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Studies of Periodic and Quasiperiodic Gold Nanohole Arrays and Their Applications

Zhaoliang Yang
The University of Western Ontario

Supervisor
Jun Yang
The University of Western Ontario

Graduate Program in Mechanical and Materials Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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STUDIES OF PERIODIC AND QUASIPERIODIC GOLD NANOHOLE ARRAYS
AND THEIR APPLICATIONS

(Thesis format: Monograph)

by

Zhaoliang Yang

Graduate Program in Mechanical and Materials Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of

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The School of Graduate and Postdoctoral Studies

The University of Western Ontario

London, Ontario, Canada

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Abstract

Wavelength to refractive index sensitivity and resonance wavelength position are two very important performance characteristics for nanohole array based surface plasmon resonance sensors while these characteristics are mostly researched on periodic nanohole arrays, instead of quasiperiodic nanohole arrays. This thesis deduces theoretical equations about the wavelength to refractive index sensitivity and resonance wavelength position of quasiperiodic nanohole arrays. Theoretical analysis shows that wavelength to refractive index sensitivity is not associated with geometry pattern, hole size or pitch but with the wavelength. A novel surface plasmon resonance platform is built by transferring gold films patterned with quasiperiodic nanohole arrays to the tip of optical fibers and experimental data are acquired to validate the theoretical analysis. Compared with experimental data, the errors of theoretically predicted resonance wavelengths are within 2.3%. In the last part of this thesis, nanohole arrays are demonstrated to enhance Raman Scattering.

Keywords

Surface plasmon resonance, extraordinary optical transmission, refractive index sensitivity, nanohole array, quasiperiodic, Surface Enhanced Raman Spectroscopy, plasmonics optical fiber
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Chapter 1

1 Introduction

People have long been interested in light traveling through tiny holes and there are a lot of related applications in real world. In modern digital single lens refractive cameras, the aperture which is in essence a pinhole can be adjusted to change the exposure and depth of field. It is intuitive that the transmission of light through apertures in an optically thick metal film should decrease with the size of the aperture. By idealizing that the metal film was infinitely thin and that the metal was a perfect conductor, Bethe derived a very simple expression to calculate the transmission efficiency (normalized to the aperture area).¹

\[
T(\lambda) = \frac{1024 \pi^2}{27} \cdot \frac{r^4}{\lambda^4}
\]

where \( \lambda \) is the wavelength of the incoming light, and \( r \) is the radius of the hole. Since transmission efficiency \( T(\lambda) \) scales as \( (r/\lambda)^4 \), \( T(\lambda) \) will drop exponentially if \( \lambda > r \). Bethe’s theory can be illustrated by Figure 1-1,

![Figure 1-1](image)

Figure 1-1 Light diffracts at the edges when it scatters through apertures (a) and the transmission \( T(\lambda) \) decreases exponentially with the increase of its wavelength \( \lambda \).
However, Bethe’s theory was challenged in 1998 as Ebbesen and his co-workers discovered that the amount of transmitted light at certain wavelengths was much larger than what was predicted by Bethe’s theory when they did light transmission experiments on gold and silver thin films with nanohole arrays. This phenomenon was named extraordinary optical transmission (EOT) which resulted in high peaks at certain wavelengths in the transmission spectrum. Figure 1-2 shows the transmission spectrum of light through a two dimensional nanohole array. Two peaks exist where the spectrum should be very smooth according to classical aperture theory. In particular, the transmission efficiency (normalized to hole area) can be larger than one even though the diameter of individual hole is smaller than the wavelength of incoming light, as illustrated by the vertical axis on the left of Figure 1-2.

Figure 1-2 The light transmission spectrum of a two dimensional hole array milled in a 225 nm thick Au film on a glass substrate. The diameter of the holes is 170 nm and the pitch is 520 nm. \(I/I_0\) is the absolute transmission of the array and \(\eta\) is the transmission that is normalized to the area occupied by the holes. Figure reprinted with permission from Ref.3.
Since it was first discovered, extraordinary optical transmission has been researched both theoretically and experimentally. Most researchers have agreed that extraordinary optical resonance is caused by the interaction of light with the free electrons on the surface of the metal film or surface plasmon resonance in other words. Previous studies have demonstrated that light transmission through nanohole arrays can be influenced by metal material properties, polarization of light and hole size, shape, geometry pattern and pitch. However, almost all of these studies are based on periodic nanohole arrays and there are very few studies on light transmission through aperiodic/quasiperiodic nanohole arrays. To have a thorough understanding about light transmission through quasiperiodic nanohole arrays, the following questions should be answered:

(1) Will there be extraordinary optical transmission (EOT) phenomenon on metal films that were milled with quasiperiodic nanohole arrays?

(2) If there is EOT on quasiperiodic nanohole arrays, then what is the difference of EOT on periodic and quasiperiodic nanohole arrays? For example, is the wavelength to refractive sensitivity the same on periodic and quasiperiodic nanohole arrays?

(3) Since there are already equations to predict resonance wavelength positions of periodic nanohole arrays, what equations should be used to calculate the resonance wavelengths of quasiperiodic nanohole arrays.

Not many articles about extraordinary optical transmission have been published and a brief literature review is given as follows. The first light transmission research on quasiperiodic nanohole array was done by Sun Mei and co-workers.\textsuperscript{4} In this work, an 8-fold quasiperiodic nanohole arrays with a diameter of 220 nm was milled on a 120 nm thick Au film and a control experiment was done on an amorphous nanohole array. In the resulted transmission spectra illustrated by Figure 1-3, there is a resonance peak in the transmission spectrum of quasiperiodic nanohole array (solid line) while no such peak appears in that of amorphous nanohole array (dashed line). That means periodicity is not necessary to generate extraordinary optical transmission but extraordinary optical transmission does not happen on random nanohole arrays. Please note that the peaks that center at about 490 nm in both spectra are attributed to the intrinsic optical properties.
(low absorption) for bare gold surfaces. Therefore the answer to Question (1) is YES and extraordinary optical transmission does exist on quasiperiodic nanohole arrays.

Figure 1-3 Light transmission spectra of quasiperiodic nanohole array (solid line) and random nanohole array (dashed line). Figure reprinted with permission from Ref.4.

More features of the transmission spectrum of quasiperiodic nanohole array were researched by Ebbesen and co-workers. A five-fold Penrose tiling nanohole array was used in Ebbesen’s work and by changing the rhombus edges from 350 to 900 nm while keeping the hole diameter fixed to 150 nm, the maxima dispersion of the spectrum were tracked and were found to closely follow Bragg conditions, as illustrated by figure 1-4, which means that the enhanced transmission peaks in quasiperiodic metallic arrays are related to Fourier space of the array, similar to the case of periodic nanohole arrays. However, Ebbesen and co-workers only discussed the relationship of maxima with Rhombus length and detailed mathematical equations were not shown and thus it’s not a complete answer to Question (3). This work further proved that the propagation length of
quasiperiodic nanohole arrays was less than that of periodic nanohole arrays as the loss of periodicity increased the localized character of surface plasmon modes, which is a partial answer to Question (2).

Figure 1-4 Maxima dispersions of modes as a function of Rhombus edge $P$ (Open circles and open triangles). The solid lines are peak positions that are predicted by Bragg conditions. The open circles and triangles are modes that are excited on the metal-air interface while the filled circles and triangles are modes that are excited on the metal-glass interface. Figure reprinted with permission from Ref.5.

Another study relative to Question (3) was done by Domenico Pacifici and co-workers.\textsuperscript{6} They predicted the resonance wavelengths by using momentum matching equations but found that what they predicted were only minima, excluding maxima, as illustrated by Figure 1-5.
Figure 1-5 Momentum matching condition $k_{sp} = G$ failed at predicting the position of the transmission maxima but the predictions which were shown by the vertical lines coincide very precisely with the experimental transmission minima. Figure reprinted with permission from Ref. 6.

As far as I know, both maxima and minima should be predicted by using momentum matching condition as both minima and maxima fit the momentum matching equations. However, detailed equations to calculate the resonance wavelengths of the Penrose tile nanohole array were not shown in their academic work. In Figure 1-5 it is unknown why they cannot predict maxima and such questions should be answered by researchers in the future.

In addition, there are also surface plasmon resonance research based on quasiperiodic aperture arrays within Terahertz regions instead of visible and near-infrared regions and correspondingly the holes are usually within or larger than micro scale. Even though those researchers seldom researched about the detailed transmission properties such as sensitivity or resonance wavelength, their works are still inspiring. Amit Agrawal and
co-workers have done amazing work on enhanced light transmission through aperiodic aperture arrays. In their work published in Nature in 2007, enhanced transmission in Terahertz regions was demonstrated in quasiperiodic aperture arrays with long-range order but no short-range order and other aperiodic structures with no long-range or short-range order but whose structure factor might contain a number of discrete Fourier transform vectors. The transmission spectra are illustrated by Figure 1-6 in which the resonances peaks correspond to the reciprocal vectors of the hole array.

Figure 1-6 Transmission spectra of three Penrose type quasiperiodic perforated films with different rhomb edge lengths, $d_3$, showing resonances $F^{(i)}$ and anti-resonances $AR_i$. Figure reprinted with permission from Ref. 7.

In their work published in 2008, they further demonstrated that aperture arrays with short-range order but lack long-range order, as illustrated by Figure 1-7(a) could also perform enhanced transmission and that the resonances could be engineered to yield different transmission properties.  

8
Figure 1-7 (a). Subwavelength aperture array that exhibits short-range order. (b) The THz transmission spectra of the structures in (a) with aperture diameter D=500 μm (red curve) and D=600 μm (blue curve) respectively and the dotted lines are corresponding random aperture structures. Figure reprinted with permission from Ref.8.

Until now a lot of fundamental work has been done to research the wavelength to refractive index sensitivity and resonance wavelengths of the periodic nanohole array, which are very important performance characteristics for surface plasmon resonance sensors. However, there is almost not much similar research about quasiperiodic nanohole arrays and therefore this thesis will study the sensitivity and resonance wavelength of quasiperiodic nanohole arrays with both theoretical and experimental methods. Besides surface plasmon resonance, another important application of nanohole array, surface enhanced Raman Spectroscopy, which has an advantage of molecular specificity over surface plasmon resonance, is also demonstrated in the end of this thesis.
Chapter 2

2 Theoretical Analysis

Wavelength to refractive index sensitivity and resonance wavelength are two important performance characteristics for nanohole array based surface plasmon resonance devices. Current research has developed equations to calculate these two characteristics on periodic nanohole arrays. However, not enough research has been done on quasiperiodic nanohole arrays. Therefore Chapter 2.2 and 2.3 mainly show the deduction procedures of equations to calculate wavelength to refractive index sensitivity and resonance wavelength on quasiperiodic nanohole arrays after a short introduction of basic theories of plasmonics in Chapter 2.1.

