnest sample regions (e.g., locations 5-7) small and dense silver islands are observed. With increasing film thickness, the islands grow in three dimensions. This growth increases the average particle size and decreases the size of the gaps between adjacent silver islands (locations 3 and 4). With a
further increase in thickness, the silver islands being to coalesce with neighboring particles and form larger, irregular shapes (location 2). With further increases in film thickness, these larger particles coalesce, resulting ultimately in contact between neighboring silver islands and the formation of a continuous silver film (location 1).

Additional detail regarding the film’s morphology can be seen through analysis of the particle size distribution and coverage as provided by the AFM images (Figure 2.4). By approximating the particles as spherical in shape, the distribution of particle radii can be determined as a function of sample position (Figure 2.4A). At location 7, the silver islands have an average radius of ~8 nm. With increasing film thickness, the average particle radius increases to ~10 nm at locations 5 and 6. As the films grows thicker, the average radius continues to increase and the distribution of particle sizes broadens. This is indicative of the growth mechanism involving individual particles growing in size and then coalescing with increasing thickness. The average particle size in terms of projected area shows this increase in particle size along the surface with increasing film thickness (Figure 2.4B), with the largest particle size appearing at the thickest sample region. While the particle size increases with increasing film thickness, the total number of distinct particles also decreases (Figure 2.4C). This decrease in particle number is the result of the coalescence of individual particles into larger islands as the film thickness increases. Overall, these results show the change from a film consisting of individual small particles into an interconnected film.
As noted earlier (Figure 2.2A), the color of the silver film varies significantly across the sample surface. This behavior can be viewed in greater detail via measurement of the optical transmission spectrum of the sample at various locations (Figure 2.3). A pronounced absorbance band centered at around 520 nm is observed in the spectra for the thinnest sample region (location 7). This absorbance is attributed to the excitation of localized surface plasmon resonance (LSPR) within the film associated with isolated nanoparticles in this region of the film. AFM measurements indicated that this surface region consisted of isolated nanoparticles with an average radius of 8...
nm. The LSPR peak associated with these particles is similar to what is seen for solution-phase silver nanoparticles,\textsuperscript{47} although somewhat red-shifted to longer wavelengths. This sample region is also transparent at wavelengths above ~750 nm. As the film thickness increases when moving from sample region 7 to region 2, the location of LSPR absorbance band shifts to longer wavelengths. This red-shifting of the LSPR peak is accompanied by a broadening in the peak shape such that it begins to extend into the near-infrared region. With increasing film thickness, as indicated in regions 4-2, the peak continues to red shift and broaden, with an increasing absorbance extending into the near-infrared and into the mid-infrared (> 2500 nm). The observation of a LSPR peak then vanishes for the thickest sample region (location 1), which exhibits a mirror-like reflectance similar to that of a continuous silver film. This change in the optical response is consistent with the changing morphology of the silver film as the thickness increases.

Figure 2.5 Optical transmission spectra of Ag gradient film on glass substrate as a function of position along the surface as denoted by location numbers 1 to 7.
The location of the LSPR absorbance peak is a strong function of the silver film morphology and is influenced by the shape, size, and coverage of the metal islands on the surface. The optical response shown in Figure 2.5 can be explained by considering the increase in the particle size with increasing film thickness as well as greater connectivity between neighboring islands as the film thickens. As the metal islands grow and the gap between particles decreases, the tail of LSPR band gradually extends further into near infrared region. This is the result of increasing interaction of the LSPR at neighboring particles through dipole-dipole interactions as the separation between particles decreases. This behavior becomes more pronounced with increasing film thickness as the silver islands become larger and the gaps between adjacent silver islands decreases. The behavior of the thickest silver region is consistent with that of a continuous metal film. In this region, a LSPR peak is no longer observed, which is presumably due to the fact that the film has grown to where there is sufficient connectivity between neighboring metal islands such that electron propagation can freely occur across the surface. The optical response of location 1 is consistent with the computed transmission spectrum for a ~20 nm thick continuous silver film with a 30% open area (Figure S2.5, Supporting Information).

In order to verify that there is a change in the connectivity of the film across the sample as the film thickness is varied, the electrical conductivity across the gradient silver film was measured as several locations. The conductivity was determined by measuring the electrical impedance using a two-probe technique (Figure S2.4, Supporting Information). Electrode contacts were positioned at either side of the sample at each of the locations specified as 1-7 with a gap distance of ~1 cm. The electrical impedance was then measured over a frequency range of ~1 Hz to ~10 kHz. The results of these measurements are illustrated in Figure 2.6.
Figure 2.6 (A) Electrical impedance spectra of silver nanoparticle film at locations 1 to 7. (B) Impedance measured at 3 kHz as a function of position along the surface.

The impedance spectra (Figure 2.6A) show a clear difference between location 1, where the film is thickest, and the other regions (2-7). In regions 2-7, the frequency response is consistent with that of a pure capacitor, indicating the lack of measurable electrical conductivity. This behavior can be attributed to a film comprised of isolated particles with no path for electronic conductivity along the surface. At location 1, however, the frequency response changes dramatically to one that is several orders of magnitude smaller and with a constant impedance.
value that is independent of frequency, indicative of a highly conductive film. The change in electrical conductivity between the different film regions can be more readily seen by plotting the impedance at a fixed frequency (Figure 2.6B). This plot shows a critical change in the conductivity between regions 1 and 2, where region 1 is a low resistance, conductive surface with an impedance of ~100 Ohm cm, whereas region 2 (and 3-7) exhibit electrical resistance values that are at least 5 order of magnitude higher. One could consider the transition from region 2 to region 1 as representing the percolation threshold, where the film converts from isolated islands to a continuous, conductive network.\textsuperscript{49,50}

The ability of this surface to support surface enhanced infrared absorbance (SEIRA) was investigated by coating a self-assembled monolayer of 1-hexadecanethiol (HDT) onto the gradient silver film and performing infrared transmission spectroscopy measurements. HDT films form spontaneously on coinage metals to create a dense monolayer via covalent bonding between the metal and the thiol group.\textsuperscript{51} Following monolayer formation, SEIRA measurements were performed in a standard FTIR instrument that utilized a transmission sample holder mounted to a translation stage with an optical aperture to control the location and extent of the sampling region (Figure S2.2, Supporting Information). Results of these measurements are summarized in Figure 2.7. Each curve shows transmission spectra at different locations on the sample. The curves show absorbance peaks that can be assigned to CH stretching vibrations of HDT as follows: antisymmetric CH\textsubscript{2}, 2918 cm\textsuperscript{-1} and symmetric CH\textsubscript{2}, 2850 cm\textsuperscript{-1}.\textsuperscript{52} A notable change in absorbance peak intensity is observed at various regions of the sample. Both peaks are clearly observed at location 7, which corresponds to a substrate region where the underlying silver film consists of isolated spherical islands. As the film thickness increases, the magnitude of the vibrational signals
increases until a maximum intensity is observed at region 2. This maximum is followed by a significant drop in the magnitude of the absorbance peaks when region 1 is reached.

**Figure 2.7** Infrared transmission spectra of a hexadecane thiol (HDT) monolayer on Ag gradient film at different locations (1 to 7) along glass substrate. The spectra are offset vertically for clarity.

The change in magnitude of the absorbance peak intensities as a function of position can be more readily seen in Figure 2.8. In this plot, the absorbance signals have been converted into an Enhancement Factor (EF), which is the measured absorbance magnitude divided by that measured for an equivalent HDT monolayer on a bare glass substrate (Figure S2.4, Supporting Information). The trend in the enhancement factor is consistent between both the symmetric (2849 cm\(^{-1}\)) and asymmetric (2918 cm\(^{-1}\)) vibrational modes. The thinnest substrate region (location 7) shows an EF
value of ~600. A continuous increase in enhancement is observed when moving from the thin sample region to the thicker regions. A maximum EF is observed at location 2, where it approaches ~1,400. A dramatic decrease in enhancement is then observed between locations 2 and 1, which corresponds to the transition between an insulating and conductive silver film.

**Figure 8.** Enhancement factor for C-H stretching vibrations of HDT monolayer as a function of different locations (1 to 7) on Ag gradient film.

The range of enhancement factors indicated in Figure 8 are consistent with the various reported values in the literature. The largest enhancement at location 2 is comparable to the best reported values. One should note that there is some inconsistency in the way in which enhancement factor is defined in the literature, which can make direct comparison between various measurements somewhat challenging. In this work, we have defined the enhancement with respect to an equivalent HDT monolayer on a glass surface in the absence of a metal film.

The role of surface plasmon resonance on SEIRA is often attributed to an electromagnetic enhancement mechanism. This mechanism is based on the formation of a locally enhanced electric field that occurs due to the excitation of a surface plasmon. Notably, the intensity of infrared absorption is proportional to the square of the electric field times the dipole moment.
change \((E \cdot \mu)^2\). The electromagnetic enhancement mechanism is therefore the result of the coupling between the dipole moment change of a molecule \((\Delta \mu)\) and a locally enhanced electric field \((E)\).

The variation in enhancement observed with the gradient metal island film is a result of the shifting resonance condition that occurs as the metal islands grow and overlap. At the thinnest metal region, the plasmonic response is one associated with a collection of individual metal islands. As the metal film grows, the islands increase in size and interact with each other. This interaction leads to a red-shifting of the plasmonic response as it extends into infrared region. As the silver islands became larger with increasing film thickness, the gaps between neighboring islands became smaller and ultimately merge with each other. The decrease in the gap distance between neighboring silver islands likely serves to produce highly SEIRA active sites or “hot spots”.\(^{53,54}\) These locations produce a much stronger electric field due to the dipole coupling between neighboring silver islands.\(^{55}\) As a result, higher SEIRA activity can be achieved in these regions. As the percolation threshold of gradient silver film is approached, the interconnected silver clusters resulting from particle coalescence produce additional “hot spots” on the surface as the gap distance continues to decrease. This evolution results in the maximum SEIRA enhancement (location 2). Once connection between neighboring islands is complete (location 1), electronic conductivity within the film suppresses LSPR and, consequently, reduces the magnitude of the enhanced surface electric field. Therefore, this transition to a conductive film results in a much lower SEIRA activity than the metal island morphology.

It is also important to note that the metal island morphology changes during the deposition process, transitioning from spherical to more nonuniform and nonspherical in shape. Indeed, the strongest LSPR is often observed for nonspherical particles and collections of particles, such as
nanoparticle aggregates or fractal structures. Nonuniformity in shape and size also leads to a greater diversity in resonance conditions, which provides a broadening of the wavelength range that resonance is observed. Near the percolation threshold of the metal film, the metal islands could be viewed as fractal structures with a broad size and shape distribution. This diversity in size and shape broadens the plasmon resonance and shifts it to longer wavelengths that extend into the infrared region, where it is better able to couple with the vibrational modes of interest for SEIRA.

To demonstrate the generality of this gradient film approach for tuning SEIRA enhancement, we have also fabricated thicker silver gradient films and gradient gold films via off-axis, sputter coating. Results of these experiments (Figures S2.7 – S2.10, Supporting Information) demonstrate that a thickness-dependent SEIRA enhancement is also observed for thicker films and for films made of gold. The primary differences in these results are that the maximum enhancement occurs at a different location on the film. Nevertheless, the greatest SEIRA enhancement in these samples also occurs where the LSPR response extends furthest into the infrared region, and at the location just prior to the onset of electrical conductivity.

2.5 Conclusions

In this work, we demonstrated a method for creating gradient metal island films via off-axis, sputter coating. These gradient films exhibited a number of position-dependent properties, including morphology, optical absorbance, and electrical conductivity. The films also showed a strikingly large variation in SEIRA enhancement for a monolayer of chemisorbed hexadecanethiol. It was noted that the maximum SEIRA activity was achieved at the percolation threshold of the gradient metal film, just prior to the onset of electrical conductivity, indicating a connectivity between neighboring islands in the film. We demonstrated that the gradient metal films could be
reproducible fabricated with different metal material, which could be used to tune the surface enhanced infrared activity along the surface. These results provide insight into the complex interplay between film properties and SEIRA enhancement, while also allowing for a method to tune for maximum enhancement.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. The material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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2.7 References


2.8 Support Information

Figure. S2.1 Schematic view of UV-Vis and Near IR transmission spectroscopy

Figure. S2.2 A) Profilier data from gradient Au film at different locations. B) Plot of Au thickness at different locations on the gradient Au film.
Figure S2.3 Experiment setup of FTIR transmission spectroscopy

Figure S2.4 Transmission FTIR of 38 nm thick film of 1-hexadecanethiol (HDT) spun coat onto a glass slide.
**Figure S2.5** Schematic of setup used for 2-electrode conductivity measurement.

**Figure S2.6** Calculated optical transmission through 20 nm silver film with 30% open area.
Figure. S2.7 Optical transmission spectra of A) thicker Ag gradient film B) Au gradient film on glass substrates as a function of position along the surface as denoted by location numbers 1 to 7.
Figure S2.8 AC impedance measurement on A) thicker Ag gradient film B) Au gradient film at different locations (1 to 7) on glass substrates.
Figure S2.9 SEIRA transmission spectra of a HDT monolayer on A) thicker Ag gradient film B) Au gradient film at different locations (1 to 7) on glass substrates.
Figure. S2.10 Enhancement factors for SEIRA of HDT monolayer on A) thicker Ag gradient film B) Au gradient film at different locations (1 to 7) on glass substrates.
3.1 Abstract

Surface enhanced infrared spectroscopy is an analytical technique for enhancing absorption signals of vibrational modes associated with analytes in infrared spectroscopy. The surface enhanced infrared absorption (SEIRA) activity is strongly related with the morphology of SEIRA active substrates. In this work, we synthesize and immobilize gold nanoparticles (AuNPs) on indium tin oxide (ITO) glass substrates by utilizing pulsed electrodeposition (PED) technique. By adjusting the overpotential and deposition cycles, the size and density of AuNPs are able to be well controlled on the surface. The prepared AuNP films are served as SEIRA active substrates in SEIRA. Scanning electron microscopy (SEM) and infrared (IR) spectroscopy are utilized to analyze the correlation between SEIRA activity and film morphology on the surface. Infrared spectra of 1-hexadecanethiol (HDT) monolayer show enhanced C-H vibrational signals on the AuNP films deposited with different deposition cycles. The maximum SEIRA enhancement occurs near the percolation threshold of AuNP films, which is related with the nano-gap regions between adjacent AuNPs. The gap distance between adjacent AuNPs would gradually become smaller with the growth of the nanoparticles and these nano-gap regions are known as “hot spots” which provide high SEIRA activity absorption sites. The film exhibited maximum SEIRA activity is able to be
monitored with optical transmission spectroscopy. This protocol provides a facile and cost effective approach to fabricate SEIRA active substrates, no template or surfactant is needed during the fabrication process. The prepared SEIRA active substrates show good reproducibility and controllability to tune SEIRA enhancement factors. It has appreciable potential to be applied in routine SEIRA applications to improve its performance.

3.2 Introduction

Surface enhanced infrared absorption (SEIRA) spectroscopy is a convenient approach for sensitively probing analytes adsorbed on metal nanostructured substrates. It provides the information of vibrational modes associated with the structure of analytes. Since Hartstein et al. discovered the enhanced infrared absorption signals by adsorbing $p$-nitrobenzoic acid on Ag island substrate in 1980, SEIRA spectroscopy technique has received much attention in the last twenty years. With its high sensitivity, various fields are able to take advantage of this technique, such as in situ characterization of species on metal electrode surfaces, biomedical sensing, and characterizing ultrathin films.

Metal island films represent the most widely used substrate for SEIRA due to the simplicity in their preparation and broad applicability. Coinage metals, such as Ag and Au, are the most widely employed metals for the SEIRA active substrates. The morphology of metal island film, such as the size, shape, density and inter particle spacing of metal nanostructures on the surface, plays an important role in SEIRA activity. Several studies have found that the maximum SEIRA enhancement of metal island films is at or near the percolation threshold of the films. However, to control the morphology of metal island films, it is significant but difficult to optimize the parameters during the film fabrication process. In recent years, engineered periodic nanostructures have also been developed for serving as SEIRA active substrates. These nanostructures could be
fabricated via electro-beam lithography, focus ion beam lithography or photolithography.\textsuperscript{19-21} Even though these periodical nanostructured substrates show good reproducibility and tunability, the complicated procedures, necessity for advanced equipment and high cost restrict their future application and limit the popularization of the SEIRA technique.\textsuperscript{22,23}

Until today, the fabrication of sensitive, reproducible and cost effective SEIRA active substrates is still not proven, which limits SEIRA spectroscopy as a routine analytical tool applied in industry. Therefore, it is critical to identify methods to manipulate the metal nanostructured surfaces by optimizing preparation parameters during the fabrication process. The controllability and reproducibility for creating SEIRA active substrates showed high SEIRA activity will be a main topic of this research.

Metal island substrates served in SEIRA can be fabricated in various ways. The common methods include physical vapor deposition,\textsuperscript{24-27} electrochemical deposition\textsuperscript{28,29} and electroless deposition.\textsuperscript{5,30} Utilizing electrochemical deposition technique to fabricate SEIRA active metal island films is very attractive. Compared with other techniques, it has a lower fabrication cost, less time consuming and easier procedures to control. Several approaches have been claimed to fabricate controllable metallic nanostructures on the conductive substrates by utilizing electrochemical deposition method, such as seed-mediated growth nanoparticles,\textsuperscript{31,32} employing a cyclic voltammetry scan,\textsuperscript{33,34} employing double potential pulses,\textsuperscript{35,36} or deposit seed at a constant potential step followed with cyclic voltammetry scan.\textsuperscript{37} However, no paper has been found on known publications about utilizing pulsed electrochemical deposition (PED) technique to control AuNPs morphology on ITO glass and serving them as substrates in SEIRA.

Previous studies concerning pulsed electrochemical deposition found that this approach favors the initiation of nucleation sites and contributes to a high dispersion of the deposits
compared with other electrochemical methods.\textsuperscript{38-40} By manipulating the parameters of the pulsed electrochemical deposition, the size and density of nanoparticles as well as the gap distance between adjacent nanoparticles can be controlled on the surface. By manipulating the metal morphology on the electrodes, it is possible to offer another route to fabricate highly sensitive and reproducible SEIRA active substrates.

In this work, the PED technique was used to prepare the gold nanoparticle films on the ITO glasses and served them as substrates in SEIRA. By adjusting the deposition potential and deposition cycles, different surface morphology would show up on the ITO glass electrode surface. Scanning electron microscope (SEM) was utilized to characterize the morphology of AuNP film prepared with different deposition cycles. A large amount of monodispersed AuNPs with a small diameter could be deposited on the electrodes with low deposition cycles. With further continuous growth of AuNPs with long deposition cycles, more and more Au would be covered on the surface. The size of gold nanoparticles became larger and the nano-gap area between neighboring nanoparticles would become smaller.

SEIRA analysis on these film were further explored by coating 1-hexadecanethiol (HDT) monolayer on the top. In infrared spectra, the C-H vibrational mode showed different enhancement factors on films prepared with different deposition cycles. It has been proven that SEIRA activity has a strong correlation with the nanoparticle film morphology and the maximum SEIRA enhancement occurs at the percolation threshold of AuNP films. Optical transmission spectroscopy would be useful to monitor the changes of film morphology near the percolation threshold since the spectral features sharply react to the slight changes of morphology. By utilizing PED technique, we were able to control the size and density of the AuNP films on the surface. The location of localized surface plasmon resonance (LSPR) peak in transmission spectra could be tuned as well.
This protocol provides a conveniently tool to control the growth of surface confined AuNPs and the prepared films showed good tunability and high sensitivity in SEIRA. These characteristics enable this approach to be a potential tool for preparing controllable SEIRA active substrates and improve the performance of SEIRA spectroscopy in the future.

3.3 Experimental

**Materials and Reagents.** Indium tin oxide (ITO) glasses (sheet resistance 8-12 Ω/sq; size, 25*75*1.1mm) were purchased from Delta Technologies (Loveland, CO). Gold (III) chloride trihydrate was obtained from Sigma Aldrich (St. Louis, MO). Sulfuric acid, ethanol, acetone and isopropanol were obtained from Fisher Chemical (Waltham, MA). 1-Hexadecanethiol (HDT, 99%) was purchased from Sigma Aldrich (St. Louis, MO). Deionized water with electrical resistivity more than 18 MΩ cm was used for aqueous solutions and rinsing the samples (NANOPure, Barnstead, Dubuque, IA).

**Pulsed Electrochemical Deposition (PED) of Gold Nanoparticles (AuNPs).** Prior to deposition, ITO glasses were first successively cleaned in acetone, ethanol and isopropanol for at least 20 minutes each with sonication and then dried under a stream of N₂ gas. The AuNPs were then deposited on clean ITO glass substrates by PED in 0.25mM HAuCl₄ and 20mM H₂SO₄ solution with a CHI900 electrochemical workstation (CH Instruments Inc., Austin, TX) in differential pulse amperometry mode with a standard three electrode system (Figure 3.1A). The cell was completed by using a piece of ITO glass as the working electrode, a stainless steel sheet as the counter electrode and an Ag/AgCl reference electrode. The schematic diagram of the PED process was shown in Figure 3.1B. The lower potential limit E₁ indicated the deposition potential and the upper potential limit E₂ indicated the potential where zero current was applied. Each cycle
consisted of an on-time \((t_1)\) and an off-time \((t_2)\). Each time length was set as 1s. The deposition was completed by regulating the pulse amplitude and deposition cycles. After the deposition was finished, the Glass/ITO/AuNPs electrode was removed from the cell. The electrode was gently rinsed further with DI water and dried under a stream of \(\text{N}_2\) gas for further analysis.

**UV-Vis Transmission Spectroscopy.** Transmission spectra were collected by a custom built apparatus. White light from a broadband, halogen source fiber illuminator (Thorlabs, Inc., Newton, NJ) passed through a 2mm diameter aperture before illuminating the sample. The transmitted light was collected through a 600µm fiber optic UV-Vis spectrometer (400-1100nm, SD2000, Ocean Optics, Inc., Dunedin, FL). The reference spectra were taken from the clean ITO glass surface on the same sample. The schematic was shown in Figure S3.1 (Support Information).

**Scanning Electron Microscopy (SEM) Characterization.** SEM images from each sample were obtained by using a JSM-6010PLUS/LA analytical scanning electron microscope (JEOL Ltd., Peabody, MA). It operates at an accelerating voltage of 20kV and using an in-lens annular secondary electron detector. Each image was further analyzed with image J.

**Self-Assembled Monolayer deposition.** 1-Hexadecanethiol (HDT) was used as probe molecule for quantitative SEIRA spectroscopy analysis. To coat the HDT monolayer on the substrate, the Glass/ITO/AuNPs electrodes were immersed in 0.01M HDT solution dissolved in ethanol for 4hrs. The thiol group can be chemically bonded with gold which forms a self-assembled monolayer on the surface. The samples were subsequently rinsed with ethanol to remove non-bonded thiols and dried with nitrogen gas.

**Infrared Transmission Microscopy.** The IR transmission spectra were collected using a Fourier Transform Infrared (FTIR) spectrometer (Nicolet iS50, Thermo Scientific, Waltham, MA).
equipped with Nicolet Continuum FTIR Microscope and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Spectra collection was conducted in transmission mode. The infrared light source would directly passed through the samples from the microscope and collected by a 15X Reflachromat objective. The schematic view was shown in Figure S3.2 (Support Information). The aperture area was 150μm*150μm. Spectra were collected from HDT coated Glass/ITO/AuNP substrate relative to the clean ITO glass surface. All the spectra were collected at a resolution of 4cm\(^{-1}\) with 32 scans.

**Figure 3.1** A) Schematic view of pulsed electrodeposition of AuNPs in a solution of 0.25mM HAuCl\(_4\) in 20mM H\(_2\)SO\(_4\). The working electrode is a clean ITO glass. The counter electrode is a piece of stainless steel sheet. B) Schematic diagram of the pulsed electrodeposition technique.
3.4 Results and Discussion

3.3.1 Pulsed electrochemical deposition of AuNPs on ITO glass.

Figure 3.2 shows a cyclic voltammogram (CV) of a clean glass/ITO electrode measured from 1.5V to -1.2V at a scan rate of 0.1V/s in a solution of 0.25mM HAuCl₄ in 20mM H₂SO₄. On the forward scan, a cathodic peak at ~190mV was observed which results from the reduction of AuCl₄⁻ to metallic Au⁰ on the electrode surface. The corresponding reaction occurs at the electrode surface was shown here: ⁴¹

\[
AuCl_4^- + 3e^- \rightarrow Au^0 + 4Cl^- \quad E^0 = 0.994V \text{ vs NHE} \quad (1)
\]

There was a second cathodic peak observed around -1.2V due to the hydrogen evolution reaction by reduction of water. The cathodic current flowed until 0.5V in the reverse scan, which is the onset for Au oxidation peak centered at around 0.8V. This indicates the AuCl₄⁻ was kept reducing to Au⁰ by reaction 1 above. It can be seen that the reduction of AuCl₄⁻ started around 0V during forward scan but remained up until 0.5V in the reverse scan, this fact comes from the nucleation and growth phenomenon of gold nuclei.

In order to reduce the AuCl₄⁻ to metallic Au, an activation barrier must be overcome to form Au nucleation sites on the electrode surface. This is the reason that a significant current from the reduction of AuCl₄⁻ does not show up until 0V in the forward scan even though the AuCl₄⁻ reduction reaction is thermodynamically possible at more positive potentials. The Au nucleation sites formed below 0V were able to catalyze the reduction of AuCl₄⁻. And the AuNP seeds make the reduction of AuCl₄⁻ thermodynamically easier as the Au seeds reduced the activation energy of the reduction reaction. This is due to the fact that Au seeds possesses large surface to volume ratio and relatively high surface energy. Therefore, Au deposition would occur at more positive potentials in the reverse scan. To synthesis Au nanoparticles on a clean glass/ITO electrode, it is
necessary to form Au nucleation sites first to overcome an energy barrier, which is achieved by applying a relative large potential (below 0V). Then the formed Au nuclei are able to catalyze the reduction of AuCl$_4^-$ at more positive potentials (until 0.5V). As a result, a characteristic cathodic current crossover until 0.5V was observed in the CV curve. This a well-known phenomenon which has been studied previously.$^{37,42}$

![Cyclic voltammogram (CV) of Glass/ITO electrode obtained in 0.25mM HAuCl4 + 20mM H2SO4 solution at a scan rate of 100mV/s. The arrows show the scan direction which begins at 1.5V and ends at -1.2V.](image)

**Figure 4.2** Cyclic voltammogram (CV) of Glass/ITO electrode obtained in 0.25mM HAuCl4 + 20mM H2SO4 solution at a scan rate of 100mV/s. The arrows show the scan direction which begins at 1.5V and ends at -1.2V.

The aims here were achieving high quality SEIRA performance on the AuNP films prepared by electrochemical deposition. And the pulsed electrochemical deposition would be the approach to fabricate controllable SEIRA-active substrates with high sensitivity. The PED method used here would be a square wave by changing the potentials periodically (Figure 3.1B). It consists of a series of pulses with a period of cathodic current at E$_1$ followed by a period with no current at E$_2$. The potential amplitude, width, concentration of electroactive species and deposition time would have a great influence on the AuNP morphology on the surface. For the sake of simplicity, the concentration of all the experiments were carried out in 0.25mM HAuCl$_4$ + 20mM H$_2$SO$_4$.
solution. The pulse width for both periods was set as 1s. Based on the CV curve collected in Figure 2, the potential of E$_2$ was set as 0.5V as no gold would be reduced on the surface at this value. The effect of potential amplitude and deposition time will be investigated in the following section.

To characterize AuNP morphology on ITO electrodes, SEM was utilized to obtain their visual representations. Figure 3.3 and Figure S3.3, S3.5 (Support Information) showed SEM images of AuNPs deposited on ITO electrodes under different conditions. The dark, grainy background corresponded to the bare ITO glass and the bright, spherical features represent the AuNPs deposited on the glass/ITO electrode. Figure S3.3 (support information) showed SEM images of Au nanoparticles deposited by PED method and direct plating method at -0.8V with 150s deposition time. As could be seen, the Au nanoparticles fabricated by the direct plating method had a larger particle size with a lower particle density on the surface. Figure S3.4 (support information) illustrated the particle size distribution for each method. The standard deviation of AuNP size of direct plating method (18.4%) was larger than the PED method (11.2%). These are due to the diffusion controlled mass transport existing during the direct electrodeposition process.$^{43}$

In the PED approach, the AuNPs appeared on the surface showed a smaller size with a larger particle density. During the deposition process, the reduction reaction on the electrode (activation process) and the mass transfer of Au ions from bulk solution through the diffusive layer toward the electrode (diffusion process) coexist. In the cathodic half cycle of PED approach, the Au ions are consumed due to the reduction reaction on the electrodes and followed with nucleation and growth mechanism. The Au ions diffuse to electrodes compensates the depletion. However, once the consumption rate is higher than the diffusion rate, a depletion layer would be formed which limits the mass transport of Au ions. In the anodic half cycle of PED approach, the consumed Au ions are replenished which eliminate the depletion layer. Therefore, PED approach facilitates
the Au ions mass transport and the Au favors the initiation of grain nuclei on the surface under cathodic half cycle. A large amount of nucleation sites could be fabricated on the surface which results better grained structures than conventionally plated techniques.\textsuperscript{44,45} As a result, Au nanoparticles with narrower size distribution were able to be fabricated on glass/ITO electrodes through PED approach.

To get more information of morphology of AuNP films deposited on ITO electrodes by PED method, Figure S3.5 (Support Information) represents SEM images of AuNPs deposited on ITO glass surfaces, respectively, with different deposition potentials ($E_1$) of -0.9V, -0.8V, -0.7V, -0.6V and -0.4V. All the films were completed with 150 deposition cycles. The size of AuNPs in the images clearly increases with decreasing electrode potentials. But the density of AuNPs decreases with decreasing electrode potentials. Based on the analysis of collected SEM images, the average diameter of AuNPs were 35±2.6, 50±5.6, 56±7.7, 72±18.4 and 110±73.1nm corresponding to different deposition potentials of -0.9V, -0.8V, -0.7V, -0.6V and -0.4V (Figure S3.6A, support information). The density of AuNPs decreased from 194 particles per 1μm$^2$ at -0.9V to 4 particles per 1μm$^2$ at -0.4V, respectively (Figure S3.6B, support information).

The difference of the particle size distribution and density at different deposition potentials is due to the nucleation and subsequent growth mechanism followed by electrochemical deposition of gold.\textsuperscript{41,43} At high overpotential (-0.9V), the electrode surfaces were deposited with small AuNPs with a large density, as the formation of gold nucleation sites is energetically favorable all over the electrode surface. A large amount of gold nucleation sites are able to be generated and leads to a smaller average diameter AuNPs. At small overpotentials, the energy is not sufficient to generate gold nucleation sites all over the surface rapidly. However, the gold nuclei could catalyze the Au reduction reaction further which leads to the preferential growth of Au around the nucleation sites.
This results a lower density of AuNPs with much larger average diameter than the AuNPs formed at more negative potentials. The energy barrier is significantly related with the electron energy which is governed by the potential.

In this work, the value of $E_1$ was set as -0.9V, as there would be a large amount of gold nucleation sites appearing on the electrode surface and it is easier to control the AuNP film morphology over the surface as its further application in SEIRA. Figure 3.3 shows a series of SEM images of AuNP films fabricated by PED method with different cycles (from 50 to 3000 cycles) from the solution of 0.25mM HAuCl$_4$ in 20mM H$_2$SO$_4$. The AuNPs were deposited at 0.9V for 1s and pulsed at 0.5V for 1s in each cycle. Based on the observation of SEM images, the morphology of AuNP films could be well controlled by adjusting electrodeposition cycles. The particle size distribution for each image is shown in Figure 3.4. With low deposition cycles (below 600 cycles), it was clear to see that the Au nanoparticles appeared on the glass/ITO electrode surface have a smaller average diameter with a narrower size distribution. By increasing deposition cycles (from 1200 to 2400 cycles), the particle size keeps increasing and the size distribution becomes broader. When the deposition time reached 3000 cycles, small particles (diameter below 140nm) could barely be found on the surface which indicate that the individual AuNPs coalesced with neighboring particles.

The average size of Au nanoparticles were 34 ± 2.6, 35 ± 3.1, 42 ± 4.8, 54 ± 8.1, 64 ± 13, 73 ± 18.6 and 72 ± 19.7 nm, respectively, for 50, 150, 300, 600, 1200, 1800 and 2400 deposition cycles in pulsed electrochemical deposition (Figure 3.5A). Therefore, the size of AuNPs on the glass/ITO electrode surface were able to be controlled by adjusting the number of electrodeposition cycles. It is worthwhile mentioning that the standard deviations of the average particle size increased with deposition cycles (7.7%, 8.8%, 11.4%, 15%, 20.4%, 25.5% and 27.3% for 50, 150,
300, 600, 1200, 1800 and 2400 deposition cycles, respectively). The particle density trend for AuNP films prepared with different deposition cycles was shown in Figure 3.5B. The density would be maximum at 150 deposition cycles, but then decreased with increasing of deposition cycles.

During the deposition process in PED technique, the Au favors forming nucleation sites over the surface due to the nucleation mechanism which results a maximum particle density at 150 deposition cycle. However, the nucleation and growth mechanism both exist during the deposition process. New nucleation sites could be formed on the surface and subsequent grew at a later time, which leads to a higher standard deviation of AuNP diameter by increasing the deposition cycles. As the deposition continues, the AuNP size are becoming larger and coalescence effect appeared on the surface which results a broader size distribution and a lower particle density on the surface.

In addition, Ostwald electrochemical coarsening mechanism could play a role in the change of particle density and size distribution in our experiment. As the particle size distribution was less uniform with increasing the deposition cycles, an electrical unbalance would occur due to the different work function of particles with different size. At electrical equilibrium, the smaller particle would have a partial positive charge and the larger particle would have a partial negative charge. In addition, the interparticle diffusion coupling effect occurs with a high density of nanoparticles on the surface. A diffusion shielding effect of nanoelectrode ensembles occurs when the small particles are close. It leads to an inhomogeneous distribution of AuCl$_4^-$ around the particles and results in non-uniform growth in subsequent electrochemical reactions. The size disparities created a gradient concentration which allowed for the diffusion of AuCl$_4^-$ toward larger particles. More Au ions would be reduced onto a larger Au nanoparticle by accepting three electrons. The larger nanoparticle would take three electrons from a neighboring smaller
nanoparticle through the conducting substrate to reestablish electrical equilibrium. The smaller particle with even more positive charge would dissolve Au ions into the solution to reestablish electrical equilibrium. Therefore, the particle density would decrease as the larger particles scavenged smaller particles on the surface. This mechanism can also be responsible for broadening AuNP size distribution with increasing deposition cycles. It was important to note that most AuNPs aggregated and showed a different morphology on the surface when the deposition cycles reached 3000 cycles. Overall, the size distribution of particles is much more uniform than conventional electrochemical deposition techniques, especially for low deposition cycles (below 600 cycles) as monodispersed AuNPs are fabricated on the electrode surfaces.
Figure 4.3 SEM images of AuNPs deposited on the ITO glass by pulsed electrodeposition method at different deposition cycles: (A) 50 cycles, (B) 150 cycles, (C) 300 cycles, (D) 600 cycles, (E) 1200 cycles, (F) 1800 cycles, (G) 2400 cycles, (H) 3000 cycles. Each cycle consists of 1s for deposition at -0.9V and 1s for pulsing at 0.5V. The scale bar represents 500nm in each image.
Figure 4.4 particle size distribution of AuNPs deposited on the ITO glass by pulsed electrodeposition method at different deposition cycles: (A) 50 cycles, (B) 150 cycles, (C) 300 cycles, (D) 600 cycles, (E) 1200 cycles, (F) 1800 cycles, (G) 2400 cycles, (H) 3000 cycles.
Figure 4.5 A) AuNP average diameter and B) density dependence on the cycles of pulsed electrochemical deposition.
4.2 Optical property characterization of AuNP film deposited on ITO/glass electrodes.

Nanometer-scale Au nanoparticles were able to absorb light in the visible and/or infrared region due to the excitation of collective electron resonance, known as localized surface plasmon resonance (LSPR).\textsuperscript{49} It occurs when the collective oscillation of the valence electrons in the Au nanoparticle are in resonance with the frequency of light and the electric field radiation drives the conduction electrons into collective oscillation at the metal surface. An enhanced electric field would be created around the metal surface and the light would be maximum absorbed at the resonant frequency.\textsuperscript{50} A series of UV-visible transmission spectra from the AuNPs/ITO/Glass substrates fabricated by PED approach with different deposition cycles were represented in Figure 3.6A. The sharp and strong bands existing around 520-600nm in spectra are contributed to LSPR effect. The wavelength of LSPR band was related with the Au nanoparticle shape, size, and local dielectric environment.\textsuperscript{51}

In the UV-vis transmission spectra, the wavelength of transmission dips (absorbance peaks) corresponding to the LSPR band was observed to increase with the number of cycles, from 50 to 3000 deposition cycles (Figure 3.6B). The absorbance peak with an obvious redshift was related with Au nanoparticle morphology on the surface. By increasing the deposition cycles, the particle size increased but the particle density decreased which lead to a decrease of gap between Au nanoparticles on the surface. The plasmon resonance wavelength is subjected to a spectral red shift with larger nanoparticles or smaller interparticle nanogaps,\textsuperscript{51} which is in agreement with the spectral shifts of the plasmon dips observed in UV-Vis transmission spectra from AuNP films synthesized with different deposition cycles.

Meanwhile, it was important to note that the LSPR band had a narrow bandwidth for AuNP films prepared with low deposition cycles (below 600 cycles), as the electrochemically formed
AuNPs had a spherical shape and high monodispersity on the surface. By increasing the number of deposition cycles, the LSPR band gradually became broader. When the number of deposition cycles reached 2400 cycles, the tail of the band extended into near infrared region. This is due to the dense, crowded Au nanoparticle morphology on the surface. With longer deposition cycles, the AuNPs would have a larger size also a shorter distance between adjacent AuNPs. The dipole of the adjacent Au nanoparticles, induced by the incident electric field, could interact with each other to broadening LSPR band in the transmission spectra owning to the dipole-dipole electromagnetic interactions. When the number of deposition cycles reached 3000 cycles, the broad absorption peak was observed at around 600nm and the LSPR signal was not very intense. It indicated that the surface morphology was close to a continuous gold film on the substrate.\textsuperscript{52} With PED approach, the location of LSPR bands were able to be adjusted by controlling the number of deposition cycles. The optical properties of the AuNP films would be a tool to monitor their SEIRA activity performance.
Figure 4.6 A) UV-Vis transmission spectra of AuNPs/ITO/Glass fabricated by pulsed electrochemical deposition method with different deposition cycles, range from 50 to 3000 cycles. B) The transmission peak of LSPR in the UV-Vis spectra versus the deposition cycles.
4.3 SEIRA Activity of the AuNPs/ITO/Glass Substrates.

The prepared AuNP films with controlled surface morphology were served as SEIRA active substrates. SEIRA activity was measured with a self-assembled monolayer coated on the AuNP film substrates. 1-Hexadecanethiol (HDT) was chosen as the probing monolayer since a monolayer could be easily adsorbed on the AuNP films. Its thiol group could form a strong Au-S bond on the gold surface. Figure 3.7 showed a series of infrared transmission spectra of HDT monolayer coated on the AuNPs/ITO/Glass substrates prepared with different deposition cycles. The transmission peaks can be assigned to CH vibrations of HDT monolayer as follows: antisymmetric CH$_2$ stretching, 2915 cm$^{-1}$ and symmetric CH$_2$ stretching, 2848 cm$^{-1}$. The peak magnitudes of C-H vibration modes were obviously changed with different deposition cycles on AuNPs/ITO/Glass substrates.

Figure 3.8 represented the transmission peak intensities of the antisymmetric and symmetric CH$_2$ stretching modes of HDT monolayer as a function of deposition cycles of the prepared AuNP films. At the early stage of AuNPs growth (below 600 cycles), the intensity of C-H vibrational modes were weak. With increasing the deposition cycles (above 1200 cycles), the IR signals became stronger and achieved the maximum intensity at 2400 deposition cycles. The signals at 2400 deposition cycles were 25 times stronger than the initial stage of Au seed film prepared with 50 cycles. When the deposition cycles reached 3000 cycles, the peak magnitude of CH vibrational modes started decreasing. The intensity clearly changed with deposition cycles contributed to different Au nanoparticle morphology on the surfaces. The maximum enhancement achieved with 2400 deposition cycles indicated this morphology was near the percolation threshold of nanoparticle film. Beyond this point, the enhancement decreased in both directions.
Figure 4.7 SEIRA measurement taken of HDT monolayer on AuNPs/ITO/Glass samples with deposition cycles. The cycles range from 50 to 3000 cycles. The spectra are offset for clarity.
Figure 4.8 Transmission peak intensity of C-H stretching vibrations of HDT monolayer as a function of different deposition cycles on AuNP samples.

The enhancement of SEIRA signals in IR spectra is strongly related with the electromagnetic field on the surface. The molecule interact with the electric field can be described in classical electromagnetic theory. The description of the process is semi-classical and the interaction is known as the semi-classical theory of quantum transition. The infrared absorption intensity of vibrational modes in spectra is proportional to $(E \cdot \mu)^2$, where $E$ is the electric field intensity and $\mu$ is the dipole moment change of vibrational modes. During the deposition process, the Au particle size, shape and density changed on the substrate. The morphological development caused drastic changes of the electromagnetic field on the AuNP films.

Besides showing different optical properties, an enhanced electric field would be produced around gold nanoparticle surface when LSPR was excited. This enhanced electric field is an evanescent field with exponential delay away from the metal surface. With the excitation of LSPR, the Au nanoparticle was polarized and a dipole was induced into the nanoparticle. When the Au particles were close to each other, the dipole inside the nanoparticle would interact with other
nanoparticles. The LSPR band could be shifted from the visible to the IR regions and IR right could more effectively couple to the nanoparticles. At such resonance a huge electromagnetic enhancement occurred in nanometer gaps due to the coherent oscillation of the free electrons in the Au nanoparticles. The narrow gap regions that harvest high electromagnetic fields were assumed to be “hot spots” that were believed to serve as the strongly SEIRA active absorption sites.

By increasing deposition cycles, more and more Au ions were reduced at the electrode and the surface coverage was increased (Figure 3.9A). As the size of AuNPs became larger, the nanogap distance between the adjacent AuNPs became smaller (Figure 3.9B). Previous studies have demonstrated that decreased separation distance could produce a stronger electric field in the gap region. At the early stage of AuNP deposition process (below 600 cycles), the nanogap distances were over 30nm which could not contribute to high SEIRA performance. At 2400 deposition cycles, the gap distance was already below 10nm. It had been demonstrated that an extremely intense electric field was produced in this range. As more “hot spots” were produced, enhanced SEIRA activity was achieved on the AuNP film. This film was able to be monitored with optical transmission spectroscopy, as the LSPR band would be extended into infrared region due to the dipole coupling between nanoparticles. By keep increasing deposition cycles to 3000, the nanogap distance increased as the particles aggregated with neighboring particles and part of the narrow gap regions were filled with Au. As less “hot spots” were produced on the surface, a lower SEIRA activity performance was achieved on the AuNP film. It could be assumed that the AuNP morphology with 2400 deposition cycles was near the percolation threshold as maximum SEIRA activity was achieved at that region. It was demonstrated that the AuNP morphology could be well controlled by pulsed electrochemical deposition approach to achieve the maximum SEIRA performance.
Figure 3.9 A) AuNP surface coverage dependence on the cycles of pulsed electrochemical deposition. B) The nanogap distance between AuNPs with different deposition cycles (100 nanogaps are analyzed).
3.5 Conclusions

In this work, we utilized pulsed electrodeposition (PED) method to control gold nanoparticle morphology on indium tin oxide (ITO) glass. The fabricated AuNP films were served as SEIRA active substrates. By manipulating the overpotential and deposition cycles, the particle size and distribution could be well controlled on the surface. Especially for low deposition cycles with high overpotential, gold nanoparticles with high monodispersity were distributed over the substrate. In addition, the nanogap distance between the adjacent gold nanoparticles could be controlled with deposition cycles. These narrow gap regions produced numerous “hot spots” on the substrate for providing high SEIRA activity performance. The maximum SEIRA activity was achieved near the percolation threshold of gold nanoparticle film, which could be monitored through optical transmission spectroscopy as the spectral features sharply react to the slight changes of nanoparticle morphology on the surface. The pulsed electrochemical deposition protocol provides an economical, feasible and reproducible method to fabricate gold nanostructures on the surface. The prepared AuNP films have the great potential to be used as controllable SEIRA active substrates for improving SEIRA performance in various applications. Besides that, the rapid, direct synthesis of monodisperse gold nanoparticles over the surface can also be further utilized to motivate future applied studies.

3.6 Acknowledgement

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3.7 References


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3.8 Support Information

Figure S3.1 Schematic view of UV-Vis transmission spectroscopy
Figure. S3.2 Schematic of Infrared (IR) microscope transmission spectroscopy
Figure S3.3 SEM images of AuNPs deposited with PED method (A) and direct plating method (B) at -0.8V with 150s deposition time. The scale bar represents 500nm in each image.
Figure. S3.4 Particle size distribution of AuNPs deposited A) with PED method and B) direct plating method at -0.8V with 150s deposition time.
Figure S3.5 SEM images of AuNPs deposited under different potentials of (A) -0.9V, (B) -0.8V, (C) -0.7V, (D) -0.6V, (E) -0.4V by PED method with 150 deposition cycles.
Figure. S3.6 A) Particle diameter and B) particle density of AuNPs deposited under different potentials of -0.9V, -0.8V, -0.7V, -0.6V, -0.4V by PED method with 150 deposition cycles.
CHAPTER 4

MECHANICAL TUNABILITY OF SURFACE PLASMON RESONANCE USING DEFORMABLE DIFFRACTION GRATINGS
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4.1 Abstract

Diffraction gratings could serve as platforms for exciting surface plasmon resonance (SPR). The spectral location of the plasmonic response could be manipulated by the grating periodicity or the light incident angle. In this work, we reported two tunable grating platforms which were able to tune the SPR response by controlling the local grating topology. One is a compressive metallic grating platform on a PDMS substrate. The other is a spontaneously chirped Au/PDMS grating platform which is fabricated through mechanical buckling approach. On both tunable grating platforms, the grating pitch could be controlled by compressing the elastomeric substrates mechanically, which shifted the corresponding wavelength of SPR peaks in spectra. The tunability of the plasmonic response from each platform was demonstrated in the infrared spectra via FTIR spectrometer. A series of measurements, including optical diffraction measurement, atomic force microscopy and optical microscopy, were carried out to compare the grating geometry with the location and intensity of corresponding plasmonic response. These results illustrated that the two substrates represented two highly tunable and flexible grating platforms for controlling the locations of SPR response. They could serve as information rich substrates for future sensor development.
4.2 Introduction

Surface plasmon resonance (SPR) phenomenon observed on noble planar metal surfaces or nanostructures has attracted wide interest for its potential applications in photonics, optics, spectroscopic techniques and chemical and biological sensors.\textsuperscript{1-6} SPR is the collective oscillations of electrons excited by impinging light at the interface of two media with positive and negative permittivity.\textsuperscript{7} Metal structures at nanoscale such as thin film islands, nanospheres, nanorods, nanoshells would show a strong light absorption and enhanced electromagnetic fields around the surface when SPR is excited.\textsuperscript{8-11} In addition, continuous metal films with specific configurations would exhibit similar SPR effects with SPR excitation.\textsuperscript{12}

It is highly desirable to tune the SPR wavelength in various applications. One motivation comes from the surface enhanced spectroscopies, such as surface enhanced Raman scattering (SERS) spectroscopy\textsuperscript{13-15} and surface enhanced infrared absorption (SEIRA) spectroscopy.\textsuperscript{16-19} By overlapping the SPR frequency with the frequency of vibrational modes, maximum plasmonic enhancement could be achieved and the performance of above techniques are improved. By tuning the SPR wavelength, more flexibility would be provided in various plasmonic sensing applications. It is significant to fabricate effective structures to manipulate SPR wavelength but the challenge still remains.

With the development over past ten years, much work has been explored for tuning the SPR wavelength. So far, researchers have demonstrated different tuning mechanisms such as optimizing thermal evaporation parameters of metal island films,\textsuperscript{20,21} altering the component of silver islands with other metals or dielectric layers,\textsuperscript{22,23} developing nanosphere lithography to precisely control geometry and spacing of the islands,\textsuperscript{9,24,25} controlling the size and shape of metal
nanoparticles,\textsuperscript{26,27} changing the component ratio of core shell nanoparticles,\textsuperscript{28,29} fabricating tunable Au opening nanoshell ordered arrays via colloidal crystals\textsuperscript{30} and changing the length of linear nanoantennas.\textsuperscript{31} However, most of the mechanisms result in fixed structures after fabrication which limit their applications. A reversible structure to tune the SPR wavelength after fabrication would provide more flexibility and find more applications.

Diffraction gratings could be used as coupler platforms for exciting SPR. It was reported that the SPR wavelength could be controlled by light incident angle or grating pitch value.\textsuperscript{32,33} With mechanical deformation, gratings would provide a highly flexible and controllable platform for SPR excitation. In this regard, the tunability of SPR spectral response on gratings would provide more versatility in plasmonic sensing applications.

In this work, the tunability of SPR response in infrared region via grating based couplers was explored. Two different tunable grating platforms were fabricated and characterized. One platform was compressive grating platform, which utilized laser interference lithography (LIL) to fabricate the holographic gratings. The topology of the gratings were transferred on a thick PDMS substrate. The mechanical compression of metallic PDMS grating substrates effectively changes the pitch value, which was able to shift the location of SPR response in infrared (IR) spectra. The other tunable platform was a spontaneously chirped grating platform fabricated via buckling of thin stiff film on elastomeric substrates using mechanical deformation. The periodicity of the grating structure was directly related with the film thickness on the surface. Here a gradient Au film was deposited on the PDMS substrate and deformed with mechanical compression. As a result, a spontaneously chirped Au/PDMS grating platform could be fabricated and the SPR response was shifted at different locations based on the corresponding pitch value on the surface. The location of SPR response from grating based couplers were presented in IR spectra. Experimental data
demonstrated that the SPR peaks were able to be shifted in a large range of wavenumbers in spectra on both tunable grating platforms with mechanical deformation. Diffraction measurement was used for characterizing the periodicity and the diffraction efficiency on both grating platforms. The magnitude and location of SPR response were strongly related with the geometry of gratings.

4.3 Experiment Section

Materials and Reagents. Microscope glass slides were purchased from Fisher (Waltham, MA). Polydimethylsiloxane silicone (PDMS) elastomer kit (SYLGARD 184) was purchased from Dow Corning (Midland, MI) and used as received. Microposit S1813 positive photoresist and Microposit 356 developer were obtained from Dow Chemical Co (Newark, DE). Gold target (99.99% purity) was purchased from AJA Intentional, Inc. (North Scituate, MA). Deionized water with electrical resistivity more than 18 MΩ cm was used to rinse and clean the samples (NANOPure, Barnstead, Dubuque, IA).

Fabrication of Compressive Grating Platform. The diffraction gratings were fabricated by using laser interference lithography (LIL) in a Lloyd’s mirror interferometer. The S1813 positive photoresist was first spun coated on clean glass slides at 4000rpm for 60s using a Laurel model WA-650MZ-23NPP spin coater (Laurell Technology Corp., North Wales, PA). The slides coated with photoresist were then placed on a hot plate at 90°C for 1min and cooled with compressed air. Then the slides were placed in the self-build Lloyd’s mirror interferometer and its apparatus was shown in Figure S4.1 (Support Information). A 405nm diode (Oxxius, Lanion, France) laser was utilized to expose the photoresist layer to fabricate a sinusoidal interference pattern on the surface. The grating periodicity was controlled by adjusting the angle of the Lloyd’s mirror which was mounted on a computer controlled rotation stage (ThorLabs, Newton, NJ). After
exposing, the slides were post baked on the hot plate at 110°C for 3min, cooled with compressed air and developed in developer solution for 1min. Finally, the slides were rinsed with DI water and dried in a stream of nitrogen gas. The grating pattern would appear on the surface. The pitch of fabricated gratings was estimated via diffraction measurement. Once desired gratings were fabricated, the topology of gratings was transferred to a PDMS master. 100nm gold was deposited on the grating surface at a rate of 1Å/s by sputter coating system (ATC 1800-F, AJA Intentional, Inc., North Scituate, MA). The gold film thickness was monitored by a quartz crystal microbalance (QCM). A Micro Vice Holder (S.T.Japan Inc., Japan) was used to compress the grating/PDMS substrate mechanically. The overall process of fabricating compressive grating platform was illustrated in Figure 4.1.

**Fabrication of Spontaneously Chirped Au/PDMS Grating Platform.** A flat PDMS master (4*4*1cm) was used as the substrate for spontaneously chirped grating platform. The sputter coating system (ATC 1800-F, AJA Intentional, Inc., North Scituate, MA) was used for depositing gradient gold film on the substrate. The deposition apparatus was shown in Figure S4.2 (Support Information). Au target was used and the base pressure of this system was below 10⁻⁵ Pa. The target was fixed at an angle of 153° towards the sample stage. The distance between target and the center of the stage would be 12.8cm. The substrate and the QCM were mounted at particular locations on the stage and not rotating during deposition process. Typical conditions were 10 SCCM (standard cubic centimeters per minute) argon gas, yielding a chamber pressure around 15mTorr. The argon gas ions would bombardment on the gold target and the gold atoms would be ejected from target to distribute on the substrate. The sputter power was set to 9W. The deposition rate of Au was around 0.04nm/s. The final mass of metal indicated on the QCM would
be 26nm. A Micro Vice Holder (S.T.Japan Inc., Japan) was then used to compress the PDMS master coated with gradient Au film. With mechanical deformation, the sinusoidal pattern would show up on the surface and its periodicity was related with the Au film thickness at each location.

**Diffracted Transmission Measurement.** Diffracted transmission measurement was used to estimate the periodicity of gratings, as well as the diffraction efficiency. The Olympus BX50 microscope (Leeds Precision Instruments Inc., Minneapolis, MN) was used to collect the diffraction images. A 40X microscope objective was applied for focusing on the grating surface. The bertrand lens and a bandpass filter (FB630-10, ThorLabs, Newton, NJ) were inserted into the observation tube during the image capture. The Bertrand lens allowed capture of diffraction images from gratings with CCD camera (ThorLabs, Newton, NJ) as it could bring the image of interference figures into focus. Collected diffraction figures were analyzed through Image J.

**Chirped Grating Surface Imaging.** Olympus BX50 microscope (Leeds Precision Instruments Inc., Minneapolis, MN) was utilized to obtain the optical microscopy images of the spontaneously chirped Au/PDMS grating platform at different locations. The whole substrate was compressed by 10% and a 40X microscope objective was inserted into the observation tube to focus the surface. A CCD camera (ThorLabs, Newton, NJ) was used to capture the corresponding surface images. All the collected images were analyzed via Image J.

**Atomic Force Microscopy (AFM) Imaging.** A dimension 3100 scanning probe microscope with Nanoscope IV controller (Veeco Metrology, LLC, Santa Barbara, CA) was utilized to collect geometry details of the grating surface. Imaging was conducted in tapping mode using silicon TESP7 AFM tips (Veeco metrology, LLC, Santa Barbara, CA) with a spring constant of ~79N/m and a resonance frequency of ~280 kHz.
Infrared Reflection Absorption Spectroscopy (IRRAS). IRRAS spectra were collected via Fourier transform infrared (FTIR) spectrometer (Nicolet iS50, Thermo Scientific, Waltham, MA) by placing the grating substrate on a specular reflectance accessory (Pike Vee-Max II, Pike Technologies, Madison, WI). The specular reflectance accessory was able to change the incident light angle from 30° to 80° as well as the polarization state allowing for both s-polarized and p-polarized light to be sent to FTIR detector. Spectra were measured at incident angle 70° and under p-polarization state for both compressive grating platform and spontaneously chirped Au/PDMS grating platform. All the spectra were collected at a resolution of 4cm⁻¹ with 64 scans.

Figure 4.1 Compressive grating platform fabrication process. Glass slides were coated with photoresist and exposed via laser interference lithography (LIL). After developing the photoresist, grating topology was transferred to a PDMS master. Grating replicas were then coated with gold film via sputter coating.
4.4 Results and Discussion

4.4.1. Grating based couplers for SPR

The gratings could work as a coupler platform for exciting SPR. Polarized light incident on plain metal film lacks the momentum to excite SPR. However, when incident on a periodic metal film e.g. on a grating surface, the incident light is diffracted at multiple orders and additional momentum is added in it to excite SPR. The SPR matching equation for grating based couplers can be described in the following equation:\(^{34}\)

\[
\frac{2\pi}{\lambda} n_d \sin \theta + m \frac{2\pi}{\Lambda} = \pm Re \left\{ \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \right\} \quad (1)
\]

where \(\lambda\) refers to the wavelength, \(n_d\) refers to the refractive index of the dielectric medium, \(\theta\) refers to the light incident angle, \(m\) refers to the diffracted order, \(\Lambda\) refers to the pitch of the grating and \(\varepsilon_d, \varepsilon_m\) are the permittivities of dielectric and metal medium, respectively. The SPR can be only excited when the electric field of incident light is normal to the grating orientation as it is able to induce a surface charge density. Therefore, p-polarized light need to be used. For the gold-air interface at infrared wavelength in our experiment, the permittivity of gold was much larger than the permittivity of air, so equation (1) could also be simplified as:

\[
\sin \theta + m \frac{\lambda}{\Lambda} = \pm 1 \quad (2)
\]

Based on the above matching equations, the wavelength of the SPR response could be tuned by adjusting the grating pitch value. Decreasing the grating pitch value will blue-shift the SPR peak and increasing the pitch value will red-shift the SPR peak in the IR spectra.
4.4.2. Compressive grating platform

Holographic gratings were fabricated by laser interference lithography in a Lloyd’s mirror interferometer apparatus. The pitch values were dependent on the wavelength of laser source $\lambda$ and interferometer angle $\theta$ and is given by the following equation:

$$\Lambda = \frac{\lambda}{2\sin \theta} (3)$$

Here we fabricated a 3300nm grating by exposing the photoresist coated glass slides with 3.5° interferometer angle. The AFM image in Figure 4.2 showed the grating morphology and height profile. The two images showed a good sinusoidal surface profile achieved by laser interference lithography. Figure 4.2B confirmed the pitch value of grating was ~3300nm and indicated the grating amplitude was ~300nm. The topology of the grating surface was then transferred on a PDMS substrate followed by gold deposition of the substrate by sputter coating. A mechanical stage was used to compress the prepared grating/PDMS substrate precisely.

In order to demonstrate the tunability of the compressive grating platform, diffraction transmission measurement was performed with different degree of mechanical deformation. A bandpass filter of 630nm was used to filter the white light source of the microscope setup. The grating was first compressed perpendicular to the grating grooves. The optical diffraction pattern images of compressive grating platform under different compression percentages were shown in Figure 3A. The images collected from the microscope exhibited three dominant features which corresponded to -1 (left), 0 (middle) and +1 (right) diffracted orders. The relationship between grating pitch and diffraction angle could be described using the following equation

$$\sin \theta_m \Lambda = m \lambda \quad (4)$$
where \( m \) is the diffracted order, \( \theta_m \) is the angle of diffracted order \( m \), \( \Lambda \) is the pitch of grating and \( \lambda \) is the wavelength of the light. The distances between \( \pm 1 \) diffracted orders and 0\(^{th} \) order are proportional to the reciprocal of the grating pitch. Therefore, the distance (\( L \)) of the diffracted spots in the diffraction image (Figure 3A) could be described by

\[
L = D \left( \frac{m\lambda}{\Lambda} \right) (5)
\]

where \( L \) is the distance between \( m^{th} \) diffracted order and zeroth order and \( D \) is a constant associated with the magnification level.\(^{35}\) Equation 4 and 5 indicated the location of 1\(^{st} \) diffracted spots would move further away from 0\(^{th} \) order with smaller grating periodicity. In Figure 4.3A, it was clear to see that the distance between \( \pm 1^{st} \) diffracted spots and 0\(^{th} \) spot kept increasing when the grating platform was compressed. This demonstrated that the pitch of the grating on the PDMS was becoming smaller with deformation.

The grating pitch could also be tuned with other deformation directions on the compressive grating platform. Figure 4.3B displayed a series of optical diffraction pattern images of compressive grating platform when the substrate was compressed parallel to the grating grooves. Based on the positions of \( \pm 1 \) diffracted orders, the grating periodicity became larger with compression.
Figure 4.2 (A) Atomic force microscopy (AFM) image and (B) height profiles of ~3300 nm pitch grating fabricated by LIL. The scale bar represents 2µm.
Figure 4.3 Optical diffraction pattern images obtained from compressive grating platform with different compression percentages. The mechanical deformation direction was (A) perpendicular with grating grooves and (B) parallel to grating grooves. The light spot in the middle was 0\textsuperscript{th} order and the two spots on the edge were ±1\textsuperscript{st} diffracted orders.

However, it was noted that other diffracted orders appeared in diffraction pattern images for the compressive grating platform with large deformation. When the grating was compressed perpendicular to the grating grooves by 23.5\%, the diffracted orders became scattered in diffraction pattern images. This should result from different periodicities of grating structure that generated on the platform (Figure S4.3, Support Information). With large deformation, the PDMS substrate
would start to bend which affected the grating pitch values on the surface. When the grating platform was compressed parallel to the grating grooves with large compression (9.1% and 13.6%), perpendicular diffracted orders appeared in the Figure 4.3B. This illustrated perpendicular grating grooves appeared on the surface which formed a 2D grating geometry. The microscopy image of grating surface compressed by 13.6% was shown in Figure S4.4 (Support Information), which indicated ~10μm pitch grating grooves perpendicular to the original grating structures were formed on the surface. These perpendicular grating grooves actually came from buckling structures of the Au film on elastomeric substrates due to the redistribution of compressive stresses produced by the uniaxial compress.

Buckling of the Au layer with applied compressive stress is an unavoidable consequence of the mismatch in equilibrium deformation states of the metal and elastomer. In order to conserve the volume, the PDMS substrate becomes higher in cross section with a decrease in width when the mechanical deformation direction was parallel to the grating grooves. Consider the grating grooves aligned in the y-axis and the compressive stress applied perpendicular or parallel to the grating grooves. The influence of a compliant substrate on the metal film was described by the stress \( \sigma \). When the stress was applied parallel to the grating grooves, the non-uniform levels of stress along the two axes (\( \sigma_x \) and \( \sigma_y \)) determine the alignment of buckling structure of Au layer. In this case, \( \sigma_y > \sigma_x \) at every point and the displacement of grating morphology relieves the stress along the x direction. Therefore, the buckling structures perpendicular to grating grooves appeared on the platform.

With proper calibration, the pitch value of grating was able to be estimated from diffraction pattern images. The scale bar 0.2µm\(^{-1}\) in the Figure 4.3 indicated the corresponding distance between \( \pm 1^{st} \) and 0\(^{th}\) diffracted order of 5µm pitch grating. Therefore the grating pitch with
different deformation could be calculated from Figure 3 and were shown in Figure 4.4. It was clear to see that the pitch value was strongly linear with the compression percentage in both mechanical deformation directions. These results indicated that this platform could be a predictable way to control the grating pitch by mechanically compressing the substrate.

Figure 4.4 Estimated pitch value of grating via diffracted transmission measurement of compressive grating platform with different compression extent. (A) Compress perpendicular with grating grooves and (B) Compress parallel to grating grooves.
Figure 4.5A displayed a series of IRRAS spectra of compressive grating platform with mechanical deformation perpendicular to grating grooves under different compressive percentages. All spectra were collected at 70 degree incidence and under p-polarization state. The plasmon was excited by coupling incident light to -1 diffracted order and resulted in a distinct and large absorbance in IRRAS spectra. The SPR peak could only be excited when the grating grooves were perpendicular to the incident light. When the PDMS substrate was at its original state, the absorbance peak appeared around 1550cm\(^{-1}\), which was predictable from the matching condition (equation 2). With compression, the SPR peak would move to larger wavenumbers (smaller wavelength). This was consistent with the SPR matching condition as the smaller grating periodicity resulted in a blue shift of SPR response in IRRAS spectra. It appeared that the surface plasmon peak would move ~500cm\(^{-1}\) away from its original position in IRRAS spectra when the compressive grating platform was compressed by 23.5%.

Figure 4.6A showed a series of IRRAS spectra of the compressive grating platform under deformation that was parallel to the grating grooves. The SPR peak moved to smaller wavenumbers (larger wavelength) in the plot as the grating pitch was becoming larger with compression. When the platform was compressed by 13.6%, the SPR peak moved ~150cm\(^{-1}\) away from its original position in IRRAS spectra. Overall, this compressive grating platform could shift SPR peak ~650cm\(^{-1}\) in IR spectra.

It was noteworthy that the magnitude of SPR peak changed during the substrate deformation. When the platform was deformed perpendicular to grating grooves, the SPR peak increased first and then slightly decreased (Figure 4.5B). When the deformation was parallel to the grating grooves, the SPR peak intensity kept decreasing with compression (Figure 4.6B). It was assumed that the SPR peak height was related with diffraction efficiency of the grating. The
diffraction efficiency was estimated by the percentage of ±1\textsuperscript{st} diffracted orders intensity from the whole light intensity. The light intensity profile of each diffraction pattern image in Figure 3 was analyzed by Image J. The relationship of SPR peak intensity and corresponding diffraction efficiency versus compression\% were plotted in Figure 4.5B and Figure 4.6B.

For the perpendicular deformation (Figure 4.5B), the grating diffraction efficiency increased with compression percentage. For sinusoidal grating, its diffraction efficiency was related with the ratio of grating amplitude/periodicity.\textsuperscript{37} When the platform was compressed perpendicular with grating grooves, the substrate would become thicker in cross section with narrowing its length by resisting a change in volume. The grating pitch became smaller and its amplitude should get larger which resulted an increased diffraction efficiency during deformation. It was assumed that more light was able to diffract through -1 diffracted order and more energy could transfer from incident photons to surface plasmons. Therefore, an enhanced SPR absorbance peak could be observed in IRRAS spectra. However with large deformation, for example with 23.5\% compression, the SPR peak became broader and lower in IRRAS spectra. This should result from the bended substrate of compressive grating platform. The curvature appeared on the surface would affect light diffraction and cause some diffraction loss, resulting in a smaller SPR peak in IRRAS spectra.

Similar phenomenon could also be observed when the compressive grating platform was deformed parallel to the grating grooves. The trend of diffraction efficiency decreased with increasing compression percentage in parallel deformation. In order to conserve the volume, the length and cross section of the substrate would both become larger under this deformation. The magnitude of SPR peak strongly decreased in the IRRAS spectra as the grating amplitude and periodicity were both increasing which resulted a low diffraction efficiency. From optical
diffraction pattern images, it could also be clear noted that less light transmitted through ±1 diffracted spots. Therefore, the grating diffraction efficiency had strong effects on the magnitude of SPR response.

Figure 4.5 (A) p-Polarized IRRAS spectra collected at 70° incidence of compressive grating platform as a function of different compression percentages. (B) Plot of SPR peak height & diffraction efficiency of compressive grating platform versus compression percentages. The mechanical compression direction was perpendicular with grating grooves.
Figure 4.6 (A) p-Polarized IRRAS spectra collected at 70° incidence of compressive grating platform as a function of different compression percentages. (B) Plot of SPR peak height & diffraction efficiency of compressive grating platform versus compression percentages. The mechanical compression direction was parallel to grating grooves.
4.4.3. Spontaneously chirped Au/PDMS grating platform

Besides fabricating gratings by LIL technique, the grating structures could also be created through mechanical buckling method. By harnessing a compliant substrate with thin stiff film on the top, the surface would buckle into a wavy, sinusoidal shape to relieve the applied stress. Overall, the thin stiff film prefers to buckle into long wavelength due to the low energy cost. In contrast, the compliant substrate favors short wavelength due to the low energy cost. In the combined system, the buckling value yields between the large and short wavelengths. The buckled sinusoidal topography of the thin stiff film could function as a diffraction grating.

Researchers have explored the energy method and developed mechanical model to estimate the grating periodicity $\Lambda$ and amplitude $A$ for the buckling system:\(^{38}\)

\[
\Lambda = \frac{2\pi h_f}{(1+\varepsilon_{pre})(1+\xi)^{1/3}} \left[ \frac{E_f(1-v_f^2)}{3E_s(1-v_s^2)} \right]^{1/3} \quad (6)
\]

\[
A = \frac{h_f}{(1+\varepsilon_{pre})(1+\xi)^{1/3}} \sqrt{\frac{\varepsilon_{pre}}{\varepsilon_c}} - 1 \quad (7)
\]

where $\xi = 5\varepsilon_{pre}(1 + \varepsilon_{pre})/32$, $\varepsilon_{pre}$ is the pre-strain, $h_f$ is the thickness of thin film, $E$ is Young’s modulus and $\nu$ is poisson’s ratio. The subscripts “s” and “f” refer to compliant substrate and thin film, respectively. $\varepsilon_c = 0.25 \left[ \frac{E_f(1-v_f^2)}{3E_s(1-v_s^2)} \right]^{1/3}$ is the minimum strain that is necessary for the buckling to occur. It indicated that the grating periodicity and amplitude were only related with the pre-strain value and thin film thickness.

Here a spontaneously chirped Au/PDMS grating platform was fabricated which showed different pitch values at different locations on a single substrate. The schematic was shown in Figure 4.6A. A gradient Au film was first deposited on a flat, thick PDMS master and a compressive stress was then applied along the substrate. The thin Au film would buckle into a
sinusoidal shape structure to relieve the applied stress. As the Au thickness varied on the substrate, the grating periodicity $\Lambda$ could be tuned in a broad range with a constant strain value.

The gradient Au film deposition was accomplished by a sputter coating system, which was illustrated in the previous report. It had been demonstrated that the Au thickness would change along the substrate. When the substrate was not compressed, different color levels appeared along the surface indicated different Au coverage (Figure 4.7B top). When the substrate was compressed by 10%, rainbow color appeared on the surface in a large area which indicated periodical buckling structures were generated (Figure 4.7B bottom). Five locations were chosen for the following characterization measurements. All the locations were from the middle of the platform and were equally spaced of 1cm between each other. From location 1 to location 5, the surface kept getting further away from metal target in sputter coating system.

The microscopy images of spontaneously chirped Au/PDMS grating platform at different locations were shown in Figure 4.8, as observed through an optical microscope using a 40X objective. The cross section profile of each image was further analyzed with Image J. It was clear to see the periodicities of the grating structures were altering along the platform. With proper calibration, the actual grating periodicity could be directly estimated from each figure. It showed that the grating pitch value changed from $\sim$5µm to $\sim$2.2µm from location 1 to location 5. It demonstrated that a spontaneously chirped Au/PDMS grating platform was fabricated through this approach. It was noticeable that good sinusoidal profile of the grating was achieved from location 2 to location 4. But at location 1 and 5, the shape of grating structures were less uniform which result from non-uniform compressive stress at the edge of the substrate. In addition, a pattern emerges with structures aligned mostly perpendicular to the grating patterns was due to the redistribution of compressive stress produced by the uniaxial strain during experiment.
Figure 4.7 A) Schematic for fabricating spontaneously chirped Au/PDMS grating platform. B) Pictures of gradient Au/PDMS substrate compressed into a chirped Au/PDMS grating platform.
Figure 4.8 Microscopy images and cross section profiles of spontaneously chirped Au/PDMS grating platform at different locations. From location 1 to 5, the Au film thickness decreases along the substrate and each location is equally spaced between each other. The scale bar in each image is 10µm.
The diffraction pattern images at each location on the chirped grating platform were shown in Figure 4.9A. It demonstrated that grating structures were generated on the surface as diffracted orders appeared in the images. Based on the distance between ±1\textsuperscript{st} diffracted orders and 0\textsuperscript{th} diffracted order, the pitch value at each location could be calculated with proper calibration which was plotted in Figure 4.9B. The pitch values were consistent with previous microscopy imaging analysis. Based on the grating periodicity at each location, the corresponding Au thickness could also be estimated from the mechanical model (equation 6) by using the following material parameters, \(E_f=79\text{GPa},\ E_s=2.6\text{MPa},\ \varepsilon_{pre}=10\%,\ \nu_f=0.42\) and \(\nu_s=0.5\). Here the modeled Au thickness was plotted in Figure 8B (dashed line). The actual Au thickness of spontaneously chirped grating platform at each location were verified via contact profilometry (Figure S4.5, support information). The actual Au thickness on the platform (black solid line) and the modeled Au thickness (black dashed line) were almost consistent in Figure 4.9B. From location 1 to location 5, the Au thickness kept decreasing along the substrate and ranged from 42 to 18\text{nm} on the spontaneously chirped grating platform.
Figure 4.9 A) Optical diffraction pattern images of spontaneously chirped Au/PDMS grating platform at different locations. B) Plot of pitch value, gold thickness and modeled gold thickness at each location. The pitch value was calculated from the diffraction pattern images. The Au thickness was collected from profilometry. And modeled Au thickness was estimated from the mechanical model based on the corresponding pitch value.
Figure 4.10 showed IRRAS spectra from the spontaneously chirped grating platform at each location with p-polarized light source at 70° incident angle. The SPR peaks coupling from -1 and -2 diffracted order of the grating platform could both be observed in the spectra. From location 1 to location 5, the wavelength of SPR response was able to be tuned in the spectra. For example, the SPR peak coupling from -1 diffracted order could be shifted ~1000 cm\(^{-1}\) on this chirped grating platform. Also it was important to note that the SPR peak intensity varied at different locations, which should be related with the diffraction efficiency of the gratings. The trend of SPR peak intensity was consistent with the corresponding diffraction efficiency at each location (Figure S4.6, Support Information). Therefore, the diffraction pattern images could be a tracker for indicating the SPR peak magnitude in spectra.

Besides the tunable SPR response in infrared spectra, the localized surface plasmon resonance (LSPR) response related with Au island morphology could also be tuned in the UV-Vis range on this spontaneously chirped grating platform. The LSPR occurred when the collective oscillation of the valence electrons of metal nanoparticles were in resonance with the frequency of light. When the LSPR was excited, light would be largely absorbed at the resonant frequency and an enhanced electric field was generated around the metal nanoparticles.\(^{39}\) The LSPR response could be characterized by transmission dips ascribed to enhanced absorption process in the UV-Vis transmission spectra. With Au thickness increasing, the absorption band shifted to longer wavelength and became broader (Figure 4.11). The red shift of LSPR response could result from the increase of Au nanoparticle size during the deposition process. And the broaden of LSPR band could result from dipole-dipole electromagnetic coupling between metal nanoparticles with a small gap distance.\(^{40}\)
Figure 4.10 p-Polarized IRRAS spectra collected at 70° light incidence from spontaneously chirped Au/PDMS grating platform at different locations.
Figure 4.11 UV-Vis transmittance spectra of spontaneously chirped grating platform at different locations without compression (left) and with compression (right).

With 10% compression, an enhanced electric field was created on the surface since the grating structures were fabricated. And an overtone enhancement was observed in the near IR spectra due to the enhanced electric field. Figure 4.12 showed UV-Vis and near IR transmission spectra at location 4 on the spontaneously chirped grating platform with and without compression, also including the spectra of flat PDMS substrate with the same compression. The peaks appeared around 1700nm were subjected to the overtone peaks of C-H vibrational mode from PDMS substrate. It was clear to see that the C-H overtone peak got enhanced on the grating platform with compression as a stronger electric field was generated around the surface.⁴¹
Figure 4.12 UV-Vis and near infrared transmittance spectra of spontaneously chirped grating platform at location 4 with and without compression and bare PDMS substrate with compression. The spectra were offset for clarity.

4.5 Conclusions

In this work, two pitch tunable diffractive grating platforms have been fabricated on elastomeric PDMS substrates. One was fabricated via the laser interference lithography technique, the other was created through sinusoidal buckled thin stiff film on a compliant substrate. The pitch tunability was achieved by deforming the grating/PDMS substrate mechanically. Based on the compressive grating platform, the grating pitch could be adjusted by compressing PDMS substrate. With spontaneously chirped grating platform, the grating pitch tunability was achieved by depositing different metal thickness along the substrate. The location of SPR response in infrared spectra could be adjusted within a large range of wavenumbers on both platforms. The tunability of SPR in infrared spectra via grating couplers could be easily designed and fabricated with the two platforms. The two tunable grating platforms both could serve as an information rich substrate
for promising applications such as optical sensors, tunable light scanners and allowed for more efficiently SPR based surface enhanced spectroscopy.

4.6 Acknowledgements

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4.7 References

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4.8 Support Information

**Figure S4.1** Laser interference lithography (LIL) apparatus for fabricating holographic gratings, including a 405nm laser, spatial filter, plane mirror and a rotatable sample stage.

**Figure S4.2** Gradient metal film fabrication apparatus by using sputter coating system. The metal target is fixed at an angle towards the sample substrate.
Figure S4.3 (A) Microscopy image of grating surface from compressive grating platform. The compress direction was perpendicular with grating grooves and the compression percentage was 23.5%. (B) Cross section profiles of the above grating surface at different positions. The scale bar in the image is 10µm.
Figure S4.4 (A) Microscopy image of grating surface from compressive grating platform. The compress direction was parallel to the grating grooves and the compression percentage was 13.6%. (B) Cross section profiles of the above grating surface. The scale bar in the image is 10µm.
Figure S4.5 Gradient Au film thickness on Si wafer at different locations via profilometer. The gradient Au film was deposited with the same apparatus of spontaneously chirped grating platform.

Figure S4.6 Plot of SPR peak height & diffraction efficiency of spontaneously chirped grating platform at each location.
CHAPTER 5

CONCLUSIONS

Surface enhanced infrared absorption (SEIRA) spectroscopy is a powerful analytical technique that amplifying vibrational signals of adsorbed molecules on rough metal island films or engineered plasmonic metallized nanostructures. It has been developed for several decades since 1980s. However, it attracted less attention than surface enhanced Raman spectroscopy (SERS) as the enhancement factor of SEIRA is much lower. But SEIRA is still an important analytical technique in surface enhanced spectroscopy. It has a unique band selection rule which only enhance the vibrational modes that dipole change is perpendicular to the metal surface. It is complementary to SERS technique and is able to be applied in a various fields, such as electrochemical dynamics, surface photochemistry, catalytic reactions and sensors in bio-spectroscopy. General background information, common SEIRA active substrates, physical details of SPR and LSPR are all illustrated in Chapter 1.

Metal island films (island size smaller than the wavelength of light) are the most widely used substrate for SEIRA measurement. It can be prepared either by physical vapor deposition or wet chemically deposition. However, the reproducibility of the SEIRA active metal island films is still on a poor level as it is quite difficult to control the deposition parameters. In Chapter 2, we focused on fabricating a gradient metal film by sputter coating method. The metal film thickness changed along the substrate. And the conductivity of the film changed from conductive to non-conductive. Based on the transmission spectra and AFM characterization, it was demonstrated that the gradient film changes from conductive, continuous silver film to non-conductive, separated silver islands. Self-assembly monolayer was coated on the gradient silver film followed with SEIRA measurement. It was observed that the vibrational signals showed maximum enhancement
at the location where the silver islands was going to change to a continuous film. This location was referred to the percolation threshold of the film and was able to be monitored with optical transmission spectroscopy or impedance measurement. The gradient metal film provide a controllable and reproducible platform to achieve maximum SEIRA activity via sputter coating approach.

In Chapter 3, we mainly focused on controlling Au nanoparticle size, density and gap distance between adjacent AuNPs on indium tin oxide substrates by pulsed electrodeposition approach. By manipulating the deposition potential and deposition cycles, numerous “hot spots” providing for high SEIRA performance would be generated on the substrates. The maximum SEIRA enhancement was achieved near the percolation threshold of metal nanoparticle film which is able to be monitored by optical transmission spectroscopy. In addition, the monodisperse gold nanoparticles were able to be directly synthesized on the surface with low deposition cycles. This protocol provides a facile, economical and reproducible approach to fabricate SEIRA active substrates with high performance. It has great potential to be utilized to motivate future applied studies.

In Chapter 4, we focused on using two tunable grating platforms to tune plasmonic response in infrared spectra. One is fabricated by the laser interference lithography technique, the other is based on mechanical buckling of sinusoidal buckled thin film on a compliant substrates. The tunability is achieved by mechanical compressing grating/PDMS system. With controlling the grating pitch, the plasmonic response can be tuned in infrared region. They both are able to serve as an information rich substrates for improving the efficiency of SEIRA spectroscopy. Based on the tunable grating system, enhanced infrared signals can be achieved by interacting SPR response with the vibrational modes.
Overall, SEIRA spectroscopy is attracting more and more attention since its discovery and it still have more spaces to be improved, both in theoretical and experiment areas. The main topic for improving SEIRA efficiency would be fabricating SEIRA active substrates with controllable morphology. Here we explored three different methods to fabricate reproducible SEIRA active substrates with high activity. The substrates fabricated with these protocols showed cost effective, high sensitivity and stability properties. It is worth keeping exploring the characteristic of SEIRA active substrates and improving the efficiency and performance of this technique.
CHAPTER 6

FUTURE DIRECTIONS

The protocols represented in this document provide multiple paths to fabricate controllable SEIRA active substrates to achieve high SEIRA activity. It is mainly focused on fabricating metal island substrates and grating platforms. While the SEIRA spectroscopy combined with grating platforms will still need to be further explored. The amplitude and shape of the grating topology have impacts on the SEIRA enhancement and the interaction between grating morphology and SEIRA spectroscopy need to be further characterized in order to achieve maximum SEIRA activity.

In addition, the AuNP films prepared by pulsed electrochemical deposition method are on separate substrates with different deposition cycles. Even though the morphology could be well controlled via this approach, it will take time and consume materials to optimize the parameters to achieve the maximum SEIRA activity. Direct synthesize a gradient AuNP film on a single substrate by electrochemical deposition will be helpful for this technique. By applying two different deposition potential on a single electrode, the potential would change linearly along the surface as long as the resistance on the surface could overload the electrons. Different potentials at each location result different particle size and density on the surface which formed a gradient AuNP film. Since multiple morphology can be achieved on one substrate, it will be more cost effective and less time consuming to prepare SEIRA active substrates. And it is easier to locate the position where show the maximum SEIRA enhancement on the surface. The directly tuning AuNP density along the surface can also be further applied in cell biology, catalysis and electronics.\textsuperscript{1-3}

Besides the metal island substrates and grating platforms, novel SEIRA active substrates can also be explored in this technique. It has been demonstrated that engineered metallic nanostructures, such as nanoantenna, split ring resonator, nanoshells, could be utilized in SEIRA
spectroscopy. Also it has been found that surface lattice plasmon could be excited at diffraction limit in the optical spectrum on periodical 2D metal nanoparticle substrates. The surface lattice plasmon involve an interplay between LSPR and diffraction grating from scattering by the periodical nanoparticles. The 2D metal nanoparticle pattern could be fabricated by combining laser interference lithography and electrochemical deposition. Since nano-hole pattern could be fabricated on the ITO glass substrate with double exposure by LIL technique, directly synthesizing AuNPs in holes could result a novel AuNP pattern on the surface. It would be interesting to explore that whether the surface lattice plasmon peak could be shifted into infrared region. The 2D AuNP pattern substrate could serve as a potential novel SEIRA active substrate. These studies provide potential work to understand the SEIRA enhancement mechanism for periodical engineered metallic nanostructured substrates and offer routes to develop novel SEIRA substrates with high sensitivity and good reproducibility.

6.1 References

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