Micro SERS sensors based on photonic-plasmonic circuits and metallic nanoparticles

Feng Tang

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Micro SERS Sensors based on Photonic-plasmonic Circuits and Metallic Nanoparticles

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Feng TANG

le 15 septembre 2017

Micro SERS Sensors based on Photonic-plasmonic Circuits and Metallic Nanoparticles

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General introduction

Surface-enhanced Raman spectroscopy (SERS) is a widely-used technique to enhance Raman signals originating from the inherently inelastic scattering of photons and molecular vibrations or rotations. Raman spectroscopy is a non-intrusive and label-free tool to identify the molecular spectral fingerprints, even for one chemical mixed with other substance. However, most SERS detections are implemented in a free space configuration such as Raman microscopes, leading to quite bulky and costly systems. This also limits its potential applications like site measurement for roadside drug detection, environmental investigation, etc. Recently, the advent of integrated optics has facilitated a number of micro-sensors or components on photonic circuits. This provides a possible approach to miniaturizing SERS machines into the microscale with integrated spectroscopic components such as arrayed waveguide gratings (AWG), planar concave gratings (PCG), and etched diffraction gratings (EDG), which can be used in Raman spectroscopy to disperse Raman signals. The fully integrated SERS-detection systems on chips with high sensitivity are one of the most desirable tools in future. It can be even implanted into smartphones and facilitate the development of on-hand labs.

Inspired by the plasmonic-photonic coupling between metallic waveguides and dielectric waveguides, this thesis presents a micro SERS sensor based on the hybrid waveguide made of a metallic slot and a dielectric strip. Using the three-dimensional finite-difference time-domain (3D-FDTD) method, the SERS processes including the excitation of surface plasmon in slots and the radiation of induced Raman dipoles are simulated. Based on the \(|E|^4\)-approximation, the enhancement factor (EF) of the sensor is analyzed by changing the geometrical parameters. It is also proved that the SERS-detection capacity can be improved dramatically due to the hotspot effect if metallic nanoparticles are added into the sensor’s metallic slot. The theoretical results show that a highly sensitive SERS sensor can be achieved based on the hybrid waveguide and metallic nanoparticles. To approve the in-reality feasibility, some prototypes of the SERS sensor are fabricated. Methylene blue (MB) molecules are used as the Raman probing molecules to characterize the SERS-detection capacity of these sensor prototypes. The preliminary experimental results show that the Raman signals of the prototypes of the SERS sensor are detectable and therefore the sensor is feasible in reality.

The 1st chapter mainly introduces the theoretical principles and instrumentation of Raman spectroscopy and surface enhanced Raman spectroscopy. The state-of-the-art describes emphatically the miniaturization tendency of the Raman spectroscopic instrumentation. Besides, some works, which are related to and inspired this thesis, are also contained in this chapter.
The 2nd chapter mainly introduces the mathematical methods to analyze the SERS sensor and the experimental techniques for nanofabrication and sample characterization. The main method is the 3D-FDTD algorithm, which can calculate numerically the electromagnetic field distribution in the sensor. An analytical model, the strong coupling model, is used to analyze the photonic-plasmonic coupling efficiency between metallic waveguides and dielectric waveguides. The fabrication procedure of the sensor prototypes is conducted by the lithography techniques, particularly the electron beam lithography (EBL). The prototype samples are tested by a commercial Raman microscope to characterize the SERS-detection capacity of the sensor.

The 3rd chapter mainly introduces the theoretical investigation of the SERS sensor based on the hybrid waveguide made of metallic slots and dielectric strips by the 3D-FDTD method. It starts with the sensor schematics and the relative material information, which is followed by a glimpse of a fully integrated SERS-detection system on a chip to show the core function of the SERS sensor. Based on the strong coupling theory, the photonic-plasmonic coupling is discussed, particularly its dependence on the geometrical parameters. Using 3D-FDTD simulations and the $|E|^4$-approximation, the enhancement factors in the metallic slot are obtained. Finally, the sensor’s detection capacity is characterized theoretically with some dye molecules. The results show that a SERS sensor can be achieved based on the hybrid waveguide with an enhancement factor of $10^2$-$10^3$ for Raman scattering of Raman-active molecules in the metallic slot.

The 4th chapter mainly introduces the theoretical investigation of the effect of in-slot metallic nanoparticles on improving the detection capacity of the SERS sensor. Using 3D-FDTD simulations, the electromagnetic field and charge distributions of the metallic sphere-slot junction are obtained and subsequently the electromagnetic interaction between the in-sphere LSP and the in-slot SPP is discussed. The $EF$ dependence of the metallic particle-slot junction on the particle’s position, size, shape, and material is demonstrated to show the strategy of optimizing the sensor’s detection capacity. On the other hand, the metallic particle-slot junction may give rise to loss of Raman signals and the related discussion is presented with the case of two nanoparticles in the slot. The results show that the averaging SERS enhancement factor around the in-slot particle can be increased dramatically, compared to the enhancement factor in the slot without metallic nanoparticles. At some points in the particle-slot junction, the enhancement factor even reaches $10^{10}$, which is enough to detect a single molecule.

The 5th chapter mainly introduces the experimental verification of the feasibility of the SERS sensor in reality. The prototypes of the sensor are obtained by fabricating some arrays of gold slots on the $\text{Si}_3\text{N}_4$ waveguides provided by the cooperators at CEA-Leti in Grenoble. The Raman probing molecules, methylene blue (MB)
in distilled water, are dropped and dried on the arrays of gold slots. The capacity of the sensor prototypes is characterized by a Raman microscope *LabRAM 800HR*. The experimental results show that the Raman signals of the sensor are detectable.

The thesis ends up with some conclusions and perspectives of the theoretical and experimental work about the SERS sensor discussed in the thesis. Following that, it is the French summary and then an appendix is attached to show the field distributions of the gold particle-slot junctions.
1. Introduction and state-of-the-art

Benefiting from the non-intrusive and label-free merits, Raman spectroscopy has attracted many interests of researchers and been developed into a well-established technique to analyze chemical and biological molecules in fundamental research and numerous applications like pharmacology, food safety, etc[1]–[4]. However, its drawback is the low signal, which in normal conditions (non-SERS) is weaker approximately 10 million times than Rayleigh scattering. To enhance Raman signals, enormous efforts have been made over the past decades. Surface-enhanced Raman spectroscopy (SERS) is one of the widely used Raman-detection techniques in labs and industries. However, its conventional configurations are always completed in a complex and costly system, preventing Raman spectroscopy from being used more widely and more flexibly. Recent advances in integrated optics provide a possible approach to miniaturizing SERS machines into micro-photonic circuits which are cheap, reliable and portable.

The 1st chapter mainly introduces the theoretical principles and instrumentation of Raman spectroscopy and surface enhanced Raman spectroscopy. The state-of-the-art describes emphatically the miniaturization tendency of the Raman spectroscopic instrumentation. Besides, some works, which are related to and inspired this thesis, are also contained in this chapter.

1.1 Principles of Raman scattering and surface-enhanced Raman spectroscopy (SERS)

Raman scattering is actually the inelastic scattering in the light-matter interaction due to energy exchange between incident photons and molecules. This section introduces the basic principles of Raman scattering and the enhancement mechanism of surface-enhanced Raman spectroscopy (SERS). Some important concepts of Raman scattering are presented here to demonstrate the physical origin of the effect and how to calculate the intensity of Raman signals. In the SERS part, the knowledge of plasmonics is presented firstly, which is the most important origin of the signal enhancement. Then the physical mechanism of enhanced Raman scattering with surface plasmons is shown and the related mathematical models are given out to describe the enhancement quantitatively.

1.1.1 Raman scattering

Raman scattering, an inelastic light scattering, was firstly discovered in experiments in 1928 by the Indian scientists C. V. Raman and K. S. Krishnan in liquids[5], and independently by the Soviet scientists G. Landsberg and L. in crystals[6], after being predicted in 1923 by A. Smekal[7]. The inelastic characteristic means that there is energy exchange between incident photons and
molecules during Raman scattering. When incident photons interact with molecules, most photons are scattered elastically by Rayleigh scattering, where the scattered photons have the same frequency as the incident photons. Nevertheless, a photons are scattered in the form of Raman scattering, which have frequencies lower (Stokes process) or higher (anti-Stokes process), corresponding to the photons’ energy loss or gain via the interaction of the molecular vibrations or rotations with the light.

According to the classical electromagnetic theory, the light-matter interaction can be modeled by a polarization description. The complete expression of the optical polarization, in which a dipole \( p \) is excited by the incident field \( E \), is defined as:

\[
p = \hat{\alpha}E + \hat{\beta}EE + \hat{\gamma}EEE + \cdots
\]  

(1-1)

where \( \hat{\alpha} \), \( \hat{\beta} \) and \( \hat{\gamma} \) are tensors and known as the linear polarizability, the hyperpolarizability, and the second-order hyperpolarizability respectively. The dipole \( p \) depends greatly on the incident power. Except for the cases with high-power lasers or pulsed lasers, the polarization above can be simplified as:

\[
p = \hat{\alpha}E
\]  

(1-2)

where the induced dipole \( p \) has a linear dependence on the incident field \( E \).

With the incident electric field \( E(t) \) oscillating at an angular frequency \( \omega \), the molecular polarization can be described as \( p(t) = \int_0^\infty \hat{\alpha}(\tau) \cdot E(t - \tau) d\tau \). This can be transferred by Fourier transform into the frequency domain \( p(\omega) = \hat{\alpha}(\omega) \cdot E(\omega) \) \( \hat{\alpha}(\omega) = \int_0^\infty \hat{\alpha}(\tau) e^{i\omega \tau} d\tau \). The induced dipole \( p(\omega) \) and the incident field \( E(\omega) \) the same frequency, so the tensor \( \hat{\alpha}(\omega) \) is called the linear optical polarizability or Rayleigh polarizability tensor. Raman scattering physically derives from the molecular vibrations and rotations, which can be seen as a small perturbation to the linear optical polarizability. By the one-order Taylor expansion, the tensor \( \hat{\alpha}(Q_k) \) in the normal mode coordinate system of molecules can be expressed as:

\[
\hat{\alpha}(Q_k) = \hat{\alpha}(0) + \left( \frac{\partial \hat{\alpha}}{\partial Q_k} \right)_{Q_k=0} Q_k = \hat{\alpha}(0) + \hat{R}_k Q_k
\]  

(1-3)

where \( Q_k \) is the normal mode coordinate, \( \hat{\alpha}(0) \) is the unperturbed linear optical polarizability and \( \hat{R}_k \) is the Raman tensor of the normal mode \( k \) with the frequency \( \nu_k \). The single normal coordinate of the mode \( k \) is expressed as \( Q_k = Q_k^0 \cos(2\pi \nu_k t + \phi) \), where \( Q_k^0 \) is the amplitude of the oscillation and \( \phi \) is an arbitrary phase.

Considering the polarizability and the perturbation, the induced electric dipole moment \( p \) in molecules, which is excited with the incident field \( E(t) = E_0 \cos(2\pi \nu_0 t + \phi) \) where \( \phi \) is an arbitrary phase, can be expressed as:

\[
p(t) = \hat{\alpha}E(t) = [\hat{\alpha}(0) + \hat{R}_k Q_k^0 \cos(2\pi \nu_k t + \phi)]E_0 \cos(2\pi \nu_0 t + \phi)
\]  

(1-4)

\[= \hat{\alpha}(0)E_0 \cos(2\pi \nu_0 t + \phi) + 0.5\hat{R}_k Q_k^0 E_0 \cos(2\pi (\nu_0 - \nu_k) t + \phi) + 0.5\hat{R}_k Q_k^0 E_0 \cos(2\pi (\nu_0 + \nu_k) t + \phi)\]
where the first term describes an induced dipole radiating at the incident frequency \( v_o \) corresponding to Rayleigh scattering and the latter two terms describe two induced dipoles radiating at the frequency \( v_o - v_k \) and \( v_o + v_k \), respectively corresponding to the Stokes process and the anti-Stokes process of Raman scattering. The normal mode frequency \( v_k \) characterizes one molecular vibration or rotation energy \( \hbar v_k \), so the Stokes process of Raman scattering is that the energy \( \hbar v_k \) transfers from incident photons to molecules and the anti-Stokes process is the inverse. According to the equation (1-4), the condition in which Raman scattering occurs is that \( \vec{R}_k Q_k^2 E_0 \neq 0 \). The molecules are Raman active if the optical polarizability \( \partial \alpha / \partial Q_k \) changes with the normal mode coordinate \( Q_k \) at the equilibrium, i.e. \( \vec{R}_k \frac{\partial \alpha}{\partial Q_k} Q_k=0 \neq 0 \). This is the Raman selection rule to judge whether molecules are Raman-active or not.

Although the classic description can explain Raman scattering intuitively and clearly, it can not explain that the Stokes process is much stronger than the anti-Stokes process. In the equation (1-4), the Stokes oscillation and the anti-Stokes oscillation have the same amplitude \( 0.5 \vec{R}_k Q_k^2 E_0 \). From the quantum view, the exchanged energy in Raman scattering \( \hbar v_k \) is the quantized vibration or rotation energy of the normal mode \( k \). This quantum process can be illustrated by a Jablonski diagram, so Raman scattering can be described as below in Figure 1-1.

![Jablonski Diagram](image)

Figure 1-1 Schematic representation of Raman and Rayleigh scatterings: (a) Simplified Jablonski diagram of the scattering processes. (b) Corresponding Raman and Rayleigh spectra.
In the Jablonski diagram above, Raman scattering is described as a two-step process. Actually, the scattering process is an instantaneous effect without an intermediate step like the one occurring in fluorescence. Here, the two-step description is a hypothesis to show the model clear and that is why the excitation level of molecular transitions in this diagram is a virtual state. Most molecules in the virtual state come back to the same vibrational or rotational energy level as that before excitation, which is Rayleigh scattering. In Raman scattering, molecules come back to a different vibrational or rotational energy level, leading to a transition between two energy levels. The transition energy equals the energy quantum $hv_k$ of quantized molecular vibrations and rotations. The specific energy change $hv_k$ is displayed in Raman spectra, which corresponds to a unique molecular vibrational or rotational mode. Thus, Raman spectroscopy has an extraordinarily high specificity to reveal the molecular internal structure and the peaks of Raman spectra are called the “fingerprint” of molecules. According to the quantized energy formula $E = hc/\lambda$, the molecular specificity in Raman spectra is always described by Raman shift $\Delta \nu_R$ (unit: cm$^{-1}$), which is defined as:

$$\Delta \nu_R = \frac{1}{\lambda_0} - \frac{1}{\lambda_s}$$

where $\lambda_0$ is the incident wavelength and $\lambda_s$ is the scattered wavelength.

In the Stokes process, molecules are excited to a higher vibrational or rotational level with the energy released by photons, for example from $k = 0$ to $k = 1$ in Figure 1-1. The anti-Stokes process has the inverse transition from an excited vibrational or rotational level to the ground level. The condition of the anti-Stokes process is that molecules exist in an excited state before incident photons arrive. Since most molecules are in the ground state under normal conditions, the Stokes process is always much stronger than the anti-Stokes process. A representative full Raman spectrum is shown in Figure 1-2. The Stokes peaks and the anti-Stokes peaks are located symmetrically with respect to the Rayleigh peak. The Stokes peaks are obviously higher than the anti-Stokes peaks, and therefore the Stokes scattering is usually employed in the Raman spectroscopic measurements.

![Figure 1-2](image-url)
Based on the polarization model, it is known that Raman signals come from the radiation of induced Raman dipoles in Raman-active molecules excited by the incident light. The total power \( P_R \) radiated by an induced Raman dipole in the medium \( n_m \) is given out by:[8]

\[
P_R = \frac{\omega_R^4 n_m \sqrt{L_m |p_R|^2}}{12\pi \varepsilon_0 c^3}
\]

(1-6)

where \( \omega_R \) is the angular frequency of the emitted light, \( L_m = [(n_m + 2)/3]^4 \) is a factor for the local field correction, and \( p_R \) is the moment of the induced Raman dipole. The Raman dipole \( p_R \) induced by the incident field \( E_{inc}(\omega_I) \) can be expressed as:

\[
p_R = L_m^{1/4} \alpha_R(\omega_R, \omega_I) \cdot E_{inc}(\omega_I)
\]

(1-7)

where \( \alpha_R \) is the second-rank Raman polarizability tensor. This tensor is determined by the electronic structure of molecules and it is can be calculated by theoretical and numerical methods such as the density functional theory (DFT).

To calculate the scattering intensity more conveniently, the concept, scattering cross-section, is defined in a scattering process. If a molecule has a Raman cross-section \( \sigma_R \) and it is excited by the incident field \( E_{inc} \), its Raman scattering intensity can be calculated by:

\[
P_R = S_{inc} \sigma_R
\]

(1-8)

where \( S_{inc} = 0.5\varepsilon_0 c n_m |E_{inc}|^2 \), which is the local power density at the molecule position, \( c \) is the light speed in vacuum, and \( n_m \) is the index of refraction of the medium. Considering the equations (1-6)-(1-8), the cross-section \( \sigma_R \) can be expressed as[8]:

\[
\begin{align*}
\sigma_R &= \frac{8\pi}{3} \left[ 1 + 2 \rho_R \frac{d\sigma_R}{d\Omega} \right] \\
\rho_R &= \frac{45\bar{\alpha}^2 + 4\overline{\eta}^2}{45\bar{\alpha}^2 + 7\overline{\eta}^2} \\
d\sigma_R &= \frac{L_m \omega_R^4}{16\pi^2 \varepsilon_0^2 c^4} \frac{45\bar{\alpha}^2 + 7\overline{\eta}^2}{45}
\end{align*}
\]

(1-9)

where \( \bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \) is the reduced trace of the Raman tensor \( \alpha_R \) and \( \overline{\eta}^2 = 0.5 \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 3(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right] \) is the anisotropy of the Raman tensor \( \alpha_R \). \( \alpha_{mn}(m, n = x, y) \) are the elements of the Raman tensor \( \alpha_R \). \( \rho_R \) is the depolarization ratio of the Raman tensor \( \alpha_R \). \( d\sigma_R/d\Omega \) is the absolute differential Raman cross-section and a typical differential Raman cross-section is very small, less than \( 10^{-30} \text{ cm}^2/\text{sr} \). This is much smaller than the competitive effect fluorescence. To exploit Raman spectroscopy in research and industries, it is necessary to enhance the weak Raman signal in the situations where the detectors are not sensitive enough or too expensive. For the past decades, enhanced Raman spectroscopy has always been the hottest topic in researching the
Raman-related techniques.

1.1.2 Surface-enhanced Raman spectroscopy (SERS)

Surface-enhanced Raman spectroscopy (SERS) is one of the most famous enhanced Raman spectroscopic techniques developed in the past decades. It was first observed in 1974 by Fleischmann at a silver electrode[9], and after three years researchers started to reveal the origin of the surface enhancement effect[10]. Compared to the classic Raman scattering, this enhancement effect can easily enhance Raman signals by several orders of magnitude, which is defined as enhancement factor \( (EF) \), when Raman-active molecules are close to metallic objects. The measured enhancement factor of colloidal solutions of aggregated metallic nanoparticles can be higher than \( 10^9 \)[11], [12]. When the factor is on the order of \( 10^7-10^8 \), the sensitivity is enough to detect a single molecule. As shown in Figure 1-3, the SERS spectrum of a single molecule, which is integrated in 0.05 s, has the very clear Raman shift peaks i.e. the molecular fingerprint of rhodamine 6G. On the other hand, the Raman spectroscopic features of \( 7.8 \times 10^5 \) molecules with 400 s integration time are very faint in the non-SERS case. The scattering power per molecule is enhanced by a factor \( 7.3 \times 10^9 \). Here, note that the red laser (633nm) has the energy close to an electronic transition of rhodamine 6G and the virtual state of Raman scattering in Figure 1-1 is a real state, so this kind of Raman scattering is called surface enhanced resonant Raman scattering (SERRS). One widely accepted mechanism of the enhancement is the local field amplification due to the photon-metal interaction: surface plasmons. Raman scattering is dramatically enhanced by the intense local electromagnetic field of surface plasmons, which are a collective oscillation of electrons at the interface between materials of opposite permittivities. Another widely discussed enhancement mechanism is the chemical enhancement. That is because the intrinsic Raman cross-section may be modified when molecules are adsorbed on metallic surfaces. It is generally accepted that the electromagnetic mechanism is the main origin that the SERS enhancement derives from while the chemical enhancement factor is about 2 orders of magnitude in the literature[13]. Therefore, solving the electromagnetic equations or measuring the actual electromagnetic fields is the key to obtain the Raman enhancement factor of a SERS substrate in a theoretical or experimental problem.

Surface plasmonics

Surface plasmonics is the research of plasmon polaritons that arise from a series of collective electron oscillations at the interface between materials of opposite permittivities, particularly between dielectrics and noble metals[14]. This concept was first predicted in 1957 by R. Ritchie[15]. According to the form of electron oscillations, it is often categorized into two classes: surface plasmon polaritons (SPP) and localized surface plasmons (LSP), as shown in Figure 1-4. SPP are propagating
plasmon polaritons at the plane interface between dielectrics and metals. LSP are non-propagating plasmons on metallic nanoparticles, which are smaller than the incident wavelength. Plasmon polaritons are inclined to describe the electromagnetic waves produced by the coupled oscillations between light and matter while plasmons describe electron density oscillations. When Raman-active molecules are close to metallic surfaces, Raman scattering can be excited directly by the intense local plasmonic field, i.e. the SERS occurs.

Figure 1-3 Classic Raman and SERS spectra of rhodamine 6G molecules with 633nm laser excitation (3mW). The SERS substrate is citrate-reduced silver colloids prepared by the Lee & Meisel method[8].

Figure 1-4 Schematic representation of plasmonics at metallic surfaces: (a) Surface plasmon polaritons (SPP) at planar metal/insulator interfaces. (b) Localized surface plasmons (LSP) on nanoscale metallic objects.

SPP are the electromagnetic surface modes which have exact analytical solutions by solving Maxwell’s equations on planar dielectric-metal interfaces. It has been proven that there are no surface modes on metallic surfaces when the excitation source is \( TE \)-polarized and thus they exist only in the \( TM \)-polarized case. On the dielectric-metal interface in Figure 1-4-(a), the SPP’s magnetic field is along the y-axis while the electric field lies in the x-z plane. The wave vectors \( k_{1z}, k_{2z} \) of the electromagnetic fields along the z-axis are imaginary, so the electromagnetic fields are confined to the dielectric-metal interface. In the propagation direction, the
electromagnetic wave vector $k_x$ can be expressed as:

$$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m(\omega)\varepsilon_D}{\varepsilon_m(\omega) + \varepsilon_D}}$$

(1-10)

where $\varepsilon_m(\omega)$ and $\varepsilon_D$ are the permittivities of metals and dielectrics respectively. Considering that $Re[\varepsilon_m(\omega)\varepsilon_D] < 0$, the term $Re[\varepsilon_m(\omega) + \varepsilon_D]$ should be negative to assure that the mode is propagative, i.e. $k_x$ is not imaginary. The propagation damping can be described by $Im(k_x)$. The electromagnetic fields in the dielectric $(H_D, E_D)$ can be expressed as:

$$\begin{cases}
H_D = (H_y e_y) \exp(ik_x x + ik_{1z} z) \\
E_D = \frac{H_y}{\omega \varepsilon_0 \varepsilon_D} (k_{1z} e_x - k_x e_z) \exp(ik_x x + ik_{1z} z)
\end{cases}$$

(1-11)

where $H_y$ is the transverse magnetic field on the interface. It is noted that this SPP mode cannot be excited directly by light beam because of $k_x > k_0 \sqrt{\varepsilon_D} = \omega \sqrt{\varepsilon_D}/c$, where $k_0$ is the wave vector of light in vacuum. There are many commonly-used indirect methods to excite SPP on planar metallic surfaces, such as prism coupling[16], [17], grating coupling[18] and near-field excitation[19]. If an incident field $E_{\text{inc}}$ with an incident angle $\theta_I$ is coupled into an SPP mode on a dielectric-metal interface with permittivities $\varepsilon_D$ and $\varepsilon_m = \varepsilon' + i\varepsilon''$ via a prism with permittivity $\varepsilon_I$, as shown in Figure 1-5, the amplification factor of the local plasmonic field on the interface compared to the incident field can be expressed as:

$$M_{\text{Loc}} \approx \frac{2|\varepsilon'|^{3/2}}{\varepsilon_D \varepsilon''} \eta \sqrt{\varepsilon_I \cos \theta_I}$$

(1-12)

where $\eta$ is the coupling efficiency from the photons to the SPP modes.

Figure 1-5 Kretschman configuration based on attenuated total reflection (ATR) via the prism coupling for exciting SPP modes on the dielectric-metal interface[16].

Unlike SPP, LSP are non-propagating oscillations of electrons that are restricted on metallic nanoparticles. When the incident wavelength is bigger than the metallic particle size, as shown in Figure 1-4-(b), the net charge center of the particle will move away from the geometrical center and subsequently an induced dipole moment appears inside the particle. On the other hand, a restoring force reacts upon these driven electrons. When the electromagnetic frequency of the incident light matches
the intrinsic oscillation frequency of electrons in the particle, the LSP resonance arises with intense electromagnetic fields around the particle. When the metallic particle size \( d \) is much smaller than the wavelength \( \lambda \), the LSP normal modes can be analyzed using the simple quasi-static approximation. Here, a metallic sphere with radius \( a \) is taken as an example in Figure 1-4-(b). Excited by the incident electric field \( \mathbf{E}_{\text{Inc}} \), the induced dipole in the particle is calculated by:

\[
\mathbf{p} = 4\pi \varepsilon_0 \varepsilon_D a^3 \frac{\varepsilon_m - \varepsilon_D}{\varepsilon_m + 2\varepsilon_D} \mathbf{E}_{\text{Inc}}
\]

(1-13)

where \( \varepsilon_m \) and \( \varepsilon_D \) are the permittivities of the metallic sphere and the surrounding medium respectively. The induced dipole moment is proportional to the incident field \( |\mathbf{E}_{\text{Inc}}| \), so according to the polarization equation \( \mathbf{p} = \varepsilon_0 \varepsilon_D \alpha \mathbf{E}_{\text{Inc}} \), the linear polarizability \( \alpha \) can be defined as:

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

(1-14)

It is obvious that the polarizability has its maximum value when the denominator \( |\varepsilon_m + 2\varepsilon_D| \) is minimized. Particularly, \( \text{Re}[\varepsilon_m(\omega)] = -2\varepsilon_D \), this is the condition of LSP resonances. The electric fields inside and outside the sphere can be expressed as:

\[
\begin{align*}
\mathbf{E}_{\text{in}} &= \frac{3\varepsilon_D}{\varepsilon_m + 2\varepsilon_D} \mathbf{E}_{\text{Inc}} \\
\mathbf{E}_{\text{out}} &= \mathbf{E}_{\text{Inc}} + \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{4\pi \varepsilon_0 \varepsilon_D} \frac{1}{r^3}
\end{align*}
\]

(1-15)

where \( \mathbf{n} \) is the unit vector in the direction of the concerned point \( \mathbf{P} \). If \( \mathbf{n} \parallel \mathbf{p} \), \( \mathbf{E}_{\text{out}} \) can be simplified as \( \mathbf{E}_{\text{out}} = (1 + \frac{\varepsilon_m - \varepsilon_D}{\varepsilon_m + 2\varepsilon_D} \frac{a^3}{r^3}) \mathbf{E}_{\text{Inc}} \). The enhancement factor of the outside electric field compared to the incident field can be calculated by:

\[
M_{\text{Loc}} = \frac{\mathbf{E}_{\text{out}}}{\mathbf{E}_{\text{Inc}}} = 1 + \frac{\varepsilon_m - \varepsilon_D}{\varepsilon_m + 2\varepsilon_D} \frac{a^3}{r^3}
\]

(1-16)

The quality factor of LSP resonances is defined as \( Q = \omega(d\varepsilon'/d\omega)/(2\varepsilon''^2) \), where the metallic permittivity is \( \varepsilon_m = \varepsilon' + i\varepsilon'' \). The quality factor of an air/metal nanoparticle with different materials is shown in Figure 1-6. The shaded area, which indicates the strong LSP resonances with a small absorption, is always concerned in research of plasmonics.

Figure 1-6 Quality factor \( Q \) of localized surface plasmon (LSP) resonances for an air/metal nanoparticle[8].
Electromagnetic enhancement

Electromagnetic enhancement is the main contribution to enhancing Raman signals in the SERS techniques. This is because Raman scattering results from the electromagnetic light-matter interaction and the presence of metal structures can dramatically modify the local electromagnetic fields. It has been demonstrated that Raman scattering can be described as the polarization of Raman-active molecules and the subsequent radiation of induced Raman dipoles. Thus, the enhancement of SERS can be divided into two parts: local field enhancement $M_{\text{Loc}}$ during the excitation process of induced Raman dipoles by surface plasmons, and radiation enhancement $M_{\text{Rad}}$ during the modified emission process of induced Raman dipoles near metallic objects. The enhancement factor ($EF$) can be expressed as:

$$ EF = EF_{\text{Loc}}(\omega_L)EF_{\text{Rad}}(\omega_R) $$

(1-17)

where $\omega_L$ and $\omega_R$ are the angle frequencies of the exciting incident light and the radiated scattering light respectively. The two processes both depend heavily on the local environment where Raman-active molecules are located.

According to the equation (1-7), the induced Raman dipoles of molecules have a linear dependence on the excitation field. The local field $E_{\text{Loc}}(\omega_L)$ of metallic surface plasmons is always more intense than the incident field $E_{\text{Inc}}$ that excites these plasmons. When plasmons are excited, the induced Raman dipole moment $p_R$ can be enhanced by $E_{\text{Loc}}/E_{\text{Inc}}$ times, compared to that excited by the incident field $E_{\text{Inc}}$ directly. Considering the quadratic relationship between the dipole moment and its radiation energy ($P_R \propto |p_R|^2$), the Raman dipole in SERS cases would radiate the energy by an enhancement factor:

$$ EF_{\text{Loc}}(\omega_L) = \left(\frac{|E_{\text{Loc}}(\omega_L)|^2}{|E_{\text{Inc}}|^2}\right) $$

(1-18)

All the enhancement factors $EF_{\text{Loc}}$ for the positions around a metallic object can be obtained once the electric field distribution is known by a numerical or experimental method.

Similarly, the emission properties of a dipole or emitter, are also dependent on its environment, particularly metallic objects. Under SERS conditions, the Raman dipole radiation is a modified spontaneous emission (MSE). Assuming that an induced Raman dipole $p_R=p_R e_p$ oscillates at a frequency $\omega_R$, the radiation enhancement factor is defined as:

$$ EF_{\text{Rad}}(\omega_R) = \frac{P_{\text{Rad}}(\omega_R)}{P_0(\omega_R)} $$

(1-19)

where $P_{\text{Rad}}$ is the power radiated by a dipole under SERS conditions while $P_0$ is the power emitted from the same dipole in free space. This enhancement effect would make induced Raman dipoles near metallic surfaces emit more energy than its radiation in free space by many orders of magnitude. There are several analytical methods to model this modified radiation, such as self-reaction method and Poynting
vector approach. But they are usually not straightforward except for some simple cases. On the other hand, the modified radiation of dipoles is a complex process due to its multi-factor dependence like positions and orientations of molecules, etc. It is a difficult task to estimate all the enhancement factors $EF_{\text{Rad}}$ for any given position of molecules on a SERS substrate. Thus, an approximate treatment is preferred in the calculation of $EF_{\text{Rad}}$.

The $|E|^4$-approximation has been used extensively in the SERS-related literature to estimate the electromagnetic enhancement. It is often assumed that $EF_{\text{Rad}}(\omega) \approx EF_{\text{Loc}}(\omega)$ and $\omega_R \approx \omega_L$, which means that the SERS enhancement factor $EF$ can be expressed simply as:

$$EF = EF_{\text{Loc}} EF_{\text{Rad}} = EF_{\text{Loc}}^2 = \frac{|E_{\text{Loc}}(\omega)|^4}{|E_{\text{inc}}|^4}$$

(1-20)

This approximation avoids the huge task of calculating $EF_{\text{Rad}}$ for every possible position (and for at least three orthogonal orientations) of a dipole on SERS substrates.

**Chemical enhancement**

Compared to the electromagnetic enhancement, the chemical enhancement in SERS is relatively small, but still observable in experiments[20]. The chemical mechanism includes all the constructive or destructive modification of Raman polarizability tensor caused by the molecular adsorption on metallic surfaces. Although the mechanism of chemical enhancement is still an object of debate in the literature, an explanation is the charge-transfer mechanism which is demonstrated in Figure 1-7. Because of a zero metal-molecule distance, the metal-molecule complex’s Jablonski diagram obtains a real existing electric excited state instead of the virtual state in Figure 1-1, which gives rise to the resonant Raman scattering. Without metals,

![Figure 1-7 Simplified Jablonski diagram of a metal–molecule complex where the metal Fermi level is located between two electric states in the molecule. One electron can transit across the state gap directly with a resonant photon energy as the path (a) or indirectly through the metallic tunnel with two steps as the path (b) + (c)[21].](image-url)
incident photons do not have enough energy to excite molecules onto higher electronic levels directly like the path (a) and the resonant Raman scattering does not occur. In the metal-molecule complex, electrons can be photon-driven from the highest occupied molecular orbit (HOMO) to the metal’s conducting band and then to the lowest unoccupied molecular orbit (LUMO). This is the charge-transfer process that makes the resonant Raman scattering occur with less photon-driven energy. The resonant Raman polarizability tensor is much bigger than in the non-resonant cases, so Raman scattering is enhanced by the chemical enhancement.

1.2 Raman-detection tools and miniaturization

After introducing the theoretical principles of Raman scattering and SERS, this section will present the state-of-the-art for exploiting Raman spectroscopy and the corresponding instrumentation. The most well-established Raman-detection systems are always completed in a free space configuration, particularly in a confocal microscope. Except for these high-resolution but bulky and costly systems, some small and portable Raman-detection tools are also developed based on conventional optics. With the advent of integrated optics, some spectroscopic components have been integrated on a chip by photonic circuits. This opens up a way to miniaturize a complex Raman-detection system onto a small photonic chip.

1.2.1 State-of-the-art of conventional Raman-detection tools

After the discovery of Raman scattering, it has attracted many interests from researchers to exploit Raman spectroscopy in analyzing chemical structures in labs and industries. At the same time, the Raman-detection instrumentation has experienced an enormous progress when it was combined with advanced laser sources, detectors and multiplexers. A typical demonstration is the variety of commercial Raman microscopes available on the market. Despite the commonly used Raman microscopes, the diverse SERS substrates are another important branch of the Raman-detection tools, particularly for low-concentration analytes.

◆ Raman microscopes

Raman microscopes are the most sensitive microscope-based instrument for Raman spectroscopic measurements on the commercial market. A representative schematic of confocal Raman microscopes is shown in Figure 1-8 and it refers to the LabRAM HR800 system released by Horiba, Ltd. Compared with a standard confocal microscope, the Raman microscope has additionally an excitation-blocked filter (the notch filter) and a spectrometer which contains a highly sensitive detector such as a charge-coupled device (CCD) or photomultiplier tube (PMT). The incident laser light is focused on the sample and the scattered Raman and Rayleigh signals are collected by the objective L3. The notch filter can remove the excitation wavelength, i.e. Rayleigh signals, and only Raman signals enter the spectrometer. The measured
sample can be in many forms such as solid, solution and powder. The sample can be accompanied by a metallic nanostructure substrate for SERS detections. The microscopic system has high spatial resolution, so it can be used to archive Raman imaging in 2D and 3D. According to the spectrum at every image pixel, it can generate detailed chemical images[22], [23]. With some extended accessories, a Raman microscope can also conduct macro measurements. The Raman microscope is a commonly used detection system and it can be used for many other applications such as photoluminescence (PL) and tip-enhanced Raman scattering (TERS), when combined with AFM, SEM, etc. Besides Horiba, some other companies such as Renishaw and Princeton Instruments, have also released many other Raman microscopes.

Figure 1-8 A representative schematic of confocal Raman-detection systems, which refers to the LabRAM HR800 system released by Horiba, Ltd. L1-L6 are lenses or groups of lenses. BS stands for beam splitter.

◆ SERS substrates

Over the past decades, much effort has been conducted on developing SERS substrates, which made them become a big branch of Raman-detection tools. Until now, it is still the most interesting topic of SERS to seek for highly sensitive plasmonic substrates. However, there is no standardized characterization of SERS substrates due to the complexity of the SERS process. Except for the enhancement factor, a good substrate should have good reproducibility, homogeneity, stability, etc. SERS substrates can be a planar metal-dielectric interface[24] but preferably metallic nanostructures such as nanowires[25], nanoparticles[26], [27], arrays of nanostructures [28] and hybrid structures like particle-wire junctions[29], [30]. Some SERS substrates have been commercialized, such as Klarite substrates, whose enhancement factor can reach at least $10^6$[31], compared to the Raman signals excited by the incident light directly. Some representative SERS substrates are presented in
Figure 1-9. Compared to single isolated metallic structures, the multi-structures have many nanogaps inside, which confine intense electric field and give rise to the strong enhancement effect. These nanogap areas are called hotspots. Besides that, the sharp structures like nanotips also can act as hotspots for SERS[32]. Colloidal solutions of aggregated metallic nanoparticles are a famous kind of SERS substrates. The aggregated nanoparticles can be in different shapes, sizes, and materials, as shown in Figure 1-9-(a) and -(b). The enhancement mainly comes from the LSP electric field in nanogaps or on nanotips. The metallic nanoparticle colloids could be kept in solutions as 3D substrates, or on planes as 2D substrates. However, the controllability and reproducibility of colloid solutions are not good in actual experiments. The lithography is a highly controllable technique to fabricate highly uniform and reproducible nanostructures, as shown in Figure 1-9-(c). The size, shape, and position of the nanocones can be controlled accurately. But it is an expensive and inefficient method for massive production, limiting its further exploitation. In recent years, a new kind of substrates named metal film over nanosphere (MFON) has attracted many interests. It is fabricated by nanosphere lithography, where metals are deposited on a self-assembly of plastic nanoparticles[33], [34], as shown Figure 1-9-(d). This method can fabricate metallic nanostructures over a big area with high-speed and low-cost. Generally, the enhancement of SERS substrates mainly comes from the LSP electric field of metallic nanostructures. By controlling the parameters of nanostructures, the LSP resonances of nanostructures can be adjusted to different excitation wavelengths and different analytes[35], [36].

For specific applications, some special configurations of SERS substrates are proposed. An example is microfluidics, which are widely used for quantitative analysis in clinical analysis, pharmaceutical research and analytical chemistry[39]–[41]. The fluidic devices can be fabricated on a small chip with windows for signal collections, as shown in Figure 1-10-(a). It can reach a high reproducibility by redistributing the aggregated colloid metallic particles. The oil insulates colloid particles and analytes from the channel walls to prevent metallic nanoparticles from
depositing on the channel walls. The time response of the Raman intensity to the analyte concentration is presented in Figure 1-10-(b). It is seen that the Raman intensity follows the change of the analyte concentration in real-time. The main limit of this setup is the long integrated time for each spectrum.

![Figure 1-10](image)

Figure 1-10 Microfluidics for SERS detections[40]: (a) Schematics of a typical microfluidic capillary. The white areas are the windows for signal collections. (b) Time response of the Raman intensity to the promethazine concentration, which is obtained by a conventional micro-Raman setup (LabRam Invers, Horiba, Ltd).

Except for the SERS substrates discussed above, metallic nanostructures can be fabricated directly on Raman-detection sensors like fiber heads. Merging the functions of probing and enhancement together, the optical fiber SERS sensors have attracted much attention of researchers in recent years. As shown in Figure 1-11, the core element of the Raman-detection system is an optical fiber covered by metallic nanoparticles at the end. The fiber end facet can be flat or tapered. Here, the incident light enters the optical fiber and excites the plasmons of the metallic nanoparticles at the fiber end. The enhanced Raman signals are coupled back into the fiber and then enter the spectrometer. A fiber SERS sensor is cost-effective, easy-to-use and suitable for remote and in-situ measurements in micro-environments. This design is also used in some commercial portable Raman spectrometers such as Peakseeker™ Pro released by Ocean Optics, Ltd. An issue of employing fibers in Raman detections is that the fiber material contributes to some background Raman peaks in the recorded spectrum. However, the background peaks could be removed by the calibration before measurements.

1.2.2 Miniaturization of Raman instrumentation

The instrumental miniaturization is always an attractive research topic of all the measurement techniques. With the development of optoelectronic and photonic technologies over the past decades, the Raman instrumentation can be realized in more and more compact and flexible configurations. For example, some commercial Raman systems have been miniaturized into the palm size, as shown in Figure 1-12. However, they are still built up based on the expensive conventional optical elements like those in a Raman microscope. On the other hand, advances in integrated optics open up another approach to miniaturizing the Raman-detection systems further into
the microscale. Up to now, many essential spectroscopic components have been realized with photonic circuits on a chip. Meanwhile, some efforts have been conducted on researching the micro Raman-detection sensors, which can be integrated into a micro-spectroscopic system. The goal of miniaturizing Raman instrumentation is achieving cheap and compact point-of-need Raman analysis tools and even implanting them into smartphones in future.

Figure 1-11 Schematics of the optical setup in which the fiber head is functionalized with metallic nanoparticles[42], [43].

Figure 1-12 Examples of handheld Raman-detection systems: (a) ReporteR™ from Intevac, Inc. (b) IDRaman mini 2.0 from Ocean Optics, Ltd.
Micro-photonics of spectroscopy

A typical spectroscopic system mainly contains a light source, a spectrometer (including a detector) and a sensor. With integrated optics, many spectroscopic components have been realized on a chip, such as lasers [44], [45], detectors [46], [47], arrayed waveguide gratings (AWG) [48]–[50], ring-resonator filters (RRF) [51], [52], and Bragg-grating filters (BGF) [53]. Based on these components, the fully integrated spectroscopic systems can be built up, for example, an on-a-chip system of transmission spectroscopy that is shown in Figure 1-13-(a). The core spectroscopic component is an arrayed waveguide grating (AWG), which disperses signals spatially into the arrayed output channels connected to the detector. The analyte sample is injected into a groove fabricated in the input slab waveguide of the AWG. When a broadband light propagates through the groove, it is absorbed or scattered by the analyte molecules. Because the groove, i.e. the detected volume, can be very small, the measurement precision is high. From the transmission spectra, the analyte information like concentration is obtained. With the sodium acetate solution in the sample groove, the concentration dependence of transmittance is reported in Figure 1-13-(b). It is seen that the relative error of the solution concentration is only 2.5%. This transmission system demonstrates the general framework of on-chip spectroscopic systems.

For the individual elements, it is noted that the sensor here is the sample injection groove in the AWG’s input slab waveguide. If it is replaced by a Raman-detection sensor, the on-a-chip system will become a tool for Raman detections. Except for the sensor, the other important elements are the light source, the detector, and the dispersive element AWG, of which the state-of-the-art will be introduced in the following.

Light sources and detectors are two basic photoelectric components in spectroscopic systems. Different light sources are needed in spectroscopic measurements according to the spectrum category. Infrared absorption or transmission spectroscopy needs a broadband source while Raman spectroscopy needs a
monochromatic excitation source. Much research effort has been conducted on the miniaturization of light sources such as broadband quantum-dot lasers\cite{56}, \cite{57} and monochromatic lasers\cite{44}, \cite{45}. Laser diodes are a key component of on-a-chip spectroscopic photonics, due to its compatibility with planar Si photonic circuits and electronics. Laser diodes have many structure configurations such as double heterostructure, quantum well, distributed Bragg reflector, and in-plane-emitting vertical cavity. A representative laser configuration is presented in Figure 1-14-(a), which is based on a vertical cavity resonance. The laser is mainly composed of a distributed Bragg reflector (DBR), an III–V active region, a high-index-contrast grating (HCG), and an in-plane output waveguide. The grating that is embedded in the in-plane output layer is the key building block. Except working as a highly-reflective mirror for the vertical resonance, the grating also guides the laser light into the output waveguide.

Another necessary photoelectric component in spectroscopic measurements is detectors. The highly sensitive photoelectric detectors, particularly charge-coupled devices (CCD), have been widely exploited in spectroscopic systems. For example, the spectroscopic linear CCD array, SONY 2048 from Sony Inc., has the pixel size (width/height) 14 µm × 56 µm with the lowest detectable power 2 nW. The CCD detectors are a well-established technique now and there are many commercial products. They are very compatible to be integrated on on-chip spectroscopic systems with Si photonics/electronics techniques. Except for CCD detectors, many other photoelectric detectors are also proposed in sensing applications, seeking for higher sensitivity but lower cost. For example, the photodiodes (OPD) can be utilized in on-a-chip fluorescence detections with organic excitations/detections\cite{58}. Figure 1-14-(b) shows the cross-section of an OPD detector. With the double hybrid layers of CuPC and C60, the quantum efficiency of the detector becomes much higher than single heterojunction structures, leading the sensitivity to be 23 mA/W.

![Figure 1-14 Schematics of micro light sources and detectors](image)

Except for the photoelectric components, the dispersive components are also another core building block of spectroscopic systems. The dispersive function can be
realized based on photonic circuits in many micro-configurations such as Michelson interferometers[59], space-variant gratings[60] and Fabry-Perot thin-film optical resonators[61]. In spectroscopic measurements, the main attention is focused on the arrayed waveguide grating (AWG) configuration[48], [49], [62]–[68], which is shown in Figure 1-13. Based on the AWG theory, there are several different sub-configurations such as etched diffraction gratings (EDG)[50], [69], planar concave gratings (PCG)[64], Fourier-transform dispersive planar waveguides (FDPW)[70], and curved sidewall gratings (CSG)[71]. The AWG-based micro-spectrometers have been exploited in Raman spectroscopy[72]–[74].

When light enters an AWG and comes out from an output channel, there is an optical path difference $\Delta L$ for the light passing two neighboring arrayed waveguides. When the wavelength meets the equation $\Delta L = m\lambda$ ($m$ is the diffraction order), the specific wavelength will be exported by this output channel. More principles of AWG can be found in the reference[49]. In Figure 1-15-(a), the simulated wavelength response of an AWG is presented with diffraction order $m = 33$. It was used in an on-a-chip spectral-domain optical coherence tomography (OCT) system for Raman spectroscopy of the skin. The individual colorful peaks present the output wavelengths of the AWG output channels and the spectral resolution is 0.38 nm. A Raman spectrum of cyclohexane was measured experimentally with an AWG spectrometer and it is reported in Figure 1-15-(b) where all the Raman peaks are folded into the free spectral range with diffraction order $m = 40$. The insert image shows the unfolded spectrum by a red curve and the peaks are marked with the same notations in the folded experimental spectra. With a certain diffraction order such as $m = 40$, the output wavelength range of an AWG only covers a narrow width from 800 cm$^{-1}$ (in the 1$^{st}$ output channel) to 1075 cm$^{-1}$ (in the last output channel), which is defined as a free spectral range (FSR) of the AWG. For the wavelength of 1076 cm$^{-1}$ (for example) out of the FSR of $m = 40$, it will be exported to the 1$^{st}$ output channel with $m = 41$. Because the two wavelengths of 800 cm$^{-1}$ and 1076 cm$^{-1}$ both satisfy the equation $\Delta L = m\lambda$, i.e. $\Delta L = 40\lambda_{800cm^{-1}}$ and $\Delta L = 41\lambda_{1076cm^{-1}}$. So, if the Raman spectrum spans several FSRs of an AWG, as shown by the insert image in Figure 1-15-(b), the Raman peaks in the different FSRs will overlap in the output channels, leading to the signal folding. But the Raman peaks can be distinguished once the peaks do not overlap with another one in the folded spectra, as shown in the experimental spectra below. Here, it is noted that an additional sharp peak appears around 1050 cm$^{-1}$ in the experimental spectra. This is the remnant of the excitation laser and it is exported in the FSR with $m = 45$, which is independent of the analyte. The AWG spectrometer can suppress the excitation laser if it is located between two adjacent output waveguides. To remove the laser further, a micro filter can be utilized before the Raman signals enter the spectrometer, such as ring-resonator filters (RRF)[51].
Figure 1-15 Raman spectra obtained by the AWG spectrometers. (a) Simulated wavelength response of an AWG spectrometer with diffraction order \( m = 33 \), the frame of which is shown in the insert[73]. (b) Raman spectra of cyclohexane measured by an AWG spectrometer, where all the Raman peaks are folded into the free spectral range with diffraction order \( m = 40 \)[74]. The insert image shows the distribution of unfolded Raman peaks in the 5 free spectral ranges with \( m = 39, 40, 41, 42, \) and 43.

**Micro-Raman-detection sensors**

It has been mentioned that the on-a-chip system in Figure 1-13 can become a tool for Raman detections if the sample injection groove is replaced by a Raman-detection sensor such as the optical fiber SERS sensors in Figure 1-11. Compared to a functionalized fiber head, the more compact configuration based on waveguides has attracted many interests in recent years[75], [76]. The experiment of evanescent excitation and collection of Raman signals using a high refractive index waveguide is firstly conducted in 1996[77]. The fully integrated configuration of Raman-detection systems, based on the waveguide-based Raman sensor and the micro-spectroscopic elements such as AWG spectrometers, is proposed in 2006 by a patent statement[78]. The waveguide used for Raman sensing can be bare or functionalized with metallic nanostructures for further enhancement. Close to the waveguide boundaries, the evanescent field has a high energy density due to the field confinement. If some metallic objects are present, the local electric field can be enhanced further. Meanwhile, Raman signals emitted by molecules can be coupled into waveguides via the evanescent field. This is the mechanism of Raman detections by waveguides.

Compared to confocal microscopes, one advantage of a waveguide-based Raman sensor is that the probing volume can be very large by increasing the waveguide length, as shown in Figure 1-16-(a). In the reference[79], the equivalent length \( l_{eq} \), which is the waveguide length when the waveguide can give out the same Raman signal intensity as that of a confocal microscope, is defined as:

\[
l_{eq} = \frac{2}{\eta_0} \left( \frac{\lambda_0}{n} \right)
\]  

\[\eta_0 = \frac{1}{n} \iint \frac{g \lambda_0 |E(\mathbf{r}_0)|^2}{\iint \varepsilon |E(\mathbf{r})|^2 d\mathbf{r}} d\mathbf{r}
\]  

(1-21)  

(1-22)
where $\lambda_0$ is the excitation wavelength in vacuum, $n$ is the refractive index of the medium, and $\eta_0$ is the conversion efficiency. In the definition of $\eta_0$, $n_g$ is the group index of the guided mode, $E(\vec{r})$ is the local electric field around the waveguide at the position $\vec{r}$, and $\vec{r}_0$ is the position of molecules. If $E(\vec{r})$ is set as the fundamental TE mode at $\lambda = 633$ nm of a Si$_3$N$_4$ strip (width = height = 300 nm) waveguide on a glass substrate, the conversion efficiency is $\eta_0 = 0.0019$ and the equivalent length is $l_{eq} = 0.324$ mm. The total scattered power $P_{R_{wg}}$ collected by a waveguide can be calculated by:

$$P_{R_{wg}} = \rho \sigma \eta_0 L_{wg} P_{pump}$$  \hspace{1cm} (1-23)

where $\rho$ is the molecule density, $\sigma$ is Raman cross-section, $L_{wg}$ is the waveguide length and $P_{pump}$ is the excitation power. The experimental verification of waveguide-based Raman sensors has been conducted by some research groups[80]–[84]. As shown in Figure 1-16-(b), the Raman spectrum of IPA molecules is obtained by a 1.6 cm silicon nitride waveguide. Like an optical fiber SERS sensor, an issue is that the waveguide material contributes to some background Raman peaks in the recorded spectrum, which can be calibrated before the analyte is added. The waveguide-based sensor can have high selectivity if surface techniques are used. For example, the waveguide, which is covered by an adsorbent polymer cladding, can perform the spectroscopic analysis of some low-concentration analytes such as trace gas[85], [86].

Figure 1-16 Raman detections by dielectric waveguides: (a) Schematics of the beam geometry of a confocal microscope and a waveguide-based Raman sensor[79]. (b) Raman spectra with/without IPA molecules measured by a 1.6 cm silicon nitride waveguide with a rectangular cross-section 200 nm x 700 nm[80].

Besides the classic Raman scattering, the waveguide-based sensor can also perform the SERS analysis when the waveguide is functionalized with metallic nanostructures. When metallic objects are in the vicinity of a dielectric waveguide, they can be excited evanescently[87]–[91]. If molecules are located near these excited metallic objects, their Raman scattering would be enhanced dramatically. The metallically functionalized waveguide locally boosts Raman signals, so the needed
analyte amount is much less, compared to the bare waveguide case. Besides that, the waveguide length does not need to be long.

In recent several years, some researchers in Ghent University have made much progress on the research of metallically functionalized waveguide SERS sensors[79], [92]–[95]. One of their latest achievements is presented in Figure 1-17, where a bare Si$_3$N$_4$ waveguide sensor is functionalized with an array of gold triangular bow ties. The gold bow ties are fabricated directly on top of the waveguide with the e-beam lithography. When the excitation light propagates in the Si$_3$N$_4$ waveguide, its evanescent electromagnetic fields excite the surface plasmons on the bow ties. Particularly, the very intense local electric field appears in the nanogaps of bow ties, which can be seen as hotspots for SERS detections. The Raman spectra, before and after a 4-Nitrothiophenol (NTP) coating is added on the waveguide with 40 bow ties, are presented in Figure 1-17-(b). The cyan shaded strips mark the NTP Stokes peaks while the black dashed lines mark the peaks result from the interferences between the plasmonic bow ties. Compared to the case without the metallic bow ties, the Raman signals of the NTP molecule coating are enhanced by a factor $8 \times 10^6$. With the metallic functionalization, the waveguide-based SERS sensor can be miniaturized further because the waveguide does not need a long length.

![Figure 1-17 Excitation and collection of SERS spectra with dielectric waveguides functionalized with metallic nanostructures[93]: (a) A bare Si$_3$N$_4$ waveguide functionalized with an array of gold bow ties. The insert image is the SEM image of a bow tie located directly on top of the waveguide. (b) Raman spectra without/with a 4-Nitrothiophenol (NTP) layer covering the waveguide with 40 bow ties.](image)

1.3 Background of the study

The waveguide-based SERS sensor in Figure 1-17 only exploits the local evanescent field of the dielectric waveguide. To increase the conversion efficiency of
Chapter I

the incident light to surface plasmons, a new configuration of waveguide-based SERS sensors is proposed in this thesis, almost at the same time as the configuration in Figure 1-17 appeared in the literature. The micro SERS sensor studied in this thesis is based on the photonic-plasmonic coupling between a metallic slot waveguide and a dielectric strip waveguide. It has been demonstrated that there is an efficient directional coupling between a dielectric strip waveguide and a metallic waveguide in form of wires[96], [97], strips[88], [90], [98]–[102], and slots[103]–[106]. The metallic slot waveguide is chosen preferably in the thesis because it can confine the plasmonic field in a small volume, particularly around the slot corners[107]–[113]. This structure also enhances dramatically the spontaneous emission of Raman dipoles induced in analyte molecules[114]–[116].

Figure 1-18 shows a photonic-plasmonic coupler created by a silicon strip and a copper slot. The hybrid waveguide of the slot and the strip can support two fundamental supermodes: even mode and odd mode with propagation constants $\gamma_e$ and $\gamma_o$ respectively, as shown in the inset image below. The even mode has the same phase of the electric field in the slot and in the strip while the odd mode exhibits the opposite phase. According to the field distribution below, it is known that the energy propagating in the hybrid waveguide behaves with a beating pattern. This results from the interaction of the even and odd supermodes and the beating length can be calculated by $L_c = \lambda_0/Re(\gamma_e - \gamma_o)$. It is seen at the middle of the in-slot beatings that most energy is coupled into the metallic slot to excite the surface plasmons. The coupling efficiency can reach 75%, so the input energy is used adequately to excite plasmons in the metallic slot. The space in the metallic slot is an ideal place to excite and collect Raman signals from molecules.

![Figure 1-18 Photonic-plasmonic coupling between a silicon strip and a copper slot[103]: (a) 3D view of the metal-oxide-silicon hybrid coupler. (b) $|E|^2$ field distribution on a $y$-normal plane of the hybrid waveguide with the fundamental TE mode guided in the silicon strip as the incident light. Here, $2L_c = 2.5 \mu m$ and the horizontal and vertical scale bars are 1 $\mu m$ and 0.1 $\mu m$ respectively.](image)

However, it is very difficult to fabricate a metallic slot with nanogaps about 10
nm wide (like the bow ties in Figure 1-17). To improve the SERS enhancement further, some metallic nanoparticles can be added inside the metallic slot, creating some nanogaps smaller than 10 nm. It has been shown that LSP on metallic nanoparticles can be excited by SPP propagating on a metallic surface[117]–[123] or in a metallic wire[30], [124]. If the gap in the particle-surface/wire junction is small enough, this local plasmonic field inside can be so intense that it can enhance Raman signals dramatically. Figure 1-19 shows an example of SERS excited by an Ag particle-wire junction[30]. It is seen that the Raman scattering at the junction is very strong. The SERS enhancement at the junction was found to be about $10^7$-$10^8$, compared to the Raman signals excited by the incident light directly. This enhancement factor is as high as the level achieved in colloidal solutions of metallic nanoparticles. Besides that, the coupling between SPP and LSP also provides an approach to exciting LSP on nanoparticles with a confined incident light from a remote source.

![Figure 1-19](image)

Figure 1-19 SERS of MGITC molecules excited in a metallic particle-wire junction[30]. (a) SEM image of an Ag particle-wire junction. (b) The corresponding Raman image at the Raman peak of 436 cm$^{-1}$.

1.4 Summary

In this chapter, the theoretical principles of Raman spectroscopy and surface enhanced Raman spectroscopy (SERS) are introduced. Raman scattering is the inelastic scattering in the light-matter interaction due to energy exchange. However, its drawback is the weak signal in normal conditions (non-SERS) and a typical differential Raman cross-section is very small, less than $10^{-30}$ cm$^2$/sr. SERS is one of the widely used techniques to enhance Raman signals. One widely accepted mechanism of the enhancement is the local field amplification due to the photon-metal interaction: surface plasmons. Another widely discussed enhancement mechanism is the chemical enhancement due to the modified intrinsic Raman cross-section by metallic surfaces. The electromagnetic enhancement is mainly considered in this thesis.

The state-of-the-art of exploiting Raman spectroscopy and the corresponding instrumentation are discussed. The most well-established Raman-detection systems are always completed in a free space configuration and the typical examples are the bulky and costly Raman microscopes. It limits the potential applications of Raman spectroscopy, such as site measurement for roadside drug detection, environmental
investigation, etc. However, the advent of integrated optics opens up a possible approach to miniaturizing SERS machines into the micro-photonic circuits. With integrated optics, the miniaturization of many spectroscopic components has been realized.

In the last part, the background of the study is introduced. The thesis is mainly inspired by the researches about the photonic-plasmonic coupling between a metallic slot waveguide and a dielectric strip waveguide and the LSP excitation by SPP. Based on the research background, the feasibility of the study can be predicted theoretically.
2. Mathematical methods and experimental techniques

According to the $|E|^4$-approximation in the equation (1-20), it is known that the enhancement factor of SERS substrates can be calculated by the local electric field of metallic surface plasmons. The plasmonic properties of metallic objects can be obtained by solving Maxwell’s equations with specific boundary conditions. For some simple problems, the analytical methods can give out the accurate electromagnetic solutions. But the complex cases always need the numerical methods for the solutions, which have been well-developed with computer techniques. The SERS sensor studied in this thesis is analyzed mainly by numerical methods to obtain its optimized parameters. The experiments contain the sensor fabrication and the characterization of the sensor’s SERS-detection capacity. The nanofabrication techniques involved here are mainly the optical lithography (OL) for dielectric waveguides and the electron beam lithography (EBL) for metallic waveguides. After fabrication, the sample characterization is conducted.

This chapter mainly introduces the mathematical methods to analyze the SERS sensor and the experimental techniques for nanofabrication and sample characterization. The main method is the three-dimensional finite-difference time-domain (3D-FDTD) algorithm, which can calculate numerically the electromagnetic fields in the sensor. An analytical model, the strong coupling model, is introduced to analyze the photonic-plasmonic coupling efficiency between metallic waveguides and dielectric waveguides. The fabrication procedure of the sensor is conducted by the lithography techniques, particularly the electron beam lithography (EBL). The prototype samples are tested by a commercial Raman microscope to characterize the SERS-detection capacity of the sensor.

2.1 Mathematical methods

The mathematical methods of solving Maxwell’s equations can be classified into two groups: analytical and numerical. The analytical methods can give out the accurate solutions but are limited to some simple and specific cases, such as Mie theory. Most complex electromagnetic problems are always solved by the numerical methods which do not need users to know the internal calculation process or intrinsic knowledge of physical problems. Many numerical methods such as finite element method (FEM), finite difference time domain (FDTD) and discrete dipole approximation (DDA) had been proposed and developed in the past decades. Compared to the others, the result of a 3D-FDTD simulation can provide a broadband electromagnetic response of metallic nanostructures covering a wide wavelength.
range. So, this numerical method is chosen and used here. The analytical model of the coupling between a metallic slot waveguide and a dielectric strip waveguide is also introduced in this section. The 3D-FDTD simulations in this thesis are conducted by a commercial software, *FDTD solutions*, from Lumerical Inc. while the analytical analysis is finished with homemade codes.

### 2.1.1 Finite-difference time-domain (FDTD)

The FDTD method, also called Yee’s method, was firstly proposed in 1966 by the applied mathematician Kane S. Yee[125]. Simply speaking, this method solves Maxwell’s curl equations by iteration over the time within artificial boundaries after the differentials of the equations are transferred into the differences of the time domain on grids staggered in space. Except for the space and time discretization, there are no other physical approximations. This means that it is a high-resolution method to solve Maxwell’s equations. On the other hand, this method has a considerable need for computer memory and calculating time. With developments of the computer techniques, PC machines can handle most of simple FDTD simulations but computing stations are still needed in the cases with a big simulated volume or a very fine space/time discretization. The electromagnetic analysis based on the FDTD method has been widely used in various areas of plasmonics research such as plasmon waveguides, enhanced optical absorption and scattering, and metamaterials[126]–[130].

#### Discretization of Maxwell’s equations

The discretization of space and time in Maxwell’s equations is the fundament of FDTD calculations. The discretized fields are distributed on the Yee’s cell, as shown in Figure 2-1-(a). The discretized electric fields occupy the midpoints of the cell edges while the discretized magnetic fields occupy the centers of the cell faces. The time is discretized by the time step in which the electromagnetic fields travel from one cell to the next. For simplicity, the case of the 1-dimensional FDTD is discussed here, as shown in Figure 2-1-(b). The mathematical basis of FDTD calculations consists in solving Maxwell’s curl equations:

\[
\begin{align*}
\nabla \times E &= -\mu \frac{\partial H}{\partial t} \\
\nabla \times H &= (J + \sigma E) \\
\end{align*}
\]

(2-1)

where $E$, $H$ and $J = \sigma E$ are the electric field, magnetic field, and current density respectively, and $\mu$, $\varepsilon$ and $\sigma$ are the medium magnetic permeability, permittivity, and electric conductivity respectively. Here, the medium is isotropic and dispersion-free for simplicity. Assuming that a plane electromagnetic wave propagates along the $z$-axis direction, the curl Maxwell’s equations can be simplified as the expressions below:
The electromagnetic fields $E_x$ and $H_y$ are alternately located on the z-axis with position numbers $i$ and $i + 0.5$. According to the central difference and the mean value theorem, the equations above can be discretized as:

$$
\begin{align*}
H_y^{n+0.5}(i + 0.5) &= H_y^{n-0.5}(i + 0.5) + \frac{2\Delta t}{\mu \Delta z} (E_x^n(i + 1) - E_x^n(i)) \\
E_x^{n+1}(i) &= \frac{2\epsilon - \sigma \Delta t}{2\epsilon + \sigma \Delta t} E_x^n(i) + \frac{2\Delta t}{(2\epsilon + \sigma \Delta t) \Delta z} (H_y^{n+0.5}(i + 0.5) - H_y^{n+0.5}(i + 0.5))
\end{align*}
$$

(2-3)

where $\Delta z$ and $\Delta t$ are the discretization step of space and time. With the time iteration, the electromagnetic fields of the discretized space points are obtained such as $E_x^n(i) \Rightarrow H_y^{0.5}(i + 0.5) \Rightarrow E_x^{1.5}(i) \Rightarrow H_y^{1.5}(i + 0.5) \Rightarrow \cdots$, as shown by the arrows in Figure 2-1-(b). In the 3D-FDTD case, the discretized Maxwell’s curl equations can be expressed in vector forms as:

$$
\begin{align*}
H^{n+0.5} &= H^{n-0.5} - \frac{\Delta t}{\mu} \nabla \times E^n \\
E^{n+1} &= \frac{2\epsilon - \sigma \Delta t}{2\epsilon + \sigma \Delta t} E^n + \frac{2\Delta t}{(2\epsilon + \sigma \Delta t)} \cdot \nabla \times H^{n+0.5}
\end{align*}
$$

(2-4)

The six scalar expressions of the equations above can be found in the Karl S. Kunz’s book[131].

Figure 2-1 Discretized electromagnetic fields on a Yee’s cell: (a) 3D Yee’s cell. (b) 1D Yee’s cell, which is unfolded on the time axis.

It is noted that the discretization step of time $\Delta t$ is limited by the numerical dispersion relationship:

$$
\left| \frac{1}{c \Delta t} \sin \left( \frac{\omega \Delta t}{2} \right) \right|^2 = \sum_{m=x,y,z} \left| \frac{1}{\Delta m} \sin \left( \frac{k_m \Delta m}{2} \right) \right|^2
$$

(2-5)

where $\Delta m|_{m=x,y,z}$ and $k_m|_{m=x,y,z}$ are the discretization steps of space and the wavevector components on the x-axis, y-axis, and z-axis directions respectively.
When the equation (2-5) has the space eigenvalues and the time eigenvalues at the same time, a specific condition is met, which is noted as Courant stability condition, as shown below.

\[
\frac{1}{\Delta t} \geq c \sqrt{\frac{1}{(\Delta x)^2} + \frac{1}{(\Delta y)^2} + \frac{1}{(\Delta z)^2}} \tag{2-6}
\]

#### Dispersion

The medium discussed above is assumed to be dispersion-free but many materials are actually dispersive. Particularly, the complex permittivity of metals is strongly dependent on the frequency of electromagnetic waves. To deal with the permittivity function \( \varepsilon_d(\omega) \) of dispersive materials, Maxwell’s curl equations are modified as:

\[
\begin{align*}
\frac{\partial D}{\partial t} &= \nabla \times H \\
\varepsilon_0 \varepsilon_d(\omega) E(\omega) &= \frac{\partial D}{\partial t} \\
\frac{\partial H}{\partial t} &= -\frac{1}{\mu} \nabla \times E
\end{align*} \tag{2-7}
\]

where \( D(\omega) \) is the electric displacement. Since the permittivity derives from material polarization, it is can be expressed as \( \varepsilon_d(\omega) = \varepsilon_\infty + \chi_p(\omega) \) where \( \chi_p(\omega) \) is the polarizability. Due to the time-domain basis of the FDTD method, the dispersive permittivity \( \varepsilon_d(\omega) \) should be dealt with in the time domain. Via the inverse Fourier transform, the relationship between \( E(\omega) \) and \( D(\omega) \) can be expressed as:

\[
D(t) = \varepsilon_0 \varepsilon_\infty E(t) + \varepsilon_0 \int_0^t E(t - \tau) \chi_p(\tau) d\tau \tag{2-8}
\]

Based on this equation, the permittivity of dispersive materials can be discretized in the time domain. One commonly used method to discretize the integral function over the time is the piecewise linear approximation, i.e. assuming that \( E(t) = E^n + \frac{E^{n+1} - E^n}{\Delta t} (t - n\Delta t) \). Then the equation (2-8) is discretized as:

\[
D^n = \varepsilon_0 \varepsilon_\infty E^n + \varepsilon_0 \sum_{m=0}^{n-1} \left[ E^{n-m} \chi_p^m + (E^{n-m-1} - E^{n-m}) \xi^m \right] \tag{2-9}
\]

where \( \chi_p^m = \int_{m\Delta t}^{(m+1)\Delta t} \chi_p(\tau) d\tau \) and \( \xi^m = \frac{1}{\Delta t} \int_{m\Delta t}^{(m+1)\Delta t} (\tau - m\Delta t) \chi_p(\tau) d\tau \). This equation describes the relationship between the discretized electric field \( E^n \) and the discretized electric displacement \( D^n \) on the discretized time point \( n \) in dispersive materials. The direct recursion relation from \( E^n \) to \( E^{n+1} \) is derived as:

\[
E^{n+1} = \left( \frac{1}{\varepsilon_\infty - \xi^0 + \chi^0} \right) \left( (\varepsilon_\infty - \xi^0) E^n + \frac{\Delta t}{\varepsilon_0} \nabla \times H^{n+0.5} + \Psi^n \right) \tag{2-10}
\]

where \( \Psi^n = \sum_{m=0}^{n-1} \left[ E^{n-m} \Delta \chi_p^m + (E^{n-m-1} - E^{n-m}) \Delta \xi^m \right], \Delta \chi_p^m = \chi_p^m - \chi_p^{m+1} \) and
\[ \Delta \xi^m = \xi^m - \xi^{m+1}. \]

Here, it is noted that the recursion relation from \( H^{n-0.5} \) to \( H^{n+0.5} \) is the same as that in the equation (2-4) because the dispersive permittivity does not influence the relationship between \( H \) and \( E \) in Maxwell’s curl equations. The discretization of the dispersive permittivity discussed above is not limited to a specific permittivity model such as Drude model or Lorentz model, so the equation (2-10) has a universal applicability for FDTD calculations including dispersive materials.

\[ \Delta \xi^m = \xi^m - \xi^{m+1}. \]

**Boundaries**

FDTD calculations are always conducted in a finite space limited by closed boundaries. On the boundaries, any unphysical reflection should not occur. Many boundary conditions have been proposed in the developing process of the FDTD method, such as Taylor extrapolation method, Mur absorbing boundary and perfectly matched layer (PML). Among them, the PML is the most popular absorbing boundary used in FDTD calculations, which was first proposed in 1994 by J. P. Berenger[132]. It is an artificial material with a strong absorption of electromagnetic fields. Based on the PML’s basic idea, researchers realized the excellent absorbing boundary by several different approaches. Here, the uniaxial PML proposed by S.D. Gedney[133] is introduced, which is used in the commercial software, *FDTD solutions*.

Assuming that the material besides a PML is described by the electromagnetic parameters \((\varepsilon_0, \mu_0, \mu_s)\), the material properties of PMLs can be set as: \((\varepsilon_0, \varepsilon, \mu_0, \mu_s)\). The second-rank tensor \( s \) is defined as:

\[
\begin{bmatrix}
    s_y s_z s_x^{-1} & 0 & 0 \\
    0 & s_x s_z s_y^{-1} & 0 \\
    0 & 0 & s_x s_y s_z^{-1}
\end{bmatrix} \tag{2-11}
\]

where \( s_x = \kappa_x + \frac{\sigma_x}{j\omega} \), \( s_y = \kappa_y + \frac{\sigma_y}{j\omega} \), and \( s_z = \kappa_z + \frac{\sigma_z}{j\omega} \). \( \kappa, \sigma_x, \sigma_y, \sigma_z \) are three arbitrary arithmetic numbers, and \( \kappa, \sigma_x, \sigma_y, \sigma_z \) are the attenuation coefficients. Since the PML material \((\varepsilon_0, \varepsilon, \mu_0, \mu_s)\) has the same wave impedance as the neighboring material \((\varepsilon_0, \varepsilon, \mu_0, \mu_s)\), there will be no reflection happening on the boundary. The attenuation factors \( \sigma_x, \sigma_y, \sigma_z \) can make the electromagnetic fields in PMLs disappear quickly. When \( \kappa_x = \kappa_y = \kappa_z = 1 \) and \( \sigma_x = \sigma_y = \sigma_z = 0 \), the PML material degenerates into the neighboring material. If only \( \sigma_x = \sigma_y = 0 \), the electromagnetic wave propagating along the x-axis direction will be absorbed by the PML boundary. In 3D-FDTD calculations, the simulated space is surrounded by 6 PML boundaries. According to orientations and overlaps, different PML parameters are chosen in these 6 boundaries, as shown in Figure 2-2. The parameters of a single PML plane are chosen to absorb the electromagnetic fields propagating in the normal direction. For example, the z-normal PML plane is set as \((1, 0, 1, 0, \kappa, \sigma_z)\). The twelve edges of the cuboid volume are created by the overlap of two orthogonal boundary planes, so the PML...
material should be absorptive in two directions, such as \((\kappa_x, \sigma_x, 1, 0, \kappa_z, \sigma_z)\) on a y-direction edge in the image below. Similarly, the PMLs at the eight cuboid vertexes should be chosen as \((\kappa_x, \sigma_x, \kappa_y, \sigma_y, \kappa_z, \sigma_z)\). With these parameters of MPL materials, any electromagnetic wave can be absorbed totally by the closed boundaries.

![Figure 2-2 Material parameters of PML planes, edges and vertexes surrounding a simulated cuboid volume. The figures in the brackets represent \(\kappa_x, \sigma_x, \kappa_y, \sigma_y, \kappa_z\) and \(\sigma_z\) orderly.](image)

The iteration equations of the electromagnetic waves in PMLs can be obtained by discretizing Maxwell’s curl equations with the material parameters \((\varepsilon_0\varepsilon_S, \mu_0\mu_S)\). Here, the x component of the ampere’s law is taken as an example. The recursion relation from \(E_x^n\) to \(E_x^{n+1}\) can be expressed as:

\[
D_x^{n+1}(i + 0.5, i, k) = \frac{2\varepsilon_0\varepsilon_S - \sigma_x\Delta t}{2\varepsilon_0\varepsilon_S + \sigma_x\Delta t} D_x^n(i + 0.5, i, k) + \left( \frac{2\mu_0\mu_S}{2\varepsilon_0\varepsilon_S + \sigma_x\Delta t} \right) \left( H_x^{n+1}(i + 0.5, j + 0.5, k) - H_x^{n+1}(i + 0.5, j - 0.5, k) \right) \frac{\Delta y}{\Delta z}
\]

\[
E_x^{n+1}(i + 0.5, i, k) = \frac{2\varepsilon_0\varepsilon_S - \sigma_x\Delta t}{2\varepsilon_0\varepsilon_S + \sigma_x\Delta t} E_x^n(i + 0.5, i, k)
\]

\[
\left( \frac{2\mu_0\mu_S}{2\varepsilon_0\varepsilon_S + \sigma_x\Delta t} \right) \left( H_x^{n+1}(i + 0.5, j + 0.5, k) - H_x^{n+1}(i + 0.5, j - 0.5, k) \right) \frac{1}{\Delta y} \left( \frac{1}{(2\varepsilon_0\varepsilon_S + \sigma_x\Delta t)} D_x^{n+1}(i + 0.5, i, k) - \frac{2\varepsilon_0\varepsilon_S - \sigma_x\Delta t}{2\varepsilon_0\varepsilon_S + \sigma_x\Delta t} D_x^n(i + 0.5, i, k) \right)
\]

where \(D_{x,y,z}\) are the assistant electric displacements, which are defined as: \(D_x = \varepsilon \frac{s_z}{s_x} E_x\), \(D_y = \varepsilon \frac{s_z}{s_y} E_y\), \(D_z = \varepsilon \frac{s_y}{s_z} E_z\). The recursion relations of the other electromagnetic components in PMLs could be found in the Karl S. Kunz’s book[131].

**Light sources and the time-frequency transform**

The excitation light used in FDTD calculations are always a pulse light source. The FDTD method is based on the time difference, so the source cannot be infinite in the time domain. The advantage of the pulse excitation is that the Fourier-transformed result of FDTD calculations contains the electromagnetic response of the analyzed
objects in a broadband of frequency (or wavelength). The continuous source only gives out the electromagnetic response of a single frequency. On the other hand, the partial distribution of a numerical light source can be uniform, Gaussian-shaped, or in another distribution function on a point, a line or a plane. The FDTD simulations in this thesis mainly used the fundamental mode guided by a dielectric waveguide and a point source acting as a dipole. The two sources are both modulated in the Gaussian form in the time domain. Regardless of the partial distribution, the time function of sources is expressed as:

$$E(t) = E_0 e^{-t^2/(2T^2)} \sin(\omega_0 t)$$  \hspace{1cm} (2-14)$$

where $t_{\text{offset}}$ is the time offset of the Gaussian function, $T$ is the half-width of the Gaussian function, and $\omega_0$ is the oscillating angle frequency of sources. Via the Fourier transform, the spectrum of the source can be expressed as:

$$E'(\omega) = E_0' e^{-(\omega-\omega_0)^2/2W^2} e^{-jwt_{\text{offset}}$$  \hspace{1cm} (2-15)$$

where $W = 1/T$, which describes the bandwidth of the spectrum. The source spectrum is still Gaussian modulated. A typical Gaussian modulated light source and its spectrum in the frequency domain are shown in the figure below. When all the finite-in-time light passes through the simulated space restricted by the boundaries, the FDTD calculation stops and the electromagnetic field of every position in the space is recorded. Via the Fourier-transform, the electromagnetic response is obtained.

![Figure 2-3 Gaussian modulated light sources: (a) Electric field intensity in the time domain. (b) The corresponding spectrum in the frequency domain. Here, $t_{\text{offset}} = 2 \times 10^{-14}$ s, $T=1 \times 10^{-14}$ s, and the wavelength is $1 \times 10^{-6}$ m.](image)

### 2.1.2 Strong coupling model

It has already been mentioned in the 1st chapter that the SERS sensor studied in this thesis is based on a hybrid waveguide made of a metallic slot and a dielectric strip. According to the electromagnetic interaction, the coupling process between two waveguides can be modeled analytically.

In the literature, the plasmonic-photonic coupling between metallic waveguides and dielectric waveguides is analyzed mainly by two methods: a strong coupling
model based on the Lorentz reciprocity theorem with all the electromagnetic field components[99], [102]–[104] and an approximation model ignoring the field components along the propagating direction[97], [100], [101]. When two waveguides are very close to each other, the strong coupling model describes the plasmonic-photonic coupling more accurately. Here, the compact two-waveguide system is considered, so the strong coupling model is exploited preferably.

The strong coupling model was proposed in 1987 by S. L. Chuang[134], [135]. Derived from the Lorentz reciprocity theorem within a general lossy medium, it is applicable to analyze the metallic-dielectric hybrid waveguide. The generalized Lorentz reciprocity theorem can be expressed as:

$$\nabla \cdot (E^1 \times H^2 - E^2 \times H^1) = i\omega (\varepsilon^1 - \varepsilon^2)E^1 \cdot E^2$$  

(2-16)

where \((E^1, H^1)\) and \((E^2, H^2)\) are the resolutions of Maxwell’s equations in two media \(\varepsilon^1\) and \(\varepsilon^2\) with the individual boundary conditions. On a \(z\)-normal plane, this equation can be expressed in an integral form:

$$\frac{\partial}{\partial z} \iint (E^1 \times H^2 - E^2 \times H^1) \cdot \hat{z} \, dx \, dy = i\omega \iint (|\varepsilon^2(x,y) - \varepsilon^1(x,y)|)E^1 \cdot E^2 \, dx \, dy$$  

(2-17)

When the media \(\varepsilon^1\) and \(\varepsilon^2\) involved in the equation above are isotropic, the reciprocity theorem is always valid and exact.

It is assumed that a hybrid waveguide \(p + q\) is composed by two waveguides \(p, q\), as shown in Figure 2-4. \(\varepsilon^{p,q}\) and \((E^{p,q}, H^{p,q})\) are the permittivity and the field profiles of the modes guided by the two isolated waveguides \(p, q\) and the hybrid waveguide \(p + q\) respectively. If the modal fields \((E^1, H^1)\) in the equation (2-17) is set as the modal field profiles of the hybrid waveguide \(p + q\) and propagate in the \(+z\) direction, the transverse fields of \((E^1, H^1)\) can be expressed as:

$$E^1_t = a(z)E^{p+}_t(x,y) + b(z)E^{q+}_t(x,y)$$  

$$H^1_t = a(z)H^{p+}_t(x,y) + b(z)H^{q+}_t(x,y)$$  

(2-18)

and the longitudinal fields are expressed as:

$$E^1_z = a(z)\frac{\varepsilon^P}{\varepsilon}E^{p+}_z(x,y) + b(z)\frac{\varepsilon^q}{\varepsilon}E^{q+}_z(x,y)$$  

$$H^1_z = a(z)\frac{\varepsilon^P}{\varepsilon}H^{p+}_z(x,y) + b(z)\frac{\varepsilon^q}{\varepsilon}H^{q+}_z(x,y)$$  

(2-19)

where \(a(z)\) and \(b(z)\) are the field intensity of the modal fields guided in the waveguides \(p, q\) respectively. Here, the expressions are approximated because the radiation modes are neglected and the waveguides \(p\) and \(q\) are assumed to only support a single \(TE\) (or \(TM\)) mode. The modal fields \((E^2, H^2)\) in the equation (2-17) is set as the modal field profiles of the isolated waveguide \(p\) and propagate in the \(z\)-axis direction, the transverse fields of \((E^2, H^2)\) can be expressed as:

$$E^2 = E^{p-}(x,y)e^{-i\beta_p z}$$  

$$H^2 = H^{p-}(x,y)e^{-i\beta_p z}$$  

(2-20)
Combining the equations (2-17)-(2-20), a coupling equation can be obtained as:

\[
\frac{da(z)}{dz} + \hat{C} \frac{db(z)}{dz} = i(\beta_p + \hat{K}_{pp})a(z) + i(\hat{C}\beta_p + \hat{K}_{qp})b(z) \tag{2-21}
\]

where \( \hat{K}_{mn} = 0.25\omega \iint (\epsilon^t - \epsilon^n)[E_{t,m}^n \cdot E_{t,n}^m - (\epsilon^m/\epsilon^n)E_{t,m}^n E_{t,n}^m]dxdy \), \( \hat{C} = 0.5(C_{mn} + C_{nm}) \) and \( C_{mn} = 0.5 \iint (E_{t,m}^n \times H_{t,n}^m) \cdot \hat{z}dxdy \). Here \( m, n = p, q \). When the modal fields \((E^2, H^2)\) in the equation (2-17) is set as the modal field profiles of the isolated waveguide \( q \) and propagate in the \(-z\) direction, a second coupling equation can be obtained as:

\[
\frac{\hat{C}}{dz} \frac{da(z)}{dz} + \frac{db(z)}{dz} = i(\hat{C}\beta_b + \hat{K}_{pq})a(z) + i(\beta_q + \hat{K}_{qq})b(z) \tag{2-22}
\]

Based on the equations (2-21) and (2-22) and a given initial condition: \( a(0) = 1 \) and \( b(0) = 0 \), the field fractions of the individual modes in the hybrid waveguide can be obtained by:

\[
a(z) = \left[ \cos(\varphi z) + i \Delta \sin(\varphi z) \right] e^{i\phi z} \tag{2-23}
\]

\[
b(z) = \frac{iK_{ha}}{\varphi} \sin(\varphi z)e^{i\phi z} \tag{2-24}
\]

where \( \Delta = (\gamma_q - \gamma_p)/2 \), \( \varphi = \sqrt{\Delta^2 + K_{pp}K_{qp}} \) and \( \phi = (\gamma_q + \gamma_p)/2 \). The corrected propagation constants \( \gamma_{p,q} \) are defined as \( \gamma_{p,q} = \beta_{p,q} + (\hat{K}_{pp,qq} - \hat{C}\hat{K}_{qp,qp})/(1 - \hat{C}^2) \) and the corrected coupling coefficients are defined as \( K_{pq,qp} = (\hat{K}_{pq,qp} - \hat{C}\hat{K}_{qp,pp})/(1 - \hat{C}^2) \). The power fraction in the waveguide \( q \) coupled from the waveguide \( p \) can be calculated by:

\[
\eta_{p \rightarrow q} = \text{Re}\left[ (C_{qp}a + b)(C_{pq}^*a^* + b^*) \right] \tag{2-25}
\]

Figure 2-4 Schematic diagrams for the strong coupling model between two waveguides: (a) the single waveguide \( p \), (b) the single waveguide \( q \) and (c) the hybrid waveguide \( p + q \).

### 2.2 Experimental techniques

In this thesis, the experiments mainly contain the sensor fabrication and the characterization of the SERS-detection capacity. Due to high-resolution and homogeneity, the lithography techniques are used to fabricate the hybrid waveguides made of metallic slots and dielectric strips. The techniques involved here are mainly the optical lithography (OL) for dielectric strip waveguides and the electron beam lithography (EBL) for metallic slot waveguides. Some other techniques such as physical vapor deposition (PVD) and scanning electron microscopy (SEM), are also
used in the experiments. The sensor’s SERS-detection capacity is characterized by a commercial Raman microscope *LabRAM 800HR*, released by Horiba, Ltd.

### 2.2.1 Fabrication of dielectric waveguides

The dielectric (Si$_3$N$_4$) waveguides were fabricated by our collaborators in the laboratory LETI at CEA in Grenoble. Here, a brief introduction is given out to show the fabrication process.

To fabricate a dielectric strip waveguide, the typical fabrication process is shown in Figure 2-5. Here, the waveguide is a silicon nitride (Si$_3$N$_4$) strip embedded in the silica (SiO$_2$) cladding on a silicon (Si) substrate. Before fabrication, the Si substrate is cleaned by ultrasonic within Decon 90 solution, distilled water, acetone and isopropyl alcohol (IPA) orderly. Then, the lower Si$_2$O cladding and the Si$_3$N$_4$ layer are deposited by plasma-enhanced chemical vapor deposition (PECVD), as shown in Figure 2-5-(a). The reagents of the deposition are SiH$_4$ and N$_2$O. The ratio of the two chemicals determines the product is SiO$_2$ or Si$_3$N$_4$. The photoresist layer is fabricated on the Si$_3$N$_4$ layer by spin coating, as shown in Figure 2-5-(b). The patterns of waveguides are written into the photoresist layer by the photon beam with a mask, as shown in Figure 2-5-(c). To remove the exposed photoresist, the sample is immersed in the developing solution, as shown in Figure 2-5-(d). Then, only the unexposed photoresist exists. The dry etching removes the Si$_3$N$_4$ layer except for the part covered by the resist, as shown in Figure 2-5-(e). After that, an upper Si$_2$O cladding is deposited by PECVD and the surface is planarized by the chemico-mechanical method. The desirable Si$_3$N$_4$ waveguide is obtained eventually as shown in Figure 2-5-(f).

![Figure 2-5 Fabrication of Si$_3$N$_4$ strips by the optical lithography techniques: (a) Deposition of the lower Si$_2$O cladding and the Si$_3$N$_4$ core layer on a cleaned Si substrate. (b) Spin coating of the photoresist layer on the Si$_3$N$_4$ layer. (c) Optical lithography. (d) Development. (e) Dry etching. (f) Deposition of the upper Si$_2$O cladding and chemico-mechanical planarization.](image-url)
2.2.2 Fabrication of metallic waveguides

Due to the size of dozens of nanometers, the fabrication of metallic slot waveguides is conducted by the e-beam lithography. The basic idea is to write the designed patterns in an electron-sensitive resist layer by an electron beam. The exposed area can be easily removed due to the breakdown of molecular chains if the resist is positive. If the resist is negative, the unexposed area will be removed. Subsequently, the hollowed-out patterns imprinted in the resist are filled by evaporated metals. The desirable metallic patterns are obtained after the remnant resist is removed.

The typical fabrication process of the e-beam lithography is shown in Figure 2-6. It is a top-down approach and the details are shown as:

- **Reactive-ion etching (RIE)**

RIE does not belong to the typical processes of the e-beam lithography but it is included as a preliminary step before fabricating metallic slot waveguides. This is because the Si$_3$N$_4$ waveguides are covered by a very thick (hundreds of nanometers) SiO$_2$ cladding which prevents the evanescent interaction between the Si$_3$N$_4$ waveguides and the metallic waveguides. Before the metallic waveguides are fabricated, the SiO$_2$ cladding should be etched to let the evanescent fields of the Si$_3$N$_4$ waveguides extend out.

The etching is conducted by the RIE machine *MU 400 PLASSYS*. The etching gasses are the plasma of SF$_6$ and O$_2$ with the flowing speeds 17 sccm and 6 sccm respectively. The RIE power is 90 W and the pressure is 4 mTorr in the working chamber.

Figure 2-6 Fabrication of metallic slots by the electron beam lithography techniques: (a) Spin coating of PMMA and Spacing 300z on the etched Si$_3$N$_4$ strip’s upper cladding. (b) E-beam lithography. (c) Development. (d) Deposition of metals. (e) Lift-off.
Spin coating of PMMA and Espacer 300z

Before the spin coating of PMMA and Espacer 300z, the sample is cleaned by ultrasonic within Decon 90 solution (2% - 5% of concentration in distilled water, 10 min, 50 °C), distilled water (10 min, 50 °C), acetone (5 min, 50 °C) and IPA (5 min, 50 °C). After that, the sample is dried with air.

Poly (methyl methacrylate) (PMMA) is a positive e-beam resist, the long molecular chains of which can be broken by the electron exposure. The applied PMMA is dissolved in methyl isobutyl ketone (MIBK) with a concentration of 30 g/L. The spin-coating parameters are chosen as 4000 rpm/sec in acceleration, 3000 rpm in speed and 30 sec in time. Consequently, a PMMA layer of 150 nm thickness is deposited on samples, which can be used to fabricate nanostructures with height less than 50 nm (the ratio of 3:1 between the PMMA thickness and the metallic nanostructure height is recommended). To flatten the PMMA surface, the resist is baked at 180 °C for 10 min.

Espacer 300Z is a conductive polymer, which can avoid the charging effect (charge accumulation on samples). The spin-coating parameters are chosen as 4000 rpm/sec in acceleration, 3000 rpm in speed and 30 sec in time. Then, the Espacer 300Z layer is baked at 70 °C for 10 min.

E-beam lithography

The metallic waveguides are written into the PMMA by the EBL machine Raith E-line. The filament works with the thermal field emission and the stage is positioned by laser interferometers with moving precision 2 nm. The standard writing field size is 100 µm × 100 µm with 2 nm × 2 nm pixel size, but the writing field size can vary from 500 nm × 500 nm up to 2 mm × 2 mm. The main parameters are chosen as: column voltage 10 kV, aperture 10 µm (control the electron beam current), dose 150 µc/cm² and writing field 50 µm × 50 µm.

Development

To develop the patterns written in the PMMA, the Espacer 300Z layer and the exposed PMMA are removed. Firstly, the sample is immersed in distilled water for 1 min and Espacer 300Z is dissolved. Subsequently, the sample is immersed in a solvent of MIBK and IPA with volume proportion 1:3 for 1 min to remove the exposed PMMA. To clean the remnant chemicals, the sample is immersed in IPA for 30 sec and dried with air.

Metal deposition

The physical vapor deposition (PVD) of metals is conducted by the PVD machine MEB 400 PLASSYS. To increase the adhesion of metallic nanostructures on SiO₂, a 3-nm-thick layer of Cr is deposited firstly. Cr is evaporated by e-beam and the deposition speed is 0.18 nm/sec. Au is evaporated by the thermal effect and the
deposition speed is 0.3 nm/sec. The pressure is about $1 \times 10^{-6}$ Torr in the working chamber.

◆ **Lift-off**

After the metal deposition, the sample is immersed in acetone for 24 hours to remove the unexposed PMMA and the metal on top. The sample is washed with IPA and dried with air to remove the remnant chemicals. Eventually, the patterned nanostructures (metallic slots) are fabricated on the sample.

2.2.3 **Characterization of the sensor**

The characterization mainly contains the topography and the SERS-detection capacity of the sensor.

◆ **Scanning electron microscope (SEM)**

Scanning electron microscopes (SEM) are the commonly-used tool to characterize nanostructures. Here, the SEM machine *Hitachi SU 8030* is used to obtain the morphological information of the sensor. Its filament works with the cold field emission and the electron beam is accelerated by a column voltage (1-30kV). A set of different electromagnetic lenses focus and scan the electron beam on the sample surface and the spatial resolution can reach 1.0 nm at 15 kV and 1.3 nm at 1 kV. The signals mainly contain two kinds of electrons: the secondary electrons (SE) and backscattered electrons (BSE). The secondary electrons are emitted by the sample atoms excited by the electron beam and the electron number depends on the sample topography. But it can not go deeply into the SiO$_2$ cladding of the Si$_3$N$_4$ waveguides. The backscattered electrons come from the high-energy electrons that go through the SiO$_2$ layer and interact with the embedded Si$_3$N$_4$ waveguides.

◆ **Raman microscope**

To characterize the SERS-detection capacity of the sensor, the Raman microscope *LabRAM 800HR* (Horiba, Ltd.) is used. It is equipped with a Helium-Neon laser (632.8 nm, 8.3 mW) and a Peltier CCD detector (1024 × 256 pixels). Three different objectives are convenient with parameters 10× NA 0.3, 50× NA 0.8 and 100× NA 0.9. The filter’s blocking for Rayleigh scattering is 60 dB and the dispersion grating is 600 lines/mm. The spectrum resolution is 3 cm$^{-2}$ and the moving precision of the stage is 1 µm.

In experiments, the signals of the backward Raman scattering are detected and two different detection configurations are presented in Figure 2-7. In the indirect detection configuration, a multimode fiber with a 5µm core diameter and NA 0.14 is used to connect the SERS sensor and the Raman microscope objective. The excitation laser is coupled into the fiber by the microscope objective. The other fiber head is coupled with the grating of the Si$_3$N$_4$ waveguide of the sensor. It is fixed with angle 25° on a three-axis platform to adjust the fiber head’ position. The coupling between
the Si$_3$N$_4$ waveguide and the fiber head is monitored by an observing microscope. The excitation laser enters into the sensor through the fiber and the Raman signals of the sensor enter into the microscope objective through the same fiber. The indirect detection configuration has a high coupling efficiency between the fiber and the Si$_3$N$_4$ waveguide, but the disadvantage is that the fiber will introduce its Raman spectrum as a disturbing background on the detector of the Raman microscope. The direct detection configuration in Figure 2-7-(b) is much simpler than the indirect one. The excitation laser is focused by the microscope objective directly on the grating of the Si$_3$N$_4$ waveguide and the signals of the backward Raman scattering are collected directly by the same microscope objective. The direct detection configuration removes the disturbing Raman spectrum of the fiber. The disadvantage is that the coupling of the excitation laser into the Si$_3$N$_4$ waveguide is relatively weak due to the variable injection angle (not always 25°) in a focused light beam.

![Figure 2-7 Configurations for measuring the Raman signals of the SERS sensor on chips: (a) Indirect detection configuration, where a fiber is used to connect the SERS sensor and the Raman microscope objective. The right image shows the real setup. (b) Direct detection configuration, where the Raman microscope objective and the grating of the sensor are coupled directly through free space. The right image shows the real setup.](image)

2.3 Summary

In this chapter, the principles and details of the mathematical methods and experimental techniques used in the thesis are introduced, including the FDTD algorithm, a strong coupling model, the fabrication procedure of samples and the characterization tools for the sensor.

Based on the $|E|^4$-approximation, the enhancement factors ($EF$) of SERS
substrates can be easily estimated by solving Maxwell’s equations with boundary conditions. The FDTD principles are introduced, such as discretization, dispersion, boundary and time-frequency transformation. It is one of the most popular numerical tools to simulate the electromagnetic phenomena. One FDTD simulation can provide a broadband electromagnetic response of metallic nanostructures covering a wide wavelength range. An analytical model, the strong coupling model, is also introduced to calculate the photonic-plasmonic coupling efficiency.

In this thesis, the experiments mainly contain the fabrication of the sensor and the characterization of the SERS-detection capacity. The fabrication process of the Si$_3$N$_4$ waveguides provided by our cooperators is introduced briefly. The fabrication in the thesis is mainly about the metallic slot waveguides, which is conducted via the standard process of the electron beam lithography. With the related techniques such as RIE and PVD, the fabrication process of metallic slots is detailed. Then, the morphological characterization tool SEM and two SERS-detection configurations based on a Raman microscope are introduced.
3. SERS sensors based on hybrid waveguides made of metallic slots and dielectric strips

The SERS sensor in the thesis is mainly based on the photonic-plasmonnic coupling in the dielectric-metallic hybrid waveguide, which has been mentioned in the 1st chapter. Compared to an open or half-open configuration such as Raman microscopes, the waveguide-based SERS sensor can confine all the electromagnetic fields in a micro scale, resulting in a much smaller sensing configuration with high local energy density.

This chapter mainly introduces the theoretical investigation of the SERS sensor based on the hybrid waveguide made of metallic slots and dielectric strips by the 3D-FDTD method. It starts with the sensor schematics and the relative material information, which is followed by a glimpse of a fully integrated SERS-detection system on a chip to show the core function of the SERS sensor. Based on the strong coupling theory, the photonic-plasmonnic coupling is discussed, particularly its dependence on the geometrical parameters. Using 3D-FDTD simulations and the \( |E|^4 \)-approximation, the enhancement factors in the metallic slot are obtained. Finally, the sensor’s detection capacity is characterized theoretically with some dye molecules. The results show that a SERS sensor can be achieved based on the hybrid waveguide with an enhancement factor of \( 10^2 \)-\( 10^3 \) for Raman scattering of Raman-active molecules in the metallic slot.

3.1 Sensor design

It has been mentioned that the SERS sensor under study is based on the hybrid waveguide made of metallic slots and dielectric strips. The main parameters that determine the photonic(strip)-plasmonnic(slot) coupling are the sizes of the two waveguides and the interval between them. The coupling efficiency can be optimized by tuning the geometrical parameters. Considering the dispersion of materials, particularly metals, the permittivity models should be chosen as close as possible to the actual materials in the sensor fabrication. As a core component of a fully integrated SERS-detection system, the potential extension of the sensor with other micro-photonic components is discussed at the end.

3.1.1 Sensor schematics

The schematics of the sensor in this thesis is shown in Figure 3-1, where a metallic (Au/Al) slot is located on the silica substrate while a silicon nitride (Si\(_3\)N\(_4\)) strip is embedded vertically at a distance \( s_p \). Si\(_3\)N\(_4\) is almost transparent for the visible and near-IR spectral regime, with a high dielectric constant \( \varepsilon = 4 \), which ensures a good confinement of electromagnetic fields. The slot material is chosen as gold (Au)
or aluminum (Al). Gold is one of the most promising metals for plasmonics in the red and near-infrared range with a good chemical stability. However, the fabrication of gold slots is very expensive if the sensor is massively produced. Aluminum is another choice for the slot material. Although an Al slot exhibits weaker surface plasmons, the cost can be much lower than the Au slot. Moreover, gold is a contaminant for most CMOS fabrication processes while aluminum is not, meaning aluminum can make it easy to integrate the SERS sensor with other microscale photoelectric elements fabricated by the CMOS techniques. Except for the cost and the compatibility with the COMS techniques, aluminum has another advantage that the excitation wavelength of Al surface plasmons is shorter than that of Au. According to the $1/\lambda^4$ dependence of Raman scattering in the equation (1-6), the shorter excitation wavelength can increase Raman intensity further. The shapes of the slot and strip waveguides are always kept as rectangular. $W_D$, $H_D$, $W_m$ and $H_m$ are the width and height of the dielectric strip and the metallic slot respectively. $Sp$ is the edge-edge distance between the slot and the strip. The metallic slot confines the plasmonic fields inside, into which analytes are applied. The superstrate material is taken as water, which is the environment of the excitation and radiation of induced Raman dipoles in molecules if analytes are dissolved in water. Its refractive index is set as $\varepsilon = 1.33$. The illumination is injected into the Si$_3$N$_4$ strip from one end at $z = 0$ nm. Then, the light will couple into the metallic slot from the Si$_3$N$_4$ strip and excites the intense local plasmonic fields there. The plasmonic fields can induce Raman dipoles of analyte molecules in the slot, the radiation of which will excite the plasmonic modes guided by the slot. The radiated Raman signals then couple into the Si$_3$N$_4$ strip, which is connected to dispersive components such as a spectrometer. The Raman spectra of analytes are detected finally by the photoelectric detector of the dispersive element.

![Figure 3-1 Sensor schematics](image)

**Figure 3-1 Sensor schematics:** (a) Cross section of the hybrid waveguide, where a rectangular silicon nitride (Si$_3$N$_4$) strip with sides $W_D$ and $H_D$ is located at a distance $Sp$ under a rectangular metallic (Au/Al) slot with sides $W_m$ and $H_m$ on the silica substrate. (b) 3D view of the SERS sensor, where the $L$-length metallic slot is laid above the embedded Si$_3$N$_4$ strip.

### 3.1.2 Permittivity models of materials

It has been demonstrated that the Fourier-transformed results of FDTD simulations contain the electromagnetic response covering a wide wavelength range. Due to the material dispersion, the involved permittivity should be expressed as a
function of wavelength or frequency in FDTD simulations, as shown in the part 2.1.1. The commonly-used permittivity models are analytic, such as Debye model and Lorenz model. In the commercial software *FDTD solutions*, an analytic permittivity model based on the experimental data is automatically generated. The experimental data of the main materials in this thesis are reported in Figure 3-2, where the refractive indexes of gold and aluminum are referred to E. D. Palik’s handbook[136] and silicon nitride is referred to H. R. Philipp[137]. Raman detections are always conducted in the visible and the near IR spectra. Considering the absorption of gold with the wavelength below 600 nm, the excitation wavelength of the sensor with a gold slot is set as 600 nm - 900 nm. The excitation wavelength of Al surface plasmons is shorter than that of gold, so the wavelength range is set as 200 nm – 800 nm. The corresponding analytic models of refractive indexes for gold, aluminum and silicon nitride are reported in Figure 3-3, which are fitted within the software *FDTD solutions* based on the experimental data.

![Figure 3-2 Refractive indexes of (a) gold, (b) aluminum and (c) silicon nitride, which are obtained from the experiments[136], [137].](image)

![Figure 3-3 Analytic models of refractive indexes for (a) gold, (b) aluminum and (c) silicon nitride, which are fitted within the software *FDTD solutions* based on the data in Figure 3-2.](image)

### 3.1.3 Potential extension

It has been introduced in the part 1.2.2 that many spectroscopic components have been realized with photonic circuits on a chip. By combining the SERS sensor under study with the photonic- and electronic- elements, a fully integrated SERS-detection system on a chip can be developed, as shown in Figure 3-4. The main extended components are a laser diode, a multiplexer such as an arrayed waveguide grating (AWG) and a line CCD detector. The laser provides the incident light to excite surface plasmons and analytes in the metallic slot of the SERS sensor. Raman scatterings of
analyte molecules are enhanced by the in-slot local plasmonic field. The Raman signals collected by the Si$_3$N$_4$ strip are dispersed spatially by the AWG waveguides depending on different Raman shifts and eventually detected by the radiation receivers (CCD). The entire on-chip system can be very small and even be implanted into a smart cell phone as a lab in hand. Considering the need for on-site chemical and biological detections, this SERS-detection system with a high enhancement factor is one of the most desirable tools in future.

![SERS detection system](image)

Figure 3-4 Fully integrated SERS-detection systems on a chip developed by combining the SERS sensor under study with the extended photonic- and electronic- components.

3.2 Photonic-plasmonic coupling between metallic slots and Si$_3$N$_4$ strips

The sensor is based on the hybrid waveguide made of metallic (Au/Al) slots and Si$_3$N$_4$ strips. The photonic-plasmonic coupling between the two waveguides is the basic mechanism of exciting surface plasmons and collecting Raman signals in the SERS sensor. This section focuses on the basic principles of the hybrid coupling, such as polarization, field distribution, and geometrical dependence. Particularly, the coupling efficiency is analyzed based on the strong coupling theory. With a higher efficiency, more energy can couple into the metallic slot to excite surface plasmons and enhance Raman scattering. It demonstrates the strategy to optimize the enhancement of the SERS sensor for Raman scattering.

3.2.1 Incident polarization

The incident light of the sensor is injected from the Si$_3$N$_4$ strip. According to the dominant electromagnetic field in the strip, the guided modes are classified into two polarizations: $TE (E_x > E_y, E_z)$ and $TM (E_y > E_x, E_z)$. When the fundamental $TE$ and $TM$ modes of the Si$_3$N$_4$ strip are injected into the hybrid waveguide, the $|E|$ distributions ($\lambda = 720$ nm) of the photonic-plasmonic coupling between the gold slot and the Si$_3$N$_4$ strip are shown in Figure 3-5. Here, a gold slot is used as an example to demonstrate the coupling. If not specified otherwise, all the electric field intensity in this thesis is normalized to the maximum value of the incident electric field. In the propagation direction, the field $|E|$ distributes in a beating feature in Figure 3-5-(a) and -(c), particularly in the gold slot. It is also seen in the x-normal planes that the strongest field excited by the $TE$ mode appears in the gold slot while the strongest field excited by the $TM$ mode appears in the space between the gold slot and the Si$_3$N$_4$.
strip. This can be observed more clearly in Figure 3-5-(b) and -(d). The plasmonic field excited by the TE mode mainly exists in the metallic slot but this area is “dark” in the case of the TM mode. This is because surface plasmons are the collective oscillation of surface electrons and the electric field is always perpendicular to metal surfaces. So, the TE mode with \( E_x > E_y, E_z \) preferably excites the plasmonic field in the slot while the TM mode with \( E_y > E_x, E_z \) preferably excites the plasmonic field in the spacing between the slot and the strip. The volume of the metallic slot is the main working place of the sensor, where analytes are applied. Therefore, the fundamental TE mode of the Si\(_3\)N\(_4\) strip is taken as the incident light in the SERS sensor.

![Figure 3-5 Electric field \( |E| \) distributions in the hybrid waveguide made of a gold slot and a Si\(_3\)N\(_4\) strip with spacing, which is normalized to the maximum value of the incident electric field: (a)-(b) \( |E| \) on an x-normal/z-normal plane when the incident light is the fundamental TE mode of the Si\(_3\)N\(_4\) strip waveguide. (c)-(d) \( |E| \) on an x-normal/z-normal plane when the incident light is the fundamental TM mode of the Si\(_3\)N\(_4\) strip waveguide. The incident light is injected at \( z = 0.25 \) \( \mu \)m. The geometry of the hybrid waveguide is set as: \( W_m = H_m = 30 \) nm, \( Sp = 10 \) nm and \( W_D = H_D = 200 \) nm.](image)

### 3.2.2 Supermodes and field beatings

According to the coupling theory, the bi-waveguide coupling process can be described by the supermodes of the superstructure. The beating distribution of the in-slot plasmonic field can be seen as the interaction of two supermodes guided in the hybrid waveguide, as shown in Figure 3-6. The hybrid waveguide supports two fundamental TE (\( E_x > E_y, E_z \)) supermodes: even and odd, the names of which are given based on the modal phase profiles. As shown in the top-right inserts of Figure 3-6-(b) and -(c), the even supermode has a symmetric phase profile between the slot and the strip while the phase profile of the odd supermode is anti-symmetric. When two guided modes, \( k_1 \) and \( k_2 \), propagate in the z-direction, their field amplitude superposition \( E \) can be expressed as \( E = \cos(k_1 z - \omega t) + \cos(k_2 z - \omega t) = 2 \cos[0.5(k_1-k_2)z] \cos[0.5(k_1+k_2)z - \omega t] \). It is obvious that the total field \( E \) is modulated with a periodic variation in the propagation direction by the term \( \cos[0.5(k_1-k_2)z] \), i.e. the beating distribution. Considering that \( k_{1,2} = (2\pi/\lambda) neff_{even,odd} \) the beating period \( L_{beat} \) can be expressed as:
\[ L_{\text{beat}} = \frac{\lambda}{Re(\text{n}_{\text{even}} - \text{n}_{\text{odd}})} \] (3-1)

where \( \text{n}_{\text{even}, \text{odd}} \) is the effective refractive index of the even or odd supermode, and \( \lambda \) is the vacuum wavelength. According to the equation above, the beating period \( L_{\text{beat}} \) of the two supermodes shown below is 440 nm, which agrees with the periodic variation of the in-slot electric field in Figure 3-6-(a).

\[ \eta_{\text{slot}} = Re[(C_{21}a + b)(C_{12}a^* + b^*)] \] (3-2)

\[ a(z) = [\cos(\varphi z) + i\frac{\Delta}{\varphi}\sin(\varphi z)]e^{i\varphi z} \] (3-3)

\[ b(z) = \frac{iK_{p\alpha}}{\varphi}\sin(\varphi z)e^{i\varphi z} \] (3-4)

where \( \Delta = (\gamma_b - \gamma_a)/2 \), \( \varphi = \sqrt{\Delta^2 + K_{p\alpha}K_{ab}} \) and \( \phi = (\gamma_b + \gamma_a)/2 \).

Here, the hybrid waveguide described in Figure 3-5 is taken as an example. When the fundamental TE mode (\( \lambda = 720 \) nm) of the Si\(_3\)N\(_4\) strip is injected as the incident light, the coupling efficiency of the energy coupled into the slot is reported in Figure 3-7. The strong coupling model is based on the modal fields of the two isolated waveguides, which are presented in the inserts. The modal fields of the isolated waveguides are obtained by an eigenmode expansion (EME) solver, which is included in the commercial software, FDTD solutions. In the 1\(^{\text{st}}\) beating period, the coupling

Figure 3-6 Supermodes and field beatings in the hybrid waveguide made of a gold slot and a Si\(_3\)N\(_4\) strip with spacing: (a) Electric field \( |E| \) distribution on an x-normal plane. (b) Electric field \( |E| \) of the even supermode with \( \text{n}_{\text{even}} = 3.0141 + 0.1149i \). (c) Electric field \( |E| \) of the odd supermode with \( \text{n}_{\text{odd}} = 1.3780 + 0.0022i \). The inserts present the modal phase profiles. The hybrid waveguide is the same as that described in Figure 3-5.

It is noted that the beating of the in-strip field is not so obvious as that in the slot. This is because the two individual waveguides are not identical and the hybrid waveguide is not symmetric, leading to that the supermodes are not a purely odd or purely even mode. So, there is still some energy left in the strip when the in-strip phase difference of the two supermodes is \( \pi \), i.e. the coupling efficiency is not 100%. The coupling efficiency can be calculated based on the strong coupling theory. According to the part 2.1.2, the fraction \( \eta_{\text{slot}} \) of the energy coupled into the slot from the strip can be expressed as:

It is noted that the beating of the in-strip field is not so obvious as that in the slot. This is because the two individual waveguides are not identical and the hybrid waveguide is not symmetric, leading to that the supermodes are not a purely odd or purely even mode. So, there is still some energy left in the strip when the in-strip phase difference of the two supermodes is \( \pi \), i.e. the coupling efficiency is not 100%. The coupling efficiency can be calculated based on the strong coupling theory. According to the part 2.1.2, the fraction \( \eta_{\text{slot}} \) of the energy coupled into the slot from the strip can be expressed as:

\[ \eta_{\text{slot}} = Re[(C_{21}a + b)(C_{12}a^* + b^*)] \] (3-2)

\[ a(z) = [\cos(\varphi z) + i\frac{\Delta}{\varphi}\sin(\varphi z)]e^{i\varphi z} \] (3-3)

\[ b(z) = \frac{iK_{p\alpha}}{\varphi}\sin(\varphi z)e^{i\varphi z} \] (3-4)

where \( \Delta = (\gamma_b - \gamma_a)/2 \), \( \varphi = \sqrt{\Delta^2 + K_{p\alpha}K_{ab}} \) and \( \phi = (\gamma_b + \gamma_a)/2 \).

Here, the hybrid waveguide described in Figure 3-5 is taken as an example. When the fundamental TE mode (\( \lambda = 720 \) nm) of the Si\(_3\)N\(_4\) strip is injected as the incident light, the coupling efficiency of the energy coupled into the slot is reported in Figure 3-7. The strong coupling model is based on the modal fields of the two isolated waveguides, which are presented in the inserts. The modal fields of the isolated waveguides are obtained by an eigenmode expansion (EME) solver, which is included in the commercial software, FDTD solutions. In the 1\(^{\text{st}}\) beating period, the coupling
efficiency peak is around 22% and then it vanishes quickly along the propagating direction. To enhance the in-slot Raman scattering, the high efficiency is preferred. So, the coupling efficiency can be used as one of the indicators when optimizing the geometrical parameters of the hybrid waveguide.

3.2.3 Geometrical dependence of coupling efficiencies

When the materials of metallic slots and dielectric strips are determined, the geometrical parameters are the key to optimize the photonic-plasmonic coupling. According to the coupling theory, the coupling can be strengthened by decreasing the phase velocity mismatch \( \delta = |n_{eff, slot} - n_{eff, strip}| \). Except for the mismatch \( \delta \), the overlap of the evanescent fields of two waveguides also influences the coupling when the two waveguides have a big difference of cross-sections. From the two viewpoints, the geometrical dependence of coupling efficiencies between metallic (Au/Al) slots and Si_3N_4 strips is discussed in the following.

**Au**

The hybrid geometry mainly contains the strip size \((W_D, H_D)\), the slot size \((W_m, H_m)\), and the spacing \(S_p\). When the strip size changes, the modal indexes of the fundamental modes (\(\lambda = 720\) nm) guided in the isolated Si_3N_4 strip are reported in Figure 3-8-(a). The three colorful (red, green, blue) curves present the strip modes when only \(W_D\) changes, only \(H_D\) changes, and both \(W_D\) and \(H_D\) change respectively. The index of the gold slot with \(W_m = H_m = 100\) nm is also included to show the phase velocity mismatch \(\delta = |n_{eff, strip} - n_{eff, slot}|\). Limited by the diffraction, the smallest size of the Si_3N_4 strip is \(d_{min} = \lambda/(2n_{Si3N4}) \approx 180\) nm. When the strip size increases, the modal index of the strip mode increases. Particularly, the blue curve climbs very quickly when \(W_D\) and \(H_D\) both change. At \(X = 575\) nm i.e. \(W_D = H_D = 575\) nm, the index of the strip goes across the modal index of the gold slot, meaning the phase velocity
mismatch $\delta = 0$. The coupling efficiencies between the strip and the slot are reported in Figure 3-8-(b). It is seen that the maximum values of the efficiencies appear in the range $X = 200 \text{ nm} - 300 \text{ nm}$ for the three colorful curves. Particularly, the peak of the blue curve is far from the position $X = 575 \text{ nm}$ with the phase velocity match $\delta = 0$. This is because the modal energy distributes on a bigger cross-section of the strip waveguide when the strip size $(W_D, H_D)$ increases, leading to the decrease of the evanescent energy density in the evanescent overlap of the strip and slot modes. That weakens the coupling between the strip and slot. Besides that, the strip height $H_D$ has a more obvious influence on the coupling efficiency than the strip width $W_D$. This is because increasing $H_D$ makes the strip center and the center of guided mode further away from the slot while increasing $W_D$ does not. This also can make the modal energy in the overlap decrease.

Similarly, the modal indexes of the fundamental modes guided in the isolated gold slot and Si$_3$N$_4$ strip waveguides and the corresponding coupling efficiencies are reported in Figure 3-9 when the slot size $(W_m, H_m)$ changes. The three colorful (red, green, blue) curves present the slot modes when only $W_m$ changes, only $H_m$ changes and both $W_m$ and $H_m$ change respectively. They are accompanied by the fundamental modal index of an isolated Si$_3$N$_4$ strip waveguide with $W_D = H_D = 600 \text{ nm}$. Again, the maximum values of the coupling efficiencies do not appear at the position of the phase velocity match $\delta = 0$. The coupling efficiency increases when the slot size increases, particularly increasing both $W_m$ and $H_m$, resulting from the increase of the evanescent overlap of the strip and slot modes.

After discussing the coupling dependence on the strip and the slot, a glimpse is given on the spacing between the two waveguides. Since the spacing $Sp$ affects the embedding depth of the strip in the silica substrate, the modal index of the strip is influenced by the spacing $Sp$, but not obviously, as shown in Figure 3-10-(a). On the
other hand, the modal index of the slot is not influenced by the spacing change. Here, the strip and slot sizes are set as: $W_D = H_D = 575$ nm and $W_m = H_m = 100$ nm. The phase velocity match $\delta = 0$ appears at $Sp = 10$ nm. The maximum value of the coupling efficiency is obtained at $Sp = 35$ nm, where $\delta \approx 0.0005$. This means that the phase velocity mismatch $\delta$ of the modes guided in the isolated dielectric strip and metallic slot does not determine the coupling efficiency independently. The highest efficiency 24\% is obtained around $Sp = 35$ nm while the efficiency is 16.5\% at $Sp = 10$ nm.

![Figure 3-9](image)

**Figure 3-9** Coupling dependence ($\lambda = 720$ nm) on the slot geometry: (a) Effective refractive indexes of the fundamental TE modes guided in the isolated gold slot (the colorful curves) and Si$_3$N$_4$ strip (the black curve) waveguides are presented as a function of the slot size ($W_m, H_m$). (b) Coupling efficiencies between the strip and the slot in (a) with spacing $Sp = 10$ nm.

![Figure 3-10](image)

**Figure 3-10** Coupling dependence ($\lambda = 720$ nm) on the spacing $Sp$ between the strip and slot waveguides: (a) Effective refractive indexes of the fundamental TE modes guided in the isolated Si$_3$N$_4$ strip (the green curve) and gold slot (the red curve) waveguides are presented as a function of the spacing $Sp$. (b) Coupling efficiencies between the strip and the slot in (a) as a function of spacing $Sp$.

The discussion above has analyzed the dependence of coupling efficiencies on every individual geometrical parameter when the slot is gold. For simplicity and clarity, the dielectric strip and the metallic slot of the SERS sensor are set as square, i.e. $W_D = H_D$ and $W_m = H_m$ (for convenience, the size of the square strip/slot is noted...
as \( S_D/S_m \). It has been demonstrated that a large slot is better to couple the photonic energy into the in-slot surface plasmons. However, it weakens the confinement of plasmons in the slot and reduces the in-slot local plasmonic field intensity. Considering the objective of enhancing Raman scattering in the metallic slot, the intense local plasmonic field is the directly-related factor, not the coupling efficiency. There should be a compromise between these two opposite effects to obtain the strongest enhancement in the slot. Here, the gold slot size is limited to be smaller than 70 nm. On the other hand, increasing \( S_D \) can decrease the energy density in the evanescent overlap of the strip and the slot, and then weaken the coupling. Here, the strip size is limited to be smaller than 350 nm.

Figure 3-11 presents the modal analysis of the isolated strip and the isolated slot with the geometrical parameter values concerned in the SERS sensor. The strip size \( S_D \) changes from 160 nm to 350 nm while the slot size \( S_m \) changes from 30 nm to 70 nm. The spacing \( S_p \) influences the strip mode slightly.

![Figure 3-11](image)

Figure 3-11 Effective refractive indexes of the fundamental TE modes (\( \lambda = 720 \text{ nm} \)) guided in the isolated Si\(_3\)N\(_4\) strip (the non-red colorful curves) and gold slot (the red curve) waveguides are presented: (a) as a function of the strip size \( S_D \) for several spacings while \( S_m = 40 \text{ nm} \). (b) as a function of the slot size \( S_m \) for several spacings while \( S_D = 200 \text{ nm} \).

Based on the modal profiles of the strip and slot waveguides and the corresponding modal indexes, the coupling efficiencies of the energy, which is coupled into the slot from the strip in the first beating, are calculated and presented in Figure 3-12. It is seen in Figure 3-12-(a) that the maximum values of the coupling efficiencies are obtained with \( S_D = 220 \text{ nm} \) while \( S_m = 40 \text{ nm} \). The coupling efficiency increases when the spacing \( S_p \) becomes smaller except for the case \( S_p = 0 \text{ nm} \). When the lower surface of the metallic slot touches the strip, the Si\(_3\)N\(_4\)-SiO\(_2\) boundary of the strip waveguide becomes into a Si\(_3\)N\(_4\)-Au boundary. This leads to a sudden change of the modal profile guided in the strip and subsequently to the decrease of the coupling efficiency. This efficiency decrease with \( S_p = 0 \text{ nm} \) is also seen in Figure 3-12-(b). The spacing \( S_p = 10 \text{ nm} \) is the optimized distance between the slot and the strip. In Figure 3-12-(b), the coupling efficiency climbs with the increase of the slot size \( S_m \), which is caused by the increase of the evanescent overlap.
Figure 3-12 Coupling efficiencies ($\lambda = 720$ nm) between the Si$_3$N$_4$ strip and the gold slot: (a) as a function of the strip size $S_D$ for several spacings while $S_m = 40$ nm. (b) as a function of the slot size $S_m$ for several spacings while $S_D = 200$ nm.

It is known that the in-slot plasmonic energy suffers an obvious loss in propagation, so the slot length $L$ in Figure 3-1 is set as one beating period of the field in the slot. Based on the modal analysis, the beating periods are reported in Figure 3-13. It is seen that the beating period becomes shorter when the spacing $Sp$ decreases. When the strip size increases, the beating period decreases firstly and then increases. When the slot size increases, the beating period always increases.

Figure 3-13 Beating periods of the field in the slot ($\lambda = 720$ nm): (a) as a function of the strip size $S_D$ for several spacings while $S_m = 40$ nm. (b) as a function of the slot size $S_m$ for several spacings while $S_D = 200$ nm.

**Al**

Although aluminum has a weaker plasmonic property than gold and silver, it is a cheap material and can be compatible with CMOS foundries. Besides that, aluminum plasmonics can work in the wavelength range below 600 nm, in which gold has a strong absorption. According to the $1/\lambda^4$ dependence of Raman scattering, the shorter wavelength can increase Raman intensity. Here, the wavelength is set as $\lambda = 530$ nm in the following discussion of the coupling between Si$_3$N$_4$ strips and Al slots. Like the Au slot, the dependence of coupling efficiencies on every individual geometrical parameter is discussed firstly and then the coupling is analyzed with the geometrical parameter values concerned in the SERS sensor.
When the strip size changes, the modal indexes of the fundamental modes guided in the isolated Si$_3$N$_4$ strip and aluminum slot are reported in Figure 3-14-(a). The three colorful (red, green, blue) curves present the strip modes when only $W_D$ changes, only $H_D$ changes and both $W_D$ and $H_D$ change respectively. The black curve is the slot mode when $W_m = H_m = 60$ nm. When the strip size increases, the modal index of the strip mode increases. All the three colorful curves intersect with the black curve at the positions where the phase velocity match $\delta = 0$ appears. The corresponding coupling efficiencies between the strip and the slot are reported in Figure 3-14-(b). The global trending of the three efficiency curves is decreasing when the strip size increases. The reason has been mentioned that the modal energy distributes on a bigger cross-section of the strip waveguide when the strip size ($W_D, H_D$) increases, leading to the decrease of the energy density in the evanescent overlap of the strip and slot modes. That weakens the coupling between the strip and slot. Particularly, increasing $H_D$ makes the strip center and the center of strip modes further away from the slot while increasing $W_D$ does not. So, the strip height $H_D$ has a more obvious influence on the coupling efficiency than the strip width $W_D$.

Similarly, the modal indexes of the fundamental modes guided in the isolated aluminum slot and Si$_3$N$_4$ strip waveguides and the corresponding coupling efficiencies are reported in Figure 3-15 when the slot size ($W_m, H_m$) changes. The three colorful (red, green, blue) curves present the slot modes when only $W_m$ changes, only $H_m$ changes and both $W_m$ and $H_m$ change respectively. The black curve shows the modal index of an isolated Si$_3$N$_4$ strip waveguide with $W_D = H_D = 250$ nm. Being similar with the coupling dependence on the strip size, the increase of $H_m$ makes the slot center and the center of the slot mode further away from the strip waveguide while increasing $W_m$ does not. This effect counteracts the increase of the evanescent overlap. So increasing $H_m$ makes the coupling efficiency decreases when $W_m$ is 60 nm. This also explains that the red curve is higher than the blue one in Figure 3-15-(b).
Increasing $W_m$ makes a bigger overlap size of the slot and the strip, leading to the efficiency increases, as shown by the red and blue curves below.

Figure 3-15 Coupling dependence ($\lambda = 530$ nm) on the slot geometry: (a) Effective refractive indexes of the fundamental TE modes guided in the isolated aluminum slot (the colorful curves) and Si$_3$N$_4$ strip (the black curve) waveguides are presented as a function of the slot size ($W_m, H_m$). (b) Coupling efficiencies between the strip and the slot in (a) with spacing $Sp = 10$ nm.

For the spacing $Sp$ between the strip and slot waveguides, it does not influence the slot mode but it affects slightly the strip mode by changing the embedding depth of the strip in the silica substrate, as shown in Figure 3-16-(a). Here, the strip and slot sizes are set as: $W_D = H_D = 250$ nm and $W_m = H_m = 52.5$ nm. The phase velocity match $\delta = 0$ appears at $Sp = 10$ nm. The coupling efficiency decreases monotonously when the spacing $Sp$ increases.

Figure 3-16 Coupling dependence ($\lambda = 530$ nm) on the spacing $Sp$ between the strip and slot waveguides: (a) Effective refractive indexes of the fundamental TE modes guided in the isolated Si$_3$N$_4$ strip (the green curve) and aluminum slot (the red curve) waveguides are presented as a function of the spacing $Sp$. (b) Coupling efficiency between the strip and the slot in (a) as a function of spacing $Sp$.

The discussion above has analyzed the coupling dependence on every individual geometrical parameter when the slot is aluminum. For simplicity and clarity, the dielectric strip and the metallic slot of the SERS sensor are set as square, i.e. $W_D = H_D$ and $W_m = H_m$ (for convenience, the size of the square strip/slot is noted as $S_D/S_m$). Figure 3-17 presents the modal analysis of the isolated strip and the isolated slot with
the geometrical parameter values concerned in the Raman sensor. The slot size $S_m$ changes from 30 nm to 100 nm while the strip size $S_D$ changes from 200 nm to 400 nm. The spacing $S_p$ influences the strip’s modal index slightly.

Figure 3-17 Effective refractive indexes of the fundamental TE modes ($\lambda = 530$ nm) guided in the isolated Si$_3$N$_4$ strip (the non-red colorful curves) and aluminum slot (the red curve) waveguides are presented: (a) as a function of the strip size $S_D$ for several spacings while $S_m = 30$ nm. (b) as a function of the slot size $S_m$ for several spacings while $S_D = 250$ nm.

Based on the modal profiles of the strip and slot waveguides and the corresponding modal indexes, the efficiencies of the energy, which is coupled into the slot from the strip in the first beating, are calculated and presented in Figure 3-18. It is seen in Figure 3-18-(a) that the coupling efficiency decreases monotonously when the strip size $S_D$ increases and $S_m = 30$ nm. The coupling efficiency increases when the spacing $S_p$ becomes smaller except for the case $S_p = 0$ nm. This efficiency decrease with $S_p = 0$ nm is also seen in Figure 3-18-(b). The spacing $S_p = 10$ nm is the optimized distance between the slot and the strip in Figure 3-18-(a). In Figure 3-18-(b), the coupling efficiency climbs firstly and then decreases with the increase of the slot size $S_m$. Here, the beating periods are reported in Figure 3-19. It is seen that the beating period becomes shorter when the spacing $S_p$ decreases. When the strip size increases, the beating period increases too. When the slot size increases, the beating period always decreases.

Figure 3-18 Coupling efficiencies ($\lambda = 530$ nm) between the Si$_3$N$_4$ strip and the aluminum slot: (a) as a function of the strip size $S_D$ for several spacings while $S_m = 30$ nm. (b) as a function of the slot size $S_m$ for several spacings while $S_D = 250$ nm.
Figure 3-19 Beating periods of the field in the slot ($\lambda = 530$ nm): (a) as a function of the strip size $S_D$ for several spacings while $S_m = 30$ nm. (b) as a function of the slot size $S_m$ for several spacings while $S_D = 250$ nm.

3.3 Surface-enhanced Raman scattering in the sensor

It has been demonstrated that the SERS enhancement comes from two contributions: the electromagnetic enhancement and the chemical enhancement. The former is the dominant one, which is considered in the design of the SERS sensor. Since Raman scattering can be taken as a virtual two-step process: the excitation of induced Raman dipoles and the dipole radiation, the electromagnetic enhancement of the SERS sensor can be obtained by simulating these two processes with the 3D-FDTD method. This section analyzes the excitation and the radiation of induced Raman dipoles in the metallic slot of the SERS sensor. Then, the $|E|^4$-approximation is introduced for simplifying the enhancement factor ($EF$) estimation. With the approximation, the enhancement dependence on the geometry is demonstrated, which is followed by the quantitative assessment of the sensor’s SERS-detection capability.

3.3.1 Excitation and radiation of induced Raman dipoles

The electromagnetic enhancement of SERS consists of two parts: local field enhancement $EF_{Loc}$ in the excitation process of Raman dipoles induced by the local plasmonic field, and the radiation enhancement $EF_{Rad}$ in the emission process of induced Raman dipoles modified by metallic objects. Thus, the enhancement factor ($EF$) for a single molecule can be expressed as:

$$EF = EF_{Loc}(\omega_L)EF_{Rad}(\omega_R)$$ (3-5)

where $\omega_L$ and $\omega_R$ are the angular frequencies of the excitation light and the Raman scattering light respectively.

**Excitation**

The excitation source of the sensor should be the $TE$ modes guided in the Si$_3$N$_4$ strip waveguide. With the fundamental $TE$ mode as the incident light, the plasmonic field distribution in the sensor is presented in Figure 3-20. The sensor consists of a gold slot and a Si$_3$N$_4$ strip with $W_m = 48$ nm, $H_m = 50$ nm, $W_D = H_D = 200$ nm, $Sp = 10$
nm, and $L = 0.61 \, \mu m$. The gold slot length $L = 0.61 \, \mu m$ equals one beating period of the photonic-plasmonic coupling between the slot and the strip with $\lambda = 720 \, \text{nm}$. The field distributions are displayed on three mutually orthogonal cross sections across the sensor. It is seen in Figure 3-20-(b) that the in-slot electric field is much stronger than that in the strip, particularly in the vicinity of the four slot corners. The amplified local field can excite strong Raman dipoles if Raman-active molecules are in the slot and therefore Raman scattering is enhanced. In Figure 3-20-(c) and -(d), it is seen that the in-slot electric field has some fluctuations along the z-axis, not like that in Figure 3-6-(a). This is because the gold slot has a finite length and the slot’s facet reflection leads to the interferences of the in-slot electric field. To some degree, the gold slot with a finite length can be considered as a half-open cavity and it can trap the plasmonic field inside. The trapped field distributes in the slot according to the rules of interferences. The photonic-plasmonic coupling is the route to exchange energy between the cavity (the slot) and the exterior (the strip). The charge distributions in the sensor are shown in Figure 3-21. The charges on the two slot walls are always opposite. There are some polarization charges on the strip boundaries. Along the propagation direction (the z-axis), it is seen clearly that the in-slot charges have the typical charge distribution of surface propagating plasmons (SPP).

Figure 3-20 Plasmonic field distributions ($\lambda = 720 \, \text{nm}$) in the sensor with the strip’s fundamental TE mode as incident light: (a) 3D view of the SERS sensor, where a gold slot is laid above the embedded Si$_3$N$_4$ strip. The insert image shows the field $|\mathbf{E}|$ profile of the incident light. (b)-(d) $|\mathbf{E}|$ distributions on a z-normal plane with $z = 805 \, \text{nm}$, on an x-normal plane with $x = 24 \, \text{nm}$ and on a y-normal plane with $y = 22 \, \text{nm}$ respectively.

Figure 3-21 Charge distributions ($\lambda = 720 \, \text{nm}$) in the sensor described in Figure 3-20-(a): (a) on a z-normal plane with $z = 805 \, \text{nm}$ and (b) on a y-normal plane with $y = 22 \, \text{nm}$. 
It is known that the induced Raman dipoles in Raman-active molecules have a linear relation with the excitation field. So the Raman dipole moment $p_R = \alpha_R E_{loc}(\omega_L)$ excited by the local plasmonic field $E_{loc}$ is bigger $E_{loc}/E_{inc}$ times than that excited by the incident field $E_{inc}$ directly. Considering the quadratic relationship between the dipole moment and its radiation energy, the Raman dipole induced by the plasmonic field $E_{loc}$ radiates the energy enhanced by a factor:

$$EF_{loc}(\omega_L) = \frac{|E_{loc}(\omega_L)|^2}{|E_{inc}|^2}$$

(3-6)

It is worth noting that the incident field $E_{inc}$ is always the maximum electric field value of the fundamental $TE$ mode guided in the Si$_3$N$_4$ strip if no other statement. In the FDTD simulations of this thesis, all the electric field is normalized to the maximum electric field value of the incident $TE$ mode, so the local field enhancement factor $EF_{loc}(\omega_L)$ is simplified as $EF_{loc}(\omega_L) = |E_{loc}(\omega_L)|^2$.

According to the definition, the $EF_{loc}$ distribution in the sensor’s slot can be calculated based on the field distribution obtained by FDTD simulations, as shown in Figure 3-22. An example point is chosen at the coordinates (23 nm, 22 nm, 0.805 µm) to discuss the enhancement factor near the slot walls. There are two peaks in the $EF_{loc}$ curve and the maximum value is at $\lambda = 781$ nm. The two peaks come from the interferences of the in-slot plasmonic field. The interferences are more obvious in the $EF_{loc}$ distribution in Figure 3-22-(b). The $EF_{loc}$ distribution along the $z$-axis shows a feature like some interferometric fringes. When the wavelength changes, the fringes shift gradually. The strong enhancement appears in the narrow band from 750 nm to 800 nm. When the wavelength is short, particularly smaller than 700 nm, the $EF_{loc}$ value is always very small. This is because the photonic-plasmonic coupling is weak due to the decrease of the evanescent overlap between the slot mode and the strip mode when the wavelength is short.

![Figure 3-22](image_url)

Figure 3-22 $EF_{loc}$ distributions in the sensor described in Figure 3-20-(a): (a) at an example point with the coordinates (23 nm, 22 nm, 805 nm). (b) on a line in the z-axis direction with $X = 23$ nm and $Y = 22$ nm.

◆ Radiation

Generally speaking, the radiation of an emitter is always dependent on its
environment. The Raman dipole radiation is also strongly affected by metal surfaces under SERS conditions. It is referred as modified spontaneous emission (MSE). Assuming that an induced Raman dipole $\mathbf{p}_R = p_R \mathbf{e}_p$ oscillates at a frequency $\omega_R$, the radiation enhancement factor is defined as:

$$EF_{Rad}(\omega_R) = \frac{P_{Rad}(\omega_R)}{P_0(\omega_R)}$$

(3-7)

where $P_{Rad}$ is the power radiated by the dipole under SERS conditions while $P_0$ is the power emitted in free space from the same dipole. This effect makes induced Raman dipoles near metallic surfaces emit more energy than its radiation in free space by many orders of magnitude.

Figure 3-23 shows the dipole radiation with three mutually orthogonal polarization directions in the hybrid waveguide consisting of a Si$_3$N$_4$ strip and a gold slot. Only the TE modes ($E_x > E_y, E_z$) are guidable in the metallic slot, so only the $E_x$ component is presented in Figure 3-23-(a), -(b), and -(c). It is seen that the dipoles’ radiation pattern is obviously modified by the waveguide. A fraction of radiation is collected and confined in the hybrid waveguide. The enhancement factors $EF_{Rad}$ of the three dipoles’ radiative emission are reported in Figure 3-23-(d). It is obvious that the x-polarized dipole has the biggest radiation enhancement factor. This is because the x-polarized dipole moment is perpendicular to the gold slot walls and the Green’s function at the dipole position is enhanced more dramatically. On the other hand, the x-polarized Raman dipole in molecules is preferably excited due to the TE modes ($E_x > E_y, E_z$) in the metallic slot if Raman-active molecules have an anisotropic Raman tensor. The x-polarized dipole’s radiation is also preferably coupled into the TE modes ($E_x > E_y, E_z$) of the metallic slot.

![Figure 3-23 Dipole radiation in the hybrid waveguide consisting of a Si$_3$N$_4$ strip and a gold slot: (a)-(c) Log(Re($E_x$)) distribution on an x-normal plane with $x = 0$ nm, which is excited by a dipole polarized in the x-, y-, and z-axis direction respectively. All the dipoles are located at the coordinates (0 nm, 22 nm, 2 μm). (d) Enhancement factors $EF_{Rad}$ of the three dipoles’ radiative emission, compared to their radiation power in free space. The insert image shows the geometry of the hybrid waveguide.](image-url)
In the sensor described in Figure 3-20, an x-polarized dipole source is assumed to be located at the example point with the coordinates (23 nm, 22 nm, 805 nm), which can simulate the Raman dipole radiation process of a Raman-active molecule in the slot. The radiation of the dipole can be enhanced and collected by the slot and the strip, as shown in Figure 3-24. A z-normal plane with $z = 1.3 \, \mu m$, marked by a black dash line, is defined as the output plane. On the output plane, the total field is the superposition of many guidable or leaky modes. The desirable radiation is that coupled into the fundamental $TE$ mode of the Si$_3$N$_4$ strip, which is shown in Figure 3-24-(c). The other radiation will leak out of the strip waveguide during its journey to photoelectric detectors. To know the radiation fraction guided in the desirable mode, the overlap between the field profiles of the radiation on the output plane and the strip’s fundamental $TE$ mode is calculated, which is defined as:

$$overlap = \frac{Re\left(\iint E_1 \times H_2^* \cdot ds\right)\left(\iint E_2 \times H_1^* \cdot ds\right)}{Re\left(\iint E_1 \times H_1^* \cdot ds\right)Re\left(\iint E_2 \times H_2^* \cdot ds\right)} \quad (3-8)$$

The overlap gives out the power fraction of the field profile $(E_1, H_1)$ that can propagate in the guidable mode $(E_2, H_2)$. Compared to the dipole radiation in free space, the enhancement factors $EF_{Rad}$ of the dipole radiation in the sensor are reported in Figure 3-24-(d). The total power dissipated by the dipole includes two parts, i.e. radiation and loss. The difference between the total power and the radiative power is the loss such as Ohmic heat. The blue $EF_{Rad}$ curve is for the dipole radiation that is coupled into the strip’s fundamental $TE$ mode. The difference between the radiative power and the coupled power is the radiation that leaks into free space and is coupled into other guidable or leaky modes in the hybrid waveguide. According to the blue $EF_{Rad}$ curve, it is noted that the sensor has a weak collection capacity for the short wavelength.

![Figure 3-24 Radiation of an x-polarized dipole in the SERS sensor: (a) Sensor frame, which is the same as that in Figure 3-20-(a). An x-polarized dipole is located at the example point with the coordinates (23 nm, 22 nm, 805 nm). (b) $|E|$ distribution on the z-normal output plane with $z = 1.3 \, \mu m$, which is marked by a black dash line in (a). (c) $|E|$ profile of the fundamental $TE$ mode of the Si$_3$N$_4$ strip. (d) Enhancement factors $EF_{Rad}$ of the dipole’s total, radiative and coupled (by the strip $TE$ mode) radiation, compared to the dipole radiation in free space.](image)
It has been mentioned that the $E_{\text{F,Loc}}$ distribution in the sensor’s slot is modulated by the interferences of the in-slot plasmonic field, as shown in Figure 3-22. The $E_{\text{F,Rad}}$ of the in-slot dipoles is also affected by the facet reflection and the subsequent interferences. As shown in Figure 3-25, the $E_{\text{F,Rad}}$ peaks shift when the slot length $L$ changes.

Figure 3-25 Enhancement factors $E_{\text{F,Rad}}$ of the dipole radiation coupled in the fundamental $TE$ mode of the $\text{Si}_3\text{N}_4$ strip, divided by the dipole radiation in free space, as a function of the slot length $L$. Here, except the slot length $L$, the other geometrical parameters and the dipole are the same as those in Figure 3-24.

3.3.2 $|E|^4$-approximation

The modified spontaneous emission (MSE) of an induced Raman dipole is a complex process due to its multi-factor dependence like positions and orientations of induced dipoles, etc. It is a huge task to estimate the enhancement factor $E_{\text{F,Rad}}$ of every position in the sensor’s metallic slot. Thus, an approximate treatment is preferred in the $EF$ calculation of SERS substrates. The $|E|^4$-approximation is a widely-used method to estimate the enhancement in the SERS-related literature. It is based on the assumptions of $E_{\text{F,Rad}}(\omega) \approx E_{\text{F,Loc}}(\omega)$ and $\omega_r \approx \omega_L$, which means that the global enhancement factor can be expressed simply as:

$$EF = EF_{\text{F,Loc}} EF_{\text{F,Rad}} = EF_{\text{F,Loc}}^2 = \frac{|E_{\text{F,Loc}}(\omega)|^4}{|E_{\text{Inc}}|^4} = |E_{\text{Loc}}(\omega)|^4$$ (3-9)

where $E_{\text{Inc}}$ is the maximum value of the incident electric field and it equals 1 in all the simulations in this thesis.

The $|E|^4$-approximation avoids a huge calculation task for each possible position (and for at least three orthogonal orientations) of a dipole on SERS substrates. The assumption, $E_{\text{F,Rad}}(\omega) \approx E_{\text{F,Loc}}(\omega)$, can be explained by the optical reciprocity theorem. As shown in Figure 3-26, the optical path of Raman scattering can be divided into two parts: the excitation path from incident light to molecules and the radiation path from
molecules to output. If analyte molecules are located at the middle position (z = 805 nm) of the slot, the excitation and the radiation of induced Raman dipoles have the same optical path with two opposite propagation directions. Hence, the approximation $EF_{\text{Rad}}(\omega) \approx EF_{\text{Loc}}(\omega) = |E_{\text{Loc}}(\omega)|^2$ is reasonable in the SERS sensor. However, the excitation path and the radiation path are different when molecules are not located at the longitudinal middle position of the metallic slot. Considering that the sensor is symmetrical about the z-normal plane with z = 805 nm, the radiation path of a dipole at the point (x, y, z) is the inverse path of the dipole excitation at the point (x, y, 1.61µm-z). So the $EF_{\text{Rad}}$ expression can be expressed as $EF_{\text{Rad}}^{x,y,z} \approx |E_{\text{Loc}}^{x,y,1.61\mu m-z}(\omega)|^2$. Considering that the dipole radiation has two opposite propagation directions, only half of the collected Raman signals are detected at the sensor’s output. Thus, the $|E|^4$-approximation for estimating the global enhancement factor in the SERS sensor is modified as:

$$EF_{x,y,z}^{v} = 0.5EF_{\text{Loc}}^{x,y,z}EF_{\text{Rad}}^{x,y,z} = 0.5|E_{\text{Loc}}^{x,y,z}(\omega)|^2|E_{\text{Loc}}^{x,y,1.61\mu m-z}(\omega)|^2 \quad (3-10)$$

Figure 3-26 Schematic representation of the optical reciprocity in the sensor. To explain it clearly, the sensor parameters are chosen as the same as those in Figure 3-20-(a) with $W_m = 48$ nm, $H_m = 50$ nm, $W_d = H_d = 200$ nm, $S_p = 10$ nm, and $L = 0.61$ µm.

To use the approximation for estimating the enhancement factor of the SERS sensor in this thesis, the validity of the $|E|^4$-approximation is proved. As shown in Figure 3-27, the enhancement factors are reported when a Raman-active molecule is assumed to be located at the point (23 nm, 22 nm, 805 nm) in the sensor described in Figure 3-26. The $EF_{\text{Loc}}$ and $EF_{\text{Rad}}$ curves have the same peak positions because the excitation and the radiation of Raman dipoles in the sensor are two mutually inverse processes. The enhancement factor $EF_{\text{Rad}}$ is the half of the local field enhancement $EF_{\text{Loc}}$. This is because the dipole radiation has two opposite propagation directions and only half of the collected Raman signals are detected at the sensor’s output. It is seen that $EF = EF_{\text{Loc}}EF_{\text{Rad}} \approx 0.5EF_{\text{Loc}}^2$, which proves that the modified $|E|^4$-approximation in the equation (3-10) is valid in the SERS sensor. It is worth noting that the local plasmonic field in the sensor’s metallic slot can be obtained by FDTD simulations via solving Maxwell’s equations with specific boundary conditions and incident light. Then, the $EF$ estimation for every possible position in the sensor’s slot can be conducted simply, avoiding the complex calculation of dipole radiation.
Figure 3-27 $|E|^4$-approximation in the SERS sensor described in Figure 3-26. A Raman-active molecule is assumed to be located at the point (23 nm, 22 nm, 805 nm).

3.3.3 Geometrical dependence of EF

Based on the $|E|^4$-approximation, the EF distribution in the sensor’s metallic slot can be obtained by FDTD simulations. It is known that the finitely long metallic slot of the sensor acts as not only a waveguide but also a cavity due to the slot’s facet reflection. To demonstrate the in-slot enhancement clearly, two structures are used in the FDTD simulations for analyzing the geometrical dependence of EF. As shown in Figure 3-28, one structure has an infinitely long metallic (Au/Al) slot above the embedded Si$_3$N$_4$ strip while the other has a finite slot length $L = 0.6$ µm (Au) / 1.304 µm (Al). The fundamental TE mode of the strip is injected from the left side as the incident light. When the slot length is infinite, there are several field beatings in the metallic slot and only the local plasmonic field in the first beating is used to assess the enhancement factor of the structure in Figure 3-28-(a). For simplicity and clarity, the cross-sections of the dielectric strip and metallic slot are set as square, i.e. $W_D = H_D$ and $W_m = H_m$ (for convenience, the size of the square strip/slot is noted as $S_D/S_m$).

For simplicity and clarity, the cross-sections of the dielectric strip and metallic slot are set as square, i.e. $W_D = H_D$ and $W_m = H_m$ (for convenience, the size of the square strip/slot is noted as $S_D/S_m$).

When the gold slot is infinite, as shown in Figure 3-28-(a), the geometrical dependence