2.1 Fundamentals of Plasmonics

Free electrons exist on the surface of metals and the free electrons will oscillate in response to an external electromagnetic field. The electron charges on a metal boundary can perform coherent oscillation with incoming light. The oscillation frequency $\omega$ is related with its wave vector $k$ by a dispersion relation $\omega(k)$. Figure 2-1 shows the simplest configurations of a semi-infinite plane metal surface in contact with a dielectric layer with a dielectric constant of $\varepsilon_d$. The following equations can be obtained by solving Maxwell’s equations and its boundary conditions,

$$\frac{k_{z1}}{\varepsilon_m} + \frac{k_{z2}}{\varepsilon_d} = 0 \quad (2-1)$$

$$k_{sp}^2 + k_{z1}^2 = \varepsilon_m \left(\frac{\omega}{c}\right)^2 \quad (2-2)$$

$$k_{sp}^2 + k_{z2}^2 = \varepsilon_d \left(\frac{\omega}{c}\right)^2 \quad (2-3)$$
where \( k_{z1} \) and \( k_{z2} \) are the respective component of the wave vectors that are vertical to the interface of the metal and dielectric layer, \( k_{sp} \) is the wave vector of surface plasmon and \( c \) is the velocity of light in vacuum.

By solving the above equations, the wave vector \( k_{sp} \) can be written as

\[
k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{2-4}
\]

Suppose the metal surface can be written as \( \varepsilon_m = \varepsilon'_m + \varepsilon''_m \), where \( \varepsilon'_m \) and \( \varepsilon''_m \) are the real and imaginary part of \( \varepsilon_m \) respectively. Then the real part of \( k_{sp} \) is

\[
k'_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}} \tag{2-5}
\]

The imaginary part of \( \varepsilon_m \) determines the internal damping and absorption and is ignored in this thesis. The real part of \( k_{sp} \) is plotted in Figure 2-2.
It is very important to note that the wave vector $k_{sp}$ is always smaller than that of incident light, $k_0$, at the same frequency $\omega$. An extra momentum $G$ is necessary to enable the incident wave to couple with the surface plasmons. One way to provide the missing momentum $G$ is to use a periodic/aperiodic nanohole array. This is expressed in the simple resonance condition,

$$k_{sp} = k_0 \sin \theta + G \quad (2-6)$$

While

$$G= \pm iG_x \pm jG_y \quad (2-7)$$

Where $k_0$ is the wave vector of incident light and $\theta$ is the incident angle. $G_x$ and $G_y$ are the vectors in reciprocal space and they are related to the structure of the nanohole array and thus are also called structure factor in some literature.\(^7\) Please note that equation (2-6) is also called Bragg condition in this thesis and equation (2-7) also refers to Bragg momentum and it is applicable for all two dimensional hole arrays.

**Figure 2-2 Dispersion curves of surface plasmons**

![Dispersion curves of surface plasmons](image)
2.2 Wavelength to Refractive Index Sensitivity Analysis

Sensitivity is the most commonly used parameters to quantify and compare the performance of sensors. In particular, Surface Plasmon Resonance (SPR) sensors are usually characterized by wavelength to refractive index sensitivity which describes the SPR peak position shift corresponding to the change of refractive index $n$ of the surrounding environment. Almost all current research about wavelength to refractive index sensitivity is only in experimental level and lacks support of theoretical analysis. This section will give a mathematical expression of wavelength to refractive index sensitivity for all normalized incident light induced surface plasmon resonance.

By combining equation (2-6) and (2-7), the following equation is obtained,

$$k_0 \sin \theta \pm iG_x \pm jG_y = k_{sp}$$  \hspace{1cm} (2-8)

Take the absolute value of both sides of equation (2-8)

$$|k_0 \sin \theta \pm iG_x \pm jG_y| = |k_{sp}| = k_{sp}'$$  \hspace{1cm} (2-9)

Where $k_0$ is the wave vector and $\theta$ is the incident angle of incident light. $G_x$ and $G_y$ are the vectors in reciprocal space and they are related to the structure of the nanohole array. In the case of a square lattice with lattice constant $P$, the reciprocal vectors can be determined by $G_x = G_y = 2\pi/P$. $i$ and $j$ are the scattering orders for the nanohole array.

Since

$$k = \frac{2\pi}{\lambda}$$  \hspace{1cm} (2-10)

and

$$\omega = ck$$  \hspace{1cm} (2-11)

By combining equation (2-5), (2-8), (2-10) and (2-11) we can get the following equation,

$$\sqrt{(\frac{2\pi}{\lambda} \sin \theta + iG_x)^2 + (iG_y)^2} = \frac{2\pi}{\lambda} \frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}$$  \hspace{1cm} (2-12)
In equation (2-12) the first approximation is that the film has no signification change in the plasmon dispersion and no coupling between the front and back surfaces of the metal film.

In this thesis, the wavelength to refractive index sensitivity is defined as,

\[ S = \frac{\Delta \lambda}{\Delta n} \]  

(2-13)

Where \( \Delta \lambda \) is the peak wavelength shift of the SPR spectra and \( n \) is the refractive index of the surrounding environment with dielectric constant \( \epsilon_d = n^2 \). According to the deduction process attached in Appendix 1, we can get the following equation,

\[ S = \frac{\lambda_m \epsilon'_m}{n(\epsilon'_m + n^2)} = \frac{\lambda_m \epsilon_m}{n \epsilon'_m + n^2} \]  

(2-14)

Where \( \lambda_m \) is the resonance wavelength, whether minima or maxima in the transmission spectrum. By analyzing equation (2-14), it’s not difficult to tell that the wavelength to refractive index sensitivity is not determined by the geometry or structure of any particular nanohole arrays if the incoming light is normal (\( \theta = 0 \)).

Since \( |\epsilon'_m| \gg n^2 \) at visible and near infrared region, equation (2-14) can be simplified as \( S \approx \lambda_m / n \). In water where \( n=1.3330 \), the equation can be further simplified as

\[ S \approx 0.75 \lambda_m \]  

(2-15)

Since many previous SPR experiments are carried on periodic nanohole arrays,9-11 this thesis will mainly experiment the sensitivity of quasiperiodic nanohole arrays and see whether the sensitivities of quasiperiodic nanohole arrays agree with equation (2-15).

2.3 Resonance Wavelength Analysis

As for periodic nanohole arrays, previous research has developed equations to predict resonance wavelengths, e.g. \( \lambda_m = \frac{P}{\sqrt{|\epsilon'_m|}} \sqrt{\frac{\epsilon'_m \epsilon_d}{\epsilon'_m + \epsilon_d}} \) for square lattice nanohole arrays9,
\[ \lambda_m = \frac{P}{\sqrt{\frac{4}{3} (l^2+i^2+j^2)}} \sqrt{\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}} \] for hexagonal arrays\(^9\) and \[ \lambda_m = \frac{P}{i} \sqrt{\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}} \] for nanoslit arrays\(^11\). Due to the complexity of quasiperiodic nanohole array’s reciprocal vectors, very few works have such predictions about quasiperiodic nanohole arrays.\(^6\) This section shows the detailed deduction of mathematical equations to predict the resonance wavelength. Please note that since it is not possible to acquire the reciprocal vectors of 12 fold quasiperiodic nanohole arrays used in my experiments with laser\(^12\) or x-ray\(^8\) diffraction method, the resonance wavelength analysis is based on five-fold Penrose tile quasiperiodic nanohole array whose reciprocal vectors can be obtained theoretically.

As mentioned in equation (2-6) the Bragg momentum matching conditions also work for quasiperiodic nanohole arrays. In the case of normal incidence (\(\theta = 0\)), equation (2-6) can be written as,

\[ k_{sp} = G \] (2-16)

Where \(G\) is the reciprocal vectors for quasiperiodic nanohole arrays. In real space, a Penrose tile is generated based on five lengths, \(a_m=1,5\), namely edges \(m=1\), long and short diagonals \((m=2\) and \(m=3\)) for fat rhombus and thin one \((m=4\) and \(m=5\)). Each of these lengths corresponds with the magnitude of the reciprocal vectors by

\[ \alpha_{m=1,5} = \frac{2\pi}{a_m \tau \sin \frac{\pi}{5}} \] (2-17)

In the case of a Penrose structures that exhibits five-fold rotational symmetry, \(\tau\) represents the golden mean which is \(\tau = (1 + \sqrt{5})/2 \approx 1.62\).

With all the above equations, the reciprocal vectors \(G\) can be written as,

\[ G_{m=1,5} = \pm a_m \cos \frac{2n\pi}{5} i \pm a_m \sin \frac{2n\pi}{5} j \] (2-18)

Where \(n\) is integer and goes from 0 to 4 and \(i\) and \(j\) are also integers (with \(i \geq 0, j \geq 0\)). From equation (2-16) and (2-18), it is deduced that,
\[|k_{sp}| = |G| = \sqrt{\frac{a_m^2 \cos^2 \frac{2n\pi}{5} i^2 + a_m^2 \sin^2 \frac{2n\pi}{5} j^2}{1 + \cos \frac{4n\pi}{5}} i^2 + \frac{1 - \cos \frac{4n\pi}{5}}{2} j^2} = a_m \sqrt{\frac{1 + \cos \frac{4n\pi}{5}}{2}} \]

\[(2-19)\]

Where \(\beta = \sqrt{\frac{a_m^2 \cos^2 \frac{2n\pi}{5} i^2 + a_m^2 \sin^2 \frac{2n\pi}{5} j^2}{1 + \cos \frac{4n\pi}{5}} i^2 + \frac{1 - \cos \frac{4n\pi}{5}}{2} j^2} = a_m \beta\)

Since \(|k_{sp}| = 2\pi n_{sp}/\lambda = 2\pi/\lambda_{sp}\), the resonance wavelengths in transmission spectra can be written as,

\[\lambda = \frac{2\pi n_{sp}}{a_m \beta}\]

\[(2-20)\]

where \(n_{sp}\) is the effective refractive index exerted on surface plasmon, \(\lambda_{sp}\) is effective wavelength of surface plasmons and \(\lambda\) is the wavelength of free space incident light. Insert equation (2-17) into equation (2-20) and \(\lambda_{sp}\) corresponds to basic lengths \(a_{m=1,5}\) directly by,

\[\lambda = \frac{2\pi n_{sp}}{a_m \beta} = \frac{2\pi n_{sp}}{a_m \beta} \left(\frac{2\pi}{a_{m \times \sin \frac{\pi}{5}}}\right) \approx \frac{0.9522a_m n_{sp}}{\beta} \approx \frac{0.9522a_m n_{sp}}{\beta} \]

\[(2-21)\]

Equation (2-21) shows that the resonance wavelengths are determined by the reciprocal vectors and basic lengths. According to equation (2-5) it is deduced that

\[n_{sp} = \frac{\lambda}{\lambda_{sp}} = \frac{\left(\frac{\varepsilon_{m}^e}{\varepsilon_{m}^d}\right)^{\frac{1}{2}}}{\left(\frac{\varepsilon_{m}^e}{\varepsilon_{m}^d}\right)^{\frac{1}{2}}} \]

\[(2-22)\]

Since \(|\varepsilon_{m}^e| \gg \varepsilon_{d}\) at visible and near-infrared regions, in our experiments, we can just simplified \(n_{sp}\) as
\[ n_{sp} = \sqrt{\frac{\varepsilon_n'\varepsilon_d'}{\varepsilon_m' + \varepsilon_d'}} = \frac{\varepsilon_d'}{\sqrt{1 + \frac{\varepsilon_d'}{\varepsilon_m'}}} \approx \sqrt{\frac{\varepsilon_d'}{1 + 0}} = \sqrt{\varepsilon_d'} \]  

(2-23)

It is important to note that the wavelength we see from the spectra from the optical spectrometer is \( \lambda \) instead of \( \lambda_{sp} \).
Chapter 3

3 Experimental Details

This chapter talks about the design and fabrication of quasiperiodic nanohole arrays and experimental setup and protocols. In Chapter 3.1, inflation method and generalized dual multigrid method were used to design 12 fold and 5 fold quasiperiodic nanohole arrays respectively. Chapter 3.2 shows the fabrication process of nanohole template. Briefly, the designed nanohole array was fabricated into silicon wafer with electron beam lithography which is followed by gold sputtering. Then in Chapter 3.3 and 3.4 the experimental setup and protocols are described in details.

3.1 Design of Quasiperiodic Nanohole Arrays

Quasiperiodic nanohole array displays irregular periodicity. Two common quasiperiodic nanohole arrays were chosen in this thesis, namely quasiperiodic nanohole array with 12 fold rotational symmetry and 5 fold Penrose tile quasiperiodic nanohole array. Their design methods are described respectively in this section.

3.1.1 Inflation Method to Design 12 Fold Quasiperiodic Nanohole Array

A 12 fold quasiperiodic pattern is made of only squares and equilateral triangles, and the distances of nearest circles are equal. As pre-required by electron beam lithography, a two dimensional draft of the nanohole array was drawn with DesignCAD LT 2000 (a newer version will not be compatible with the electron beam lithography software in the NanoFab of Western University) with the unit set to be NONE which means micrometer. It is drawn using inflation method and the inflation rule for this 12 fold quasiperiodic nanohole array is divided into three steps,
1. Draw the parent dodecagon which is composed of squares and triangles. A circle is drawn on each vertex. The coordinates of the circle centers of circle 1 and 2 in figure 3-1(a) are used to draw the corresponding circles by using the function of Circle in DesignCAD. The diameter of the circles is 200 nm. The coordinates of circle centers 1 and 2 are \((d, 0)\) \((d=600 \text{ nm in this case})\) and \((d + \frac{\sqrt{3}}{2}d, \frac{d}{2})\). Then the function of Circular Array of DesignCAD is used to repeat the circles circularly and parent dodecagon is illustrated in Figure 3-1(b).

2. Group all the circles in Step 1 in DesignCAD and take the parent dodecagon in Figure 3-1(b) as a vertex in Figure 3-1(a) and repeat Step 1. The coordinates of circle centers 1 and 2 are scaled by \(2 + \sqrt{3}\) correspondingly.\(^{13}\) The scaling (can also be seen as inflation) is illustrated by Figure 3-1(c). In this design, the circle group on the position of circle center 2 and circle groups that are circularly arrayed by it are rotated by the angle \(\frac{\pi}{6}\) and the DesignCAD drawing in Step 2 is illustrated by Figure 3-1(d).

3. Repeat step 2 until the whole pattern is large enough (around 100 \(\mu\text{m}\)). With this method of inflation, some circles overlap with previous ones and the overlapped circles have to be deleted in DesignCAD because overlapped holes in the drawing will result in bigger hole diameter due to repeated electron beam lithography. The SEM image of overlapped holes can be seen in Figure 3-1(e). The holes in the middle part are apparently larger than the rest.
Figure 3-1 Parent dodecagon illustration in step 1(a) and dodecagon groups illustration in step 2(c) which are reprinted from reference 1. (b) and (d) are DesignCAD drawings of parent dodecagon and dodecagon groups in step 1 and 2. (e) shows SEM image of overlapped circles which are larger than expected. (a) and (c) are reprinted with permission from Ref.9.

Extra circles are trim until the whole pattern is circular with a diameter of 120μm. Figure 3-2 shows the whole nanohole pattern drawing in DesignCAD.
3.1.2 Generalized Dual Multigrid Method to Generate 5 Gold Penrose Tile Quasiperiodic Nanohole Array

The 5 fold quasiperiodic nanohole array is Penrose tiling, one of the most famous quasiperiodic patterns. A canonic Penrose tiling consists of two kinds of rhombuses with acute angles of $2\pi/10$ and $2\pi/5$ respectively. Generalized dual multigrid method was used to define the coordinates of the vertices of the five-fold Penrose tiling in this thesis. The coordinates were then imported into DesignCAD and circles are generated on the coordinates. The following sections will introduce generalized dual multigrid method.
To generate the vertex coordinates of a five-fold Penrose tiling, five sets of equally spaced parallel lines are put together and each set rotated $2\pi/5$ radians from the other sets, as shown by Figure 3-3,

![Figure 3-3 Five sets of equally separated lines angled by $2\pi/5$ from one another](image)

These are imaginary lines and it’s not necessary to actually draw them. For reference, the five sets of lines are named from A to E and the strips between adjacent lines are numbered from 1 to N-1, n is the number of lines in each set. The set of lines can be put arbitrarily but it’s important to keep them overlapped. To locate a vertex of the Penrose tiling, the polygon formed by these intersecting lines should be considered. Take the polygon marked by a big blue dot in the above picture for example. This polygon lies within strip 3 of set A ($i_A = 3$), strip 1 of set B ($i_B = 1$), strip 1 of set C ($i_C = 1$), strip 2 of set D ($i_D = 2$) and strip 3 of set E ($i_E = 3$). The factor $(i_A, i_B, i_C, i_D, i_E) = (3, 1, 1, 2, 3)$
is assigned to the polygon to indicate which strips it lies in. The actual coordinates corresponding to the above marked polygon can be determined by the following equations,

\[ x = i_A \cos(0) + i_B \cos\left(\frac{2\pi}{5}\right) + i_C \cos\left(\frac{4\pi}{5}\right) + i_D \cos\left(\frac{6\pi}{5}\right) + i_E \cos\left(\frac{8\pi}{5}\right) \]

\[ y = i_A \sin(0) + i_B \sin\left(\frac{2\pi}{5}\right) + i_C \sin\left(\frac{4\pi}{5}\right) + i_D \sin\left(\frac{6\pi}{5}\right) + i_E \sin\left(\frac{8\pi}{5}\right) \]

Large numbers of coordinates should be generated to fulfill a large enough pattern. In this thesis, an online Mathematica program named **GridMethod.m** was used to generate a very large amount of \((i_A, i_B, i_C, i_D, i_E)\).

In Mathematica, the following command was input to get the desired factor \((i_A, i_B, i_C, i_D, i_E)\).

\[ \text{DualizeGrid}[5, -20, 20, \{\text{random}, 0\}, \text{False}, 1] \]

Here the number 5 means it was a five-fold Penrose tiling and \(N_{min} = -20\) and \(N_{max} = 20\) showed the number of lines in each set and this controlled the size of the whole pattern. Since there were a really large number of factors generated, Microsoft Office Word and Excel were used to process the data (delete unnecessary comma or brackets to make the data in good format for following processing) before they were saved into a txt file named “Penrosedata.txt” and then imported into a MATLAB program to calculate the actual coordinates \((x, y)\) and The MATLAB program could be found in Appendix 2. The data generated by MATLAB contained some duplicated coordinates and the function of Remove Duplicates was used in Microsoft Office Excel to remove the duplicated data. In the drop-down list of File in DesignCAD, clicked Import and chose the file type as XYZ, selected the saved TXT file and the window in Figure 3-4 appeared. The diameter of the circle was set to be 0.2 μm.
Figure 3-4 DesignCAD window to generate circles directly from coordinates

Similar to the case of 12 fold quasiperiodic design, extra circles in the 5 fold quasiperiodic array were deleted and the whole pattern was a big circle with a diameter of about 120 μm, as illustrated by Figure 3-5

Figure 3-5 DesignCAD drawing of the five quasiperiodic array
3.2 Fabrication of Quasiperiodic Nanohole Arrays

The design of the above quasiperiodic nanohole arrays was sent to Western NanoFabrication Facility in Western University for fabrication. As illustrated by Chapter 3.2.1, a nanohole template was fabricated by electron beam lithography and deep reactive ion etching. Then gold was sputtered directly onto the surface of nanohole template. In Chapter 3.2.2, the nanohole array film was peeled off the nanohole template and transferred to the tip of optical fibers with the help of epoxy. The residues on the silicon template can be washed off and the silicon template can be re-used.

3.2.1 Fabrication of Nanohole Array Template

The completed DesignCAD drawings were then sent to Western NanoFabrication Facility in Western University for electron beam lithography. Figure 3-6 shows the process of nanofabrication. First a 100 nm thick polymethyl methacrylate (PMMA) was spin-coated on a silicon wafer. A quasiperiodic nanohole array with a diameter of 200 nm and pitch of 600 nm was fabricated on the PMMA layer by an Electron Beam Lithography (EBL) system (LEO 1530 equipped with a nanopattern generation system). The electron beam lithography was followed by deep reactive ion etching (Alcatel 601E) to transfer the nanoholes to silicon wafer. A 100 nm thick gold was sputtered onto the silicon wafer after removing PMMA resist in piranha solution (a 3:1 mixture of sulfuric acid and hydrogen peroxide).
Figure 3-6 Fabrication process of gold nanohole pattern

Figure 3-7 show the Scanning Electron Microscope (SEM) images of the nanohole pattern silicon wafer (before gold deposition).

Figure 3-7 SEM images of 12 fold rotational symmetry nanohole array
3.2.2 Transfer Metallic Film with Nanohole Array to Optical Fiber

Optical fiber is widely used nowadays as waveguides for remote sensing. In this thesis, the gold nanohole pattern was transferred to a multimode optical fiber tip whose numerical aperture was 0.22 so that light was automatically normalized to the gold nanohole array and this setup made it easy for remote sensing. The transferring process was illustrated by Figure 3-8. A 1 μL epoxy (302-3M) was applied onto the tip of the optical fiber and then heated to 60°C for 3 hours. Once heated, the epoxy became sticky and this would not only prevent the epoxy flowing into the nanoholes but also made gold sticks to the epoxy. After 3 hours’ curing, the epoxy became solid and then was peeled off from the silicon template. Thanks to the stickiness of the cured epoxy, nanohole pattern was transferred to the optical fiber tip. After gold film was peeled off from the silicon template, gold could be re-deposited onto the silicon template after thorough washing. Therefore this is a re-usable strategy.

![Figure 3-8 Process of transferring gold nanohole array to optical fiber](image)

However, it should be noted that the whole nanohole pattern only possessed a circle of 120 μm while the cross section of the optical fiber had a diameter of 500 μm. Therefore one of the challenges was that the nanohole pattern should be within the area of optical fiber otherwise light wouldn’t travel through the nanohole arrays. In this thesis, a
transferring kit was designed with SolidWorks and fabricated with 3D printing technology. Figure 3-9 shows the design of the transferring kit in Solidworks.

Figure 3-9 Body part (a) and lid part (b) of the transferring kit

The two dimensional engineering drawing is shown in Figure 3-10.

Figure 3-10 Engineering drawing of body part
In the experiment, the optical fiber was inserted into the cylinder of the body part and the silicon template was attached to the square part of the lid with double sided adhesive tapes. Figure 3-11 best illustrates how the transferring kit works. In Figure 3-11(b) the center part is silicon as the original gold nanohole arrays have been transferred onto the tip of optical fiber.

![Figure 3-11 Transferring kit on optical fiber (a) and silicon template (after peeling off) on lid of transferring kit (b)](image)

The opening at the side allowed the blade to cut off the needless gold nanohole pattern on the optical fiber tip, illustrated by figure 3-12.
Figure 3-12 The blade cut off needless gold nanohole pattern through the opening on the side

3.3 Experimental Setup

In this experiment, two optical fibers, with nanohole array transferred to only one of them, were coupled to light source and spectrometer (USB4000, Ocean optics) respectively and a flow cell made of PDMS connected and aligned the two optical fibers. The tips of the two optical fibers were separated by about 1 mm which allowed the aqueous solutions in and out. Teflon tubes were inserted into the PDMS flow cell as inlet and outlet respectively. A syringe pump was used to suck at the end of outlet Teflon tube. Suction method was used because it wouldn’t introduce bubble when changing the solutions.
To acquire transmission spectra at different refractive indexes, DI water, 5%, 10%, 15%, 20% NaCl solution were flowed into the flow cell one by one. Table 4-1 shows the detailed protocols. Please note that the light source should be turned on 15 minutes before any experiment to stabilize the light source. In the Ocean Optics SpectraSuite software, the integration time was set 10 ms and scans to average 200, boxcar width 10 and electric dark correction was ticked. Then the stable light source was connected with spectrometer and “reference” button was clicked on the software and the reference file was saved onto the hard disk. After the shutter of the light source was turned off, the “dark” button in the Ocean Optics SpectraSuite software was clicked and then the dark file was saved onto the hard disk. Then the experimental setup was re-arranged according to Figure 3-14, which was followed by changing intensity mode to transmission mode by clicking the button “T”
in the software. In the transmission mode, light intensity of the light source could be increased until the target resonance wavelengths are very visible. The optical fiber could be moved to make a good spectrum but once the experiment began it’s very important to keep the whole platform stable.

**Table 3-1 Experimental Protocol of acquiring transmission spectra of quasiperiodic nanohole arrays with sodium chloride solutions of different concentrations flowing by at the interface at the rate of 10 μL/min**

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flow DI water for 15 min. Save spectra</td>
</tr>
<tr>
<td>2</td>
<td>Stop pump and change to 5%NaCl tube and flow 15 minutes. Save spectra</td>
</tr>
<tr>
<td>3</td>
<td>Stop pump and change to 10%NaCl tube and flow 15 minutes. Save spectra</td>
</tr>
<tr>
<td>4</td>
<td>Stop pump and change to 15%NaCl tube and flow 15 minutes. Save spectra</td>
</tr>
<tr>
<td>5</td>
<td>Stop pump and change to 20%NaCl tube and flow 15 minutes. Save spectra</td>
</tr>
<tr>
<td>6</td>
<td>Stop pump and flow DI water for 30 minutes to clean the tubes</td>
</tr>
</tbody>
</table>

In these experiments, solutions of smaller concentrations flew before solutions of larger concentrations. To prevent inducing air bubbles into the Teflon tube, the pump was stopped to stabilize the solutions in the Teflon before the solution was changed. According to the author’s experience, changing syringes would induce air bubbles that might stay in the flow cell and fail the experiments. Thus suction method was used because no syringe change was needed.
Chapter 4

4 Surface Plasmon Resonance Experimental Results and Discussion

This chapter shows the results of surface plasmon resonance experiments. Experimental data were analyzed to calculate wavelength to refractive index sensitivities and resonance wavelengths in Chapter 4.1 and 4.2 respectively. The calculated results were compared with theoretical analysis and it was found that experimental results agreed well with theoretical analysis. A concise conclusion & discussion is given in Chapter 4.3.

4.1 Wavelength to Refractive Index Sensitivity Results

In this section, the detailed procedures to calculate wavelength to refractive index sensitivities of 12 and 5 fold quasiperiodic nanohole arrays are shown respectively. Basically the position of resonance wavelengths should be obtained by fitting the half-maximum of the corresponding transmission spectrum peak or trough and then the maxima or minima position of the fitted curve is obtained. The positions of the same peak or trough of the SPR spectra red shifts with the increase of the concentration of the NaCl solution and the wavelength to refractive index sensitivity is the slope of the wavelength-refractive index curve. At the end of the chapter, the acquired quasiperiodic sensitivities are plotted along with periodic sensitivities to validate the mathematical expressions in Chapter 2.2.

4.1.1 Wavelength to Refractive Index Sensitivity of 12 Fold Quasiperiodic Nanohole Array

The spectra that were collected with experimental methods described in Chapter 4 were saved into text files. With proper data processing, the spectra in Figure 4-1 could be obtained,
Figure 4-1 Transmission spectra of quasiperiodic nanohole arrays in DI water and various concentrations of Sodium Chloride solutions
Three steps of data processing were necessary to ensure the positions of the peaks or troughs of the transmission spectra before wavelength to refractive sensitivities were calculated. First the desired wavelength ranges of the peaks or troughs were ensured according to the half maximum of corresponding transmission spectra. Second the part of transmission spectra picked in the first step was fitted at an order of 9. Finally peak or trough positions were calculated.

First the troughs and peaks of the above spectra were picked and listed in Table 4-1.

**Table 4-1 Troughs (T) and peaks (P) of the transmission spectra. Unit is nm**

<table>
<thead>
<tr>
<th>Item</th>
<th>T One</th>
<th>P One</th>
<th>T Two</th>
<th>P Two</th>
<th>T Three</th>
<th>P Three</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>769.99</td>
<td>783.48</td>
<td>808.73</td>
<td>844.03</td>
<td>867.44</td>
<td>904.8</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>770.55</td>
<td>790.19</td>
<td>812.6</td>
<td>845.66</td>
<td>870.12</td>
<td>905.68</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>773.37</td>
<td>795.4</td>
<td>817.94</td>
<td>846.56</td>
<td>873.69</td>
<td>907.43</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>776</td>
<td>799.11</td>
<td>824.54</td>
<td>850</td>
<td>876.01</td>
<td>907.6</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>776.13</td>
<td>803.19</td>
<td>829.47</td>
<td>852.71</td>
<td>877.61</td>
<td>907.78</td>
</tr>
</tbody>
</table>

According to the above data, the start and end points of each fitting peak or trough were calculated by averaging the adjacent trough and peak and the results were listed in Table 4-2.

**Table 4-2 Start and end points of each fitting peak or trough. P stands for peak and T stands for trough. Unit is nm**

<table>
<thead>
<tr>
<th>Item</th>
<th>Fitting P One</th>
<th>Fitting T One</th>
<th>Fitting P Two</th>
<th>Fitting T Two</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>start</td>
<td>end</td>
<td>start</td>
<td>end</td>
</tr>
<tr>
<td>DI water</td>
<td>776.74</td>
<td>796.11</td>
<td>796.11</td>
<td>826.38</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>780.37</td>
<td>801.4</td>
<td>801.4</td>
<td>829.13</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>784.39</td>
<td>806.67</td>
<td>806.67</td>
<td>832.25</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>787.56</td>
<td>811.83</td>
<td>811.83</td>
<td>837.27</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>789.66</td>
<td>816.33</td>
<td>816.33</td>
<td>841.09</td>
</tr>
</tbody>
</table>
Second each selected curve in Table 4-2 was fit at an order of 9, as illustrated in Figure 4-2. By fitting the original spectrum into a simple curve, the uncertainty of the spectra caused by surrounding environment was decreased and the spectrum was simplified. Figure 4-2 illustrates the fitted curve of DI water’s fitting peak One.

![Figure 4-2](image)

**Figure 4-2 Original DI water curve (black) and its fitting curve (red)**

Finally the peak position of the fitted curve was found with 1st derivative method. Figure 4-3 illustrates the peak position of the fitted curve in Figure 4-2 (red).
With the above three steps, the peak or trough positions of all the curves could be calculated and the results were listed in Table 4-3. Unit is nm.

**Table 4-3 The maxima or minima positions of each fitting curve**

<table>
<thead>
<tr>
<th>Item</th>
<th>Fitting P One</th>
<th>Fitting T One</th>
<th>Fitting P Two</th>
<th>Fitting T Two</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>783.72</td>
<td>810.95</td>
<td>843.23</td>
<td>867.23</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>790.08</td>
<td>814.21</td>
<td>845.61</td>
<td>870.57</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>794.62</td>
<td>818.15</td>
<td>847.90</td>
<td>873.26</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>799.25</td>
<td>822.77</td>
<td>850.41</td>
<td>875.64</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>803.78</td>
<td>826.76</td>
<td>852.57</td>
<td>877.93</td>
</tr>
</tbody>
</table>

Each column of data in Table 4-3 could be plotted and the slope of their linear fit represented the wavelength to refractive index sensitivity, as illustrated by Figure 4-4. There were all together four sensitivities calculated but only the biggest sensitivity was
desired and used in the following section. Please note that in Figure 4-4 P stands for peak and T stands for trough.

Figure 4-4 Results of wavelength to refractive index sensitivities of selected peaks and troughs of 12 fold quasiperiodic nanohole array

4.1.2 Wavelength to Refractive Index Sensitivity of 5 Fold Quasiperiodic Nanohole Array

With similar methods as mentioned above, the peak or trough positions and wavelength to refractive index sensitivities of 5 fold quasiperiodic nanohole array were calculated. Figure 4-5 shows the transmission spectra obtained in the experiments.
Figure 4-5 Transmission spectra of 5 fold quasiperiodic nanohole array
Similarly, the peak and trough positions of each spectrum should be recorded before fitting the spectrum. The peak and trough positions were listed in Table 4-4. Compared to the 12 quasiperiodic array, more peaks and troughs were picked for 5 fold quasiperiodic array.

**Table 4-4** Troughs and peaks of the transmission spectra of 5 fold quasiperiodic nanohole array. T stands for Trough and P stands for Peak. Unit is nm.

<table>
<thead>
<tr>
<th>Item</th>
<th>T1</th>
<th>P1</th>
<th>T2</th>
<th>P2</th>
<th>T3</th>
<th>T4</th>
<th>P3</th>
<th>T5</th>
<th>P4</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>721.34</td>
<td>731.69</td>
<td>755.47</td>
<td>783.48</td>
<td>818.67</td>
<td>859.91</td>
<td>863.5</td>
<td>876.54</td>
<td>912.32</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>724.99</td>
<td>733.98</td>
<td>756.98</td>
<td>789.26</td>
<td>819.96</td>
<td>859.55</td>
<td>868.51</td>
<td>879.75</td>
<td>912.84</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>726.33</td>
<td>738.75</td>
<td>763.59</td>
<td>795.4</td>
<td>820.32</td>
<td>860.27</td>
<td>872.44</td>
<td>883.12</td>
<td>913.71</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>727.67</td>
<td>741.23</td>
<td>769.99</td>
<td>796.89</td>
<td>823.62</td>
<td>862.24</td>
<td>873.69</td>
<td>884.01</td>
<td>915.1</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>733.41</td>
<td>747.32</td>
<td>771.68</td>
<td>807.44</td>
<td>824.35</td>
<td>864.75</td>
<td>876.37</td>
<td>887.02</td>
<td>917.37</td>
</tr>
</tbody>
</table>

With the above data, the start and end point of each fitting peak or trough were calculated, as shown by Table 4-5.

**Table 4-5** Start and end point of each fitting peak or trough. Unit is nm

<table>
<thead>
<tr>
<th>Item</th>
<th>Fitting P1</th>
<th>Fitting T1</th>
<th>Fitting P2</th>
<th>Fitting T2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>start</td>
<td>end</td>
<td>start</td>
<td>end</td>
</tr>
<tr>
<td>DI water</td>
<td>726.52</td>
<td>743.58</td>
<td>743.58</td>
<td>769.48</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>729.49</td>
<td>745.48</td>
<td>745.48</td>
<td>773.12</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>732.54</td>
<td>751.17</td>
<td>751.17</td>
<td>779.50</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>734.45</td>
<td>755.61</td>
<td>755.61</td>
<td>783.44</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>740.37</td>
<td>759.5</td>
<td>759.5</td>
<td>789.56</td>
</tr>
</tbody>
</table>
The selected curves were then fitted and their peaks and trough positions calculated. The calculation results were listed in Table 4-6.

**Table 4-6 The maxima or minima position of each fitting curve**

<table>
<thead>
<tr>
<th>Item</th>
<th>Fitting P1</th>
<th>Fitting T1</th>
<th>Fitting P 2</th>
<th>Fitting P3</th>
<th>Fitting T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>731.57</td>
<td>754.03</td>
<td>783.42</td>
<td>863.51</td>
<td>875.64</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>734.38</td>
<td>757.84</td>
<td>787.99</td>
<td>868.98</td>
<td>879.21</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>737.68</td>
<td>763.34</td>
<td>792.73</td>
<td>871.80</td>
<td>882.34</td>
</tr>
<tr>
<td>15% NaCl</td>
<td>741.95</td>
<td>768.63</td>
<td>797.02</td>
<td>874.11</td>
<td>885.21</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>745.85</td>
<td>772.64</td>
<td>805.73</td>
<td>876.05</td>
<td>888.08</td>
</tr>
</tbody>
</table>

The corresponding wavelength to refractive index sensitivities were then calculated according to Table 4-6 and the results were shown by Figure 4-6.

![Figure 4-6](image)

**Figure 4-6 Results of wavelength to refractive index sensitivities of selected peaks and troughs of 5 fold quasiperiodic nanohole array**
4.1.3 Equation Validation with Experimental Data

In our previous research, wavelength to refractive index sensitivities acquired by other groups were summarized, as shown by Appendix 4, but none of those sensitivities was acquired on quasiperiodic nanohole arrays. The sensitivities acquired on quasiperiodic nanohole arrays were plotted together with those on periodic nanohole arrays to see whether the trend of experimental sensitivities agree with curve of equation (2-15) (black line).

![Figure 4-7 Theoretical (black line) and experimental sensitivities of both periodic (blue dots) and quasiperiodic (green dots) nanohole arrays](image)

Apart from one dot around 1500 nm, other dots were all very close to the curve of equation (2-15), the black line in Figure 4-7. The green triangular were also very close to the black line. Given the many factors that might affect the sensitivities, equation (2-15) demonstrated good capability to calculate the sensitivity. Of course a thorough validation still waits for further proofs.
4.2 Resonance Wavelength Results

The calculating process of the resonance wavelengths of 5 fold Penrose tile nanohole array based on equations in Chapter 2.3 is shown in this section. Basically the $\beta$ defined in Chapter 2.3 is first calculated with the values of $n$ goes from 0 to 4 and a MATLAB program is used to calculate the predicted resonance wavelengths corresponding to each combination of $(i, j, \beta)$. To make a clear comparison the predicted resonance wavelengths are listed together with those obtained by experimental data as illustrated in Table 4-8. At the end of this section the errors of our predictions are calculated and turn out to be within 2.3%. The detailed calculation procedures are as follows.

According to equation (2-21) resonance wavelengths can be written as $\lambda = \frac{a_m n \sqrt{\sin \frac{\pi}{5} \cdot \tau}}{\beta}$, where $\beta = \sqrt{\frac{1 + \cos \frac{4 \pi}{5}}{2} i^2 + \frac{1 - \cos \frac{4 \pi}{5}}{2} j^2}$. Since the values of $a_m, n, \sqrt{\sin \frac{\pi}{5}}$ are known thus the only variable in equation (2-21) is $\beta$ which is calculated in Table 4-7.

<table>
<thead>
<tr>
<th>Value of $n$</th>
<th>$\cos(4n\pi/5)$</th>
<th>Simplified $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$i$</td>
</tr>
<tr>
<td>1</td>
<td>-0.8090</td>
<td>$\sqrt{0.0955i^2 + 0.9045j^2}$</td>
</tr>
<tr>
<td>2</td>
<td>0.3090</td>
<td>$\sqrt{0.6545i^2 + 0.3455j^2}$</td>
</tr>
<tr>
<td>3</td>
<td>0.3090</td>
<td>$\sqrt{0.6545i^2 + 0.3455j^2}$</td>
</tr>
<tr>
<td>4</td>
<td>-0.8090</td>
<td>$\sqrt{0.0955i^2 + 0.9045j^2}$</td>
</tr>
</tbody>
</table>

With the MATLAB program in Appendix 3, $(i, j)$ and corresponding $\beta$ and predicted wavelength were obtained. In this case, all $(i, j)$ integer pairs within the range of $0 \leq i \leq 10$ and $0 \leq j \leq 10$ were used in the calculation. Table 4-8 shows the values of $i, j, \beta$ and the predicted values of resonance wavelengths $\lambda_{pre}$ and corresponding resonance wavelengths (in bold) obtained by experiments. In Table 4-8 T represents for trough and P represents for peak.
Table 4-8 The predicted and experimental resonance wavelength corresponding to $i$, $j$ and $\beta$

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>$\beta$</th>
<th>$\lambda_{pre}/n_{sp}$</th>
<th>$\lambda^1_{exp}/n^1_{sp}$</th>
<th>$\lambda^2_{exp}/n^2_{sp}$</th>
<th>$\lambda^3_{exp}/n^3_{sp}$</th>
<th>$\lambda^4_{exp}/n^4_{sp}$</th>
<th>$\lambda^5_{exp}/n^5_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>1.62</td>
<td>446.33</td>
<td>T455.66</td>
<td>T452.49</td>
<td>T449.55</td>
<td>T446.56</td>
<td>T443.58</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2.36</td>
<td>494.49</td>
<td>P497.90</td>
<td>P496.10</td>
<td>P494.52</td>
<td>P492.84</td>
<td>P490.71</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>2.16</td>
<td>540.17</td>
<td>T541.94</td>
<td>T539.90</td>
<td>T538.04</td>
<td>T536.36</td>
<td>T535.47</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.81</td>
<td>547.84</td>
<td>P548.81</td>
<td>P547.31</td>
<td>P546.23</td>
<td>P545.79</td>
<td>P545.05</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>1.76</td>
<td>563.69</td>
<td>T565.66</td>
<td>T564.79</td>
<td>T565.23</td>
<td>T565.42</td>
<td>T564.63</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.00</td>
<td>584.25</td>
<td>P587.71</td>
<td>P587.26</td>
<td>P586.99</td>
<td>P586.30</td>
<td>P588.81</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1.93</td>
<td>606.37</td>
<td>T613.93</td>
<td>T611.02</td>
<td>T608.27</td>
<td>T605.71</td>
<td>T602.86</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1.85</td>
<td>630.20</td>
<td>P631.91</td>
<td>P628.81</td>
<td>P625.85</td>
<td>P622.92</td>
<td>P620.25</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.56</td>
<td>637.32</td>
<td>T645.21</td>
<td>T641.12</td>
<td>T637.88</td>
<td>T634.63</td>
<td>T630.91</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.81</td>
<td>644.02</td>
<td>P647.79</td>
<td>P647.62</td>
<td>P645.54</td>
<td>P643.01</td>
<td>P640.20</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.95</td>
<td>645.94</td>
<td>T656.89</td>
<td>T655.25</td>
<td>T653.34</td>
<td>T651.18</td>
<td>T648.99</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.72</td>
<td>678.78</td>
<td>P683.76</td>
<td>P680.01</td>
<td>P676.34</td>
<td>P673.19</td>
<td>P669.99</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1.43</td>
<td>696.53</td>
<td>T712.24</td>
<td>T707.42</td>
<td>T702.80</td>
<td>T698.04</td>
<td>T693.23</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.00</td>
<td>722.18</td>
<td>P727.03</td>
<td>P722.43</td>
<td>P718.12</td>
<td>P713.99</td>
<td>P709.98</td>
</tr>
</tbody>
</table>

According to Table 4-8, Figure 4-8 was designed to visually show the positions of the predicted wavelength and experimental wavelength. In order to eliminate the influence of refractive index of different concentrations of sodium chloride solutions, the $x$ axis was divided by $n_{sp} = \sqrt{\varepsilon_d}$ and thus the predicted resonance wavelength divided by $n_{sp}$ could be written as

$$\frac{\lambda}{n_{sp}} = \frac{2\pi}{a_m \beta} \approx \frac{0.9522 a_m}{\beta}$$

The above equation also simplified the calculation of predicted resonance wavelengths.
According to Figure 4-8, the equation (2-21) successfully predicted both peak and trough wavelengths because its parent equation (2-19) included both resonance peaks and resonance troughs. Equation (2-21) could predict the resonance wavelengths with very acceptable accuracy. To further investigate equation (2-21)’s capability of predicting resonance wavelengths, the prediction error was defined as,

$$\delta = \frac{\lambda_{pdt} - \lambda_{exp}}{\lambda_{exp}} = \frac{\lambda_{pdt} - \lambda_{pdt}/n_{sp}}{\lambda_{pdt}/n_{sp}}$$

where $\lambda_{pdt}$ and $\lambda_{exp}$ represented predicted and experimental resonance wavelengths respectively and $n_{sp}$ was the effective refractive index of surface plasmon waves.

The error of each predicted wavelength was shown by Figure 4-9.
Figure 4-9 Error of predicted resonance wavelengths. The horizontal dashed line is $\delta = 0$

Figure 4-9 shows that the errors of the predicted wavelengths are well within 2.3% which is quite acceptable.

4.3 Conclusion and Discussion

In Chapter 4, the data obtained in Chapter 3 were analyzed to calculate wavelength to refractive index sensitivities and resonance wavelengths. The experimental data were then used to validate the theoretical analysis in Chapter 2.

Experimental wavelength to refractive index sensitivities from nanohole arrays that are in different patterns (periodic or quasiperiodic), diameters and pitches are in a linear trend around the theoretical line. The two indications by theoretical analysis are well supported by experimental data. First, wavelength to refractive index sensitivities are not associated with the geometry or structure of the nanohole arrays. Second, wavelength to refractive index sensitivities are in a rough linear relationship with the wavelengths.
Experimental resonance wavelengths were compared with theoretical results calculated by equations in Chapter 2 and the errors turned out to be within 2.3% which is quite acceptable. Therefore the equations deduced in this thesis are acceptable for calculating resonance wavelengths. This is different from previous research in which only trough wavelengths were predicted and peak wavelengths were not able to be predicted.\(^6\) The reasons may lie in the calculation of reciprocal vectors.

To better validate the wavelength to refractive index sensitivity equation, it is suggested that more kinds of quasiperiodic nanohole arrays of different diameters and pitches be used. Since each kind of nanohole array has a different structure factor and thus the equation to calculate resonance wavelength is different. However, different nanohole arrays share the same calculating approach of resonance wavelengths, namely Bragg condition. Some people doubt the usage of Bragg condition in calculating resonance wavelengths and more research should be done to thoroughly explain about this problem.\(^6\)
Chapter 5

5 Surface Enhanced Raman Spectroscopy on Nanohole Arrays

Other than surface plasmon resonance, another important application of nanohole array is surface enhanced Raman Spectroscopy which has an advantage of molecular specificity over surface plasmon resonance. This chapter aims to demonstrate that Raman Scattering is enhanced on the substrate of nanohole arrays. The experimental setup, materials, methods and experimental results are described. Please note that since silicon wafers with periodic nanohole array are commercially available and have a much larger area than customized quasiperiodic nanohole arrays, this chapter will use periodic instead of quasiperiodic nanohole arrays.

5.1 Introduction

Surface-enhanced Raman Spectroscopy (SERS) is another important application of nanohole arrays. As mentioned in Chapter 2, surface plasmon resonance detection method relies on the changes in refractive index at the metal-dielectric interface and provides good sensitivity. However, surface plasmon resonance (SPR) lacks molecular specificity and antibodies have to be used to capture specific proteins, which increase the complexity and uncertainty. Unlike SPR, SERS provides excellent molecular specificity and thus has been a hot research field since it was first discovered. Many works have been published that use nanohole arrays to enhance Raman Scattering but few works have been done to incorporate the nanohole arrays onto an optical fiber which is a natural waveguide and can be used for remote detection. By guiding excitation laser with optical fiber instead of the common microscope, the SERS device becomes portable and the price is decreased. This thesis demonstrates the feasibility of using a nanohole array for SERS and a prototype of optical fiber based SERS device is proposed.
5.2 Fundamentals of Surface Enhanced Raman Spectroscopy

Surface enhanced Raman Spectroscopy is a surface sensitive technology that enhances Raman scattering by analytes adsorbed on rough or nanostructured surfaces. The principle of Raman Scattering is illustrated by Figure 5-1. When incoming photons are scattered from an atom or molecule, most scattered photons have the same energy (frequency and wavelength) as the incident photon and this kind of scattering is called Rayleigh scattering. A small fraction of the scattered photons have lower frequency than that of the incident photons and such scattering is called Raman scattering.

![Figure 5-1 Principle of Raman scattering](image)

In this thesis, Raman scattering is expressed by the wavenumber shift from the wavenumber of excitation source or Rayleigh scattering, the calculation equation is shown below,

\[
k = k_{exc} - k_{vib} = \frac{1}{\lambda_{exc}} - \frac{1}{\lambda_{vib}}
\]  

where \(k_{exc}, \lambda_{exc}\) are the wavenumber and wavelength of the excitation laser; \(k_{vib}, \lambda_{vib}\) are the wavenumber and wavelength of the vibration of Raman scattering atoms or molecules. The unit of \(k\) is \(cm^{-1}\) in this section.

Since Raman scattering photons only account for 1 in 10 million scattering photons and thus the signal of Raman Scattering is very weak, which limited the application of Raman
Scattering until the technique of surface enhanced Raman Spectroscopy was discovered. Both electromagnetic (EM) enhancement and chemical (CE) enhancement account for the SERS enhancement. The intense electromagnetic field arises from the localized surface plasmons and EM is the main contributor of the enhancement. Chemical enhancement originates from the charge transfer between the surface and the adsorbed analytes. According to previous literature, the Raman signal is strongest when the nanohole array, if nanohole milled metallic surface is used, has a resonant transmission closer to the wavelength of the excitation laser.

5.3 Experimental Procedure

A typical reflective surface enhanced Raman Spectroscopy experimental setup was used in this section. The nanohole patterned gold film was transferred to silicon wafer with the method introduced in Chapter 3.2. Two typical SERS active chemicals 4-Mercaptopyridine (4-MP) and Rhodamine 6G (R6G) were applied onto the nanohole patterned gold film and other substrates as control experiments. At the end of this chapter, the transmission spectrum of the nanohole patterned gold film is shown and its transmission almost reaches its peak at the wavelength of excitation laser, which is a pre-condition to generate strong enhanced Raman scattering.

5.3.1 Experimental Setup

In the SERS experimental setup illustrated by Figure 5-2, the excitation laser, with a wavelength of 785 nm, was focused onto Au-air interface through a 10× objective lens. The scattering light (containing Raman information) was reflected into the objective and then collected by a spectrograph. The silicon wafer with a layer of gold film was mounted on an XYZ microscope stage.
Figure 5-2 Experimental setup for Surface Enhanced Raman Spectroscopy. The laser wavelength is 785 nm and the analytes are adsorbed at the Au-air interface.

5.3.2 Application of Analytes

In this section, the two analytes were used, namely 4-Mercaptopyridine (4-MP, $C_5H_5NS$) and Rhodamine 6G (R6G, $C_{28}H_{31}N_2O_3Cl$) to demonstrate the Raman enhancement of nanohole arrays. Their chemical structures illustrated in Figure 5-3 show that 4-MP is a smaller molecule and its sulfur atom will form a Au-S with gold surface while R6G is a larger molecule and will form hydrogen bonds with gold surface.
Figure 5-3 Chemical structures of 4-Mercaptopyridine (a) and Rhodamine 6G (b)

After being transferred to clean silicon wafer by epoxy (refer to Chapter 3.2), the gold film was cleaned in UV ozone for 20 minutes, washed with deionized (DI) water and dried with nitrogen gas. Then the substrates (both patterned and unpatterned gold film) were immersed in 3 mM 4-MP or 100 μM R6G water solutions for 3h in room temperature to form a self-assembled monolayer (SAM). Here unpatterned gold films were used as a control experiment. The immersion procedure is illustrated by Figure 5-4.
5.3.3 Characterization of SERS Nanohole Array

The nanohole array in the surface enhanced Raman Spectroscopy experiment is periodic, with a diameter of 200 nm, thickness of 100 nm and pitch of 400 nm. Previous research shows that the Raman signal is strongest when the resonant transmission peak wavelength of the nanohole array is close to the laser wavelength. The resonant transmission spectra of the nanohole array in the SERS experiment as shown in Figure 5-5 illustrates that the nanohole array has a pretty high transmission of 53% which is very close to that of the peak wavelength. Therefore this nanohole array is expected to yield strong SERS signal at the excitation of 785 nm laser source.
Figure 5-5 Transmission spectra of nanohole array of which peak wavelength is very close to the wavelength of exciting laser, 785 nm

5.4 Results and Discussion

To demonstrate that gold nanohole arrays were able to enhance Raman scattering signals, two analytes were used, namely 4-Mercaptopyridine (4-MP) and Rhodamine (R6G). For each analyte, 4 kinds of substrates were prepared. The first substrate was solid materials of 4-MP/R6G on clean silicon wafer. The Raman scattering signals of other substrates were compared with that of solid 4-MP/R6G to help judge whether their Raman scattering signals were from 4-MP/R6G. The second substrate was patterned gold nanohole arrays which had been immersed in 4-MP/R6G aqueous solutions for 3 hours. The Raman scattering signals of gold nanohole arrays were compared with the third substrate, unpatterned gold films which had also been immersed in 4-MP/R6G aqueous solution for 3 hours, to demonstrate the Raman Scattering enhancement on patterned gold nanohole arrays. Some people might doubt whether the gold nanohole arrays with no 4-MP or R6G might generate similar spectra to 4-MP/R6G by any chance and thus the
Raman scattering signals of gold nanohole arrays before immersing into 4-MP/R6G solutions were collected to help demonstrate whether the Raman Scattering signals from substrate patterned and unpatterned gold films were purely from the analytes or from gold nanoholes. In the following sections, the Raman scattering results of 4-MP and R6G were separately shown with a focus on 4-MP as R6G results were similar.

5.4.2 Results of 4-MP

4-Mercaptopyridine (4-MP) is widely used in surface enhanced Raman Spectroscopy (SERS) studies because it can form a self-assembled monolayer on metal surfaces and has a large scattering cross section. The microscope image of solid material of 4-MP and its Raman scattering spectrum is illustrated by Figure 5-6.
Figure 5-6 Microscope image (a) and Raman scattering spectrum (b) of solid 4-MP

Figure 5-6(b) was the raw spectrum before baseline correction and the peaks of Raman shift were marked. The unique and sharp Raman shift peaks would help distinguish different analytes.

The Raman scattering spectra of patterned and unpatterned gold films are listed below for comparison. Please note that for solid 4-MP/R6G the exposure time is 1s, accumulation 1 and laser power 50 mW, while in the case of the other substrates the exposure time for 10s, accumulations 2 and laser power 20 mW. The Raman scattering intensities of different substrates are not absolutely quantitatively comparable because the focusing of microscope influence the intensity of the Raman scattering signals and it is very difficult to make the focus the same in different experiments. Therefore the Raman scattering is only used for semi-quantitative test and it’s best to focus on the peak positions of the Raman shift data rather than the intensity of the Raman shift data. Please note that laser
power varies with literature, some use laser power as low as 0.5 mW$^{16-18}$ and others use as high as 35 mW$^{15,19}$. 

The Raman scattering spectrum of gold nanohole arrays and unpatterned gold films are shown below. The gold nanohole array and unpatterned gold film were on one single substrate (only part of the whole gold film was patterned) and the patterned gold and unpatterned gold were different in color, as illustrated by Figure 5-7(a) and Figure 5-8(a).
Figure 5-7 Microscope image (a) and Raman scattering spectrum (b) of 4-MP on gold nanohole arrays

Even though 4-MP was not visible from Figure 5-7(a), the Raman scattering signal was pretty strong and the peaks were very obvious, especially at the Raman shift of 1093 cm$^{-1}$. To further demonstrate the signal enhancement of nanohole arrays, the spectrum of 4-MP on unpatterned gold film is shown in Figure 5-8.
Figure 5-8 Microscope image (a) and Raman scattering spectrum of 4-MP on unpatterned gold film
Although Raman Scattering is only semi-quantitative, the too big difference in intensity between nanohole array and unpatterned gold film can still lead to the conclusion that the Raman scattering on nanohole arrays is much stronger than that on unpatterned gold film. Another difference between the two substrates is that the signal to noise ratio of 4-MP on nanohole arrays is much bigger than that of 4-MP on unpatterned gold. The peak positions of the two Raman shift spectra are marked and it is not difficult to tell that the two substrates have different peak positions.

In Figure 5-9, Raman scattering spectra from both patterned and unpatterned gold films were compared with that of solid 4-MP and unlike the above spectra, the Raman scattering spectra were baseline corrected which made the peaks more obvious.
Figure 5-9 Baseline corrected Raman Scattering spectra of solid 4-MP(a), 4-MP on nanohole arrays (b) and unpatternd gold film (c)
Three peaks were picked out for comparison from Figure 5-9(c), namely 598 cm\(^{-1}\), 874 cm\(^{-1}\), 1275 cm\(^{-1}\). However, none of these three peaks corresponded with the peaks in the Raman scattering spectrum of solid 4-MP as shown in Figure 5-9(a). Even if the exposure was increased to exposure time 10s, 5 accumulations and laser power 50 mW, the Raman scattering spectrum in Figure 5-10 was acquired and still no corresponding peaks could be found in the Raman spectrum of solid 4-MP. Therefore the 4-MP on unpatterned gold films could not be detected without enhancing its Raman scattering signal.

**Figure 5-10 Raman scattering of 4-MP on unpatterned gold film under larger exposure**

However, peaks of the spectrum of 4-MP on patterned gold films found their counterparts in the spectrum of solid 4-MP, as shown by Table 5-1. Please note that 520 cm\(^{-1}\) is the Raman scattering peak of silicon and it’s not included in Table 5-1.
Table 5-1 Raman scattering peak positions of 4-MP on nanohole arrays and solid 4-MP

<table>
<thead>
<tr>
<th>4-MP on nanohole arrays (cm(^{-1}))</th>
<th>Solid 4-MP (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>716</td>
<td>721</td>
</tr>
<tr>
<td>1000</td>
<td>988</td>
</tr>
<tr>
<td>1060</td>
<td>1078</td>
</tr>
<tr>
<td>1093</td>
<td>1104</td>
</tr>
<tr>
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<td>1226</td>
</tr>
<tr>
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<td>1597</td>
</tr>
<tr>
<td>1607</td>
<td>1618</td>
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</tbody>
</table>

In table 5-1, only peaks of large intensities were picked and the peaks agreed well with previous research. All Raman scattering peaks of 4-MP on nanohole arrays could find their counterparts in those of solid 4-MP. It was found that the Raman scattering peaks of 4-MP on nanohole arrays were slightly blue shifted compared to those of solid 4-MP, except for 1000 cm\(^{-1}\) which was red shifted, in the same case of Ref.20. The blue shift happened when 4-MP adsorbs onto the gold nanohole array by forming an Au-S bond and thus the ring became perpendicular to the surface. Chemical bond change and environment change would lead to the peak shift. According to this comparison, it can be concluded that the Raman scattering spectra in Figure 5-9(b) does show the Raman scattering of 4-MP which is not shown in the control experiment (4-MP on unpatterned gold) according to Figure 5-9(c).

Before concluding that the nanohole arrays can enhance the Raman scattering signals, some may doubt the Raman scattering of nanohole arrays may come from the nanohole array itself instead of the analytes on nanohole arrays. That doubt can be solved by the fourth substrate, nanohole arrays without being immersed into analyte solution, whose Raman scattering spectra is shown in Figure 5-11. Please note that to enhance the signals and increase signal to noise ratio the exposure time is 10s, accumulations 3 and laser power 50 mW.
Figure 5-11 Raman Scattering graph of clean nanohole arrays without immersing into analyte solution

It is obvious that no 4-MP peaks can be found in Figure 5-11. Therefore it is valid to conclude that gold nanohole arrays can enhance Raman scattering. Actually it enables the detection of 4-MP self-assembled monolayers (SAM) because SAMs on unpatterned gold film cannot be detected even if exposure is enlarged as shown by Figure 5-10.

5.4.3 Results of R6G

To make the conclusion more convincing, similar experiments were conducted with Rhodamine 6G (R6G). In the R6G experiments, 3 substrates were prepared. The first one was solid R6G on silicon wafer. Please note that Raman scattering of silicon (520 cm\(^{-1}\)) was not seen on solid R6G’s Raman Scattering spectra as the laser focus point was too far from the silicon wafer. The second and third substrates were gold films with and without nanohole arrays immersed in 100 μM R6G aqueous solutions for 3 hours before thorough washing.
At first the Raman scattering of solid R6G was tested to help judge whether the Raman scattering spectra from the next two substrates were R6G and the result was shown in Figure 5-12. As for solid R6G, the exposure time was 1s, accumulations 3 and laser power 10 mW. However, for the patterned and unpatterned gold films, the exposure time was 10s, accumulations 2 and laser power 20 mW.
Figure 5-12 Microscope image of solid R6G (a) and both original (b) and baseline corrected (c) Raman Scattering spectra of solid R6G
According to Figure 5-12, it is obvious that solid R6G has really strong Raman Scattering signals with very narrow bandwidth. Figure 5-13 shows the Raman scattering spectrum of nanohole arrays immersed in R6G aqueous solutions.
Figure 5-13 Microscope image of nanohole arrays immersed in R6G solution (a) and both original (b) and baseline corrected (c) Raman Scattering spectra
Table 5-2 is given to compare the peak positions of patterned gold immersed in R6G solutions in figure 5-13(c) and solid R6G in 5-12(c). Please note that 520 cm\(^{-1}\) is not included Table 5-2 as 520 cm\(^{-1}\) is from silicon.

**Table 5-2 Raman scattering peak positions of R6G on nanohole arrays and solid R6G**

<table>
<thead>
<tr>
<th>R6G on nanohole arrays (cm(^{-1}))</th>
<th>Solid R6G (cm(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>611</td>
<td>611</td>
</tr>
<tr>
<td>773</td>
<td>768</td>
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<tr>
<td>1509</td>
<td>1516</td>
</tr>
</tbody>
</table>

Although the peaks of the two graphs are not exactly the same, it is still safe to say that R6G is detected in that random errors may exist in the measurement and that the peaks are picked out manually which will inevitably cause some error.

To demonstrate that there was Raman scattering enhancement on nanohole arrays, unpatterned gold film worked as the control experiment and the result was shown in Figure 5-14.
It is obvious that intensity of R6G on unpatterned gold film is much weaker than that of nanohole array patterned gold film. Another point is that the signal to noise ratio is too low and there are no very obvious peaks. That means R6G is not detected on the third substrate of R6G experiments. Similar to the result in 4-MP experiments, the Raman Scattering spectra of R6G on nanohole arrays cannot be caused by the nanohole arrays itself. It is concluded that the Raman scattering is enhanced on nanohole arrays.

5.5 Conclusion

In summary, 4-MP and R6G self-assembled monolayers (SAMs) are formed on nanohole array substrates and unpatterned gold substrates and the Raman scattering spectra on nanohole array substrates are much stronger than that on unpatterned gold substrates.
Raman scattering enhancement is found on gold films milled with nanohole arrays and this enhancement can be used in low concentration Raman spectroscopy.
6 Thesis Summary and Future Direction

This thesis focuses on two important features of nanohole array based surface plasmon resonance spectra: wavelength to refractive index sensitivity and resonance wavelength. Mathematical equations are deduced to analyze the two features and theoretical analysis is supported by experimental data. In the last part of the thesis, nanohole array is demonstrated to be able to enhance Raman scattering. The contents of this thesis are summarized according to the structure of the thesis and future directions of related research are also discussed.

6.1 Thesis Summary

This thesis mainly researches two important features of surface plasmon resonance transmission spectra of quasiperiodic nanohole arrays, namely wavelength to refractive index sensitivity and resonance wavelength. Mathematical equations are established to calculate the sensitivity and resonance wavelength and the theoretical analysis is further validated by experimental data. At the end of this thesis, surface-enhanced Raman Spectroscopy of nanohole array is also demonstrated.

Chapter 2 introduces the basic theory of surface plasmon resonance and resonance equation is established according to Bragg condition for any two dimensional nanohole lattices. The mathematical equations to calculate wavelength to refractive index sensitivity and resonance wavelength are developed respectively based on Bragg condition. The mathematical expression of refractive index sensitivity shows that sensitivity roughly linearly increase with resonance wavelength and is not associated with the specific pattern of the nanohole array.

In chapter 3, inflation method to design 12 fold quasiperiodic nanohole array and generalized dual multigrid method to design 5 five Penrose tile nanohole array are
described. The nanohole arrays are fabricated using electron beam lithography which is followed by gold sputtering. The patterned gold film is then mounted onto the tip of optical fiber with a 3D printed transferring kit. Two optical fibers which are connected with light source and spectrometer respectively were aligned by a flow cell. DI water and NaCl solutions with different concentrations were flown by the surface of nanohole arrays and the transmission spectra were collected for data analysis.

In Chapter 4, the spectra obtained by the experiments in Chapter 3 were analyzed and compared with theoretical analysis. First, the sensitivities of quasiperiodic nanohole arrays together with sensitivities of periodic nanohole arrays are used to validate the wavelength to refractive index sensitivity equations developed in Chapter 2. It is found that even though the nanohole pattern varies (periodic or quasiperiodic) and the parameters of the pattern (diameter, pitch, thickness) vary, the experimental sensitivities are in a pretty good linear trend and the pattern does not affect the sensitivity at all. Second, the mathematical equation to calculate resonance wavelength is validated with experimental data and the errors turn out to be within 2.3%. The acceptable errors demonstrate the feasibility of the applying the mathematical equation to calculate resonance wavelengths.

Other than surface plasmon resonance, another important application of nanohole array, surface enhanced Raman Spectroscopy is demonstrated in Chapter 5. Self-Assembly Monolayers (SAM) of 4-MP and R6G are formed on patterned gold film and show much enhanced Raman scattering on the control experiments on unpatterned gold film.

In conclusion, this thesis deduces mathematical equations to calculate resonance wavelengths and wavelength to refractive index sensitivities and these equations are validated with experimental data. Raman Scattering enhancement is also demonstrated on nanohole arrays.
6.2 Future Direction

Fundamental research of nanohole array based surface plasmon resonance (SPR) and surface enhanced Raman Spectroscopy (SERS) has been discussed in this thesis and the future direction of this research is to make next-generation SPR and SERS sensors which are discussed respectively as below.

The current SPR experimental platform can be used to detect some diseases. Specific antibodies can attach to the surface of gold nanohole arrays and corresponding antigens captured by the antibodies will result in red shift of SPR spectrum. The BioNanoTechnology lab has designed a novel principle to detect prostate cancer. In the future, it is possible to make a portable SPR sensor based on nanohole arrays by engineering the current SPR platform.

Since a lot of diseases or toxic materials are characterized by specific proteins/molecules while Raman scattering has molecular specificity, nanohole array based SERS sensors will be widely used in fields like medical diagnosis and food safety. Ideally disease or toxic materials can be detected by immersing the nanohole arrays into solutions that contain target molecules. Similar to the SPR experimental platform described in this thesis, nanohole array based SERS sensors can also be engineered onto the tip of optical fibers and thus the SERS sensor can be portable.
Reference


Appendices

Appendix 1 Derivation of Wavelength to Refractive Index Sensitivity Equation

The optical spectrometer used for the experiments discussed in this thesis only covers visible and near infrared regions ranging from 340 nm and 1040 nm. Then it is reasonable to suppose that the dielectric constant does not change in this narrow wavelength range.

\[
\sqrt{\left( \frac{2\pi}{\lambda} \sin \theta + iG_x \right)^2 + (iG_y)^2} = \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}}
\]

\[
\sqrt{\left( \frac{2\pi}{\lambda} \sin \theta + iG_x \right)^2 + (jG_y)^2} = \frac{2\pi}{\lambda} \sqrt{\frac{i\varepsilon'_m n^2}{\varepsilon'_m + n^2}}
\]

\[
\sqrt{(\sin \theta + \frac{\lambda}{2\pi} iG_x)^2 + (\frac{\lambda}{2\pi} jG_y)^2} = \sqrt{\frac{\varepsilon'_m n^2}{\varepsilon'_m + n^2}}
\]

\[
\frac{\lambda^2}{4\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) + \frac{\lambda}{\pi} iG_x \sin \theta + \sin^2 \theta = \frac{\varepsilon'_m n^2}{\varepsilon'_m + n^2} \quad (1)
\]

Take \( \frac{\Delta \lambda}{\Delta n} \) at both sides of the equation (1),

\[
\frac{\lambda}{2\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) \frac{\Delta \lambda}{\Delta n} + \frac{iG_x \sin \theta \Delta \lambda}{\pi \Delta n} = \left( -\frac{\varepsilon'_m}{1 + \frac{\varepsilon'_m}{n^2}} \right) \left( -\frac{2\varepsilon'_m}{n^3} \right)
\]

\[
= \frac{\varepsilon'_m n^2}{\varepsilon'_m + n^2} \cdot \frac{2\varepsilon'_m}{n(\varepsilon'_m + n^2)} \quad (2)
\]

When the incoming light is normal, which means \( \theta = 0 \), equations (1) and (2) can be simplified as,

\[
\frac{\lambda^2}{4\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) = \frac{\varepsilon'_m n^2}{\varepsilon'_m + n^2} \quad (3)
\]
\[
\frac{\lambda}{2\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) \Delta \lambda \Delta n = \frac{\varepsilon_m n^2}{\varepsilon_m n^2 + n e_n^2} \cdot \frac{2 e_m'}{n (\varepsilon_m + n^2)} \tag{4}
\]

Insert equation (3) into equation (4) and we can get,

\[
\frac{2}{\lambda} \cdot \frac{\lambda^2}{4\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) \Delta \lambda \Delta n = \frac{\lambda^2}{4\pi^2} \left( i^2 G_x^2 + j^2 G_y^2 \right) \cdot \frac{2 e_m'}{n (\varepsilon_m + n^2)}
\]

Thus

\[
\frac{\Delta \lambda}{\Delta n} = \frac{\lambda e_m'}{n (\varepsilon_m + n^2)} = S
\]

Please note that even if there is no approximation that \( e_d = n^2 \) which is illustrated by equation (6-8), we can still get a similar deduction, which is shown below,

\[
\frac{\Delta}{\Delta n} \left( \frac{\varepsilon_m e_d'}{\varepsilon_m + e_d} \right) = \frac{\Delta}{\Delta n} \left( \frac{\varepsilon_m'}{\varepsilon_m + 1} \right) = \left( \frac{\varepsilon_m'}{\varepsilon_m + 1} \right) \left( \frac{\varepsilon_m}{\varepsilon_m' + e_d} \right) \frac{\Delta e_d}{\Delta n} = \frac{\varepsilon_m e_d'}{\varepsilon_m + e_d} \cdot \frac{\varepsilon_m}{\varepsilon_m' + e_d} \frac{\Delta e_d}{\Delta n}
\]

Thus

\[
\frac{\Delta \lambda}{\Delta n} = \frac{\lambda}{2} \frac{e_m'}{e_d (e_m'^2 + e_d)} \frac{\Delta e_d}{\Delta n}
\]

Furthermore, even if \( e_m' \) changes with refractive index \( n \), we can still get the following equation,

\[
\frac{\Delta}{\Delta n} \left( \frac{\varepsilon_m e_d'}{\varepsilon_m + e_d} \right) = \left( \frac{\varepsilon_m'}{\varepsilon_m + 1} \right) \left( \frac{\varepsilon_m}{\varepsilon_m' + e_d} \right) \frac{\Delta e_d}{\Delta n} + \left( \frac{\varepsilon_d}{\varepsilon_m' + e_d} \right) \left( \frac{\varepsilon_m'}{\varepsilon_m + 1} \right) \frac{\Delta e_d}{\Delta n} = \frac{\varepsilon_m e_d'}{\varepsilon_m + e_d} \cdot \frac{\varepsilon_m}{\varepsilon_m' + e_d} \frac{\Delta e_d}{\Delta n} + \frac{\varepsilon_d}{\varepsilon_m' + e_d} \frac{\Delta e_m'}{\Delta n}
\]

Thus

\[
\frac{\Delta \lambda}{\Delta n} = \frac{\lambda}{2} \left[ \frac{\varepsilon_m e_d'}{\varepsilon_m + e_d} \frac{\Delta e_d}{\Delta n} + \frac{\varepsilon_d}{\varepsilon_m' + e_d} \frac{\Delta e_m'}{\Delta n} \right]
\]
Appendix 2 MATLAB Program to generate vertex coordinates of 5 fold Penrose Tiling

clear all;

A =load('Penrosedata.txt');

vars=fieldnames(A);

B =zeros(length(vars),2);

for n=1:length(vars)
    B(n,1)=A(n,1)*cos(0)+A(n,2)*cos(2*pi/5)+A(n,3)*cos(4*pi/5)+A(n,4)*cos(6*pi/5)+A(n,5)*cos(8*pi/5);
    B(n,2)=A(n,1)*sin(0)+A(n,2)*sin(2*pi/5)+A(n,3)*sin(4*pi/5)+A(n,4)*sin(6*pi/5)+A(n,5)*sin(8*pi/5);
end

save result B;
Appendix 3 MATLAB Program to Calculate Predicted Resonance Wavelength

clear all;

A = load('scattering order.txt');

B = zeros(600,4);

for m=1:120

    for n=1:5

        B(5*-m+n+1,1)=A(m,1);

        B(5*-m+n+1,2)=A(m,2);

        B(5*-m+n+1,3)=A(m,1);

    end

    B(5*-m+4,4)= 0.9522*645.16/B(5*-m+3,3);

    B(5*-m+3,4)= 0.9522*758.43/B(5*-m+3,3);

    B(5*-m+2,4)= 0.9522*1043.89/B(5*-m+2,3);

    B(5*-m+1,4)= 0.9522*398.73/B(5*-m+1,3);

    B(5*-m,4)= 0.9522*1227.16/B(5*-m,3);

end

save result B;
C=zeros(600,4)

for m=1:120
    for n=1:5
        C(5*m-n+1,1)=A(m,1);
        C(5*m-n+1,2)=A(m,2);
        C(5*m-n+1,3)=(0.0955*A(m,1)^2+0.9045*A(m,2)^2)^0.5;
    end
    C(5*m-4,4)=0.9522*645.16/C(5*m-4,3);
    C(5*m-3,4)= 0.9522*758.43/C(5*m-3,3);
    C(5*m-2,4)= 0.9522*1043.89/C(5*m-2,3);
    C(5*m-1,4)= 0.9522*398.73/C(5*m-1,3);
    C(5*m,4)= 0.9522*1227.16/C(5*m,3);
end

save result C;

D=zeros(600,4)

for m=1:120
    for n=1:5
        D(5*m-n+1,1)=A(m,1);
    end
D(5*m-n+1,2)=A(m,2);

D(5*m-n+1,3)=(0.6545*A(m,1)^2+0.3455*A(m,2)^2)^0.5;

end

D(5*m-4,4)=0.9522*645.16/D(5*m-4,3);

D(5*m-3,4)= 0.9522*758.43/D(5*m-3,3);

D(5*m-2,4)= 0.9522*1043.89/D(5*m-2,3);

D(5*m-1,4)= 0.9522*398.73/D(5*m-1,3);

D(5*m,4)= 0.9522*1227.16/D(5*m,3);

end

save result D;
Appendix 4 List of Periodic Sensitivities (Copied with permission from Ref.13)

<table>
<thead>
<tr>
<th>Publication</th>
<th>SPR wavelength (nm)</th>
<th>Metal/Dielectric</th>
<th>Sensitivity(nm/RIU)</th>
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<td>Au/Water</td>
<td>615</td>
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<td>Seeing protein monolayers with naked eye through plasmonic Fano resonances</td>
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<td>Au/water</td>
<td>690</td>
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<td>Integrated nanoplasmic-nanofluidic biosensors with targeted delivery of analytes</td>
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<td>Au/water</td>
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<td>Attomolar protein detection using in-hole surface plasmon resonance</td>
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<td>On-chip surface-based detection with nanohole arrays</td>
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<td>Au/water</td>
<td>333</td>
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<td>Nanoholes as nanochannels: flow-through plasmonic sensing</td>
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<td>EOT or Kretschmann configuration?</td>
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<td>Comparative study of the plasmonic modes in gold nanohole arrays</td>
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<td>Large-area subwavelength aperture arrays fabricated using nanoimprint lithography</td>
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<td>513</td>
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</table>
Curriculum Vitae

Name: Zhaoliang Yang

Post-secondary Education and Degrees:

Huazhong University of Science and Technology
Wuhan, Hubei Province, China
2007-2012 Bachelor of Engineering Science

The University of Western Ontario
London, Ontario, Canada
2012-2015 Master of Engineering Science

Honours and Awards:

Outstanding Individual Award for Science & Technology
Innovation Activities
Huazhong University of Science and Technology
2010

Second Prize of National Mechanical Innovative Design Contest in Hubei Province
Hubei Province, China
2011

Related Work Experience

Research/Teaching Assistant
The University of Western Ontario
2013-2014

Thesis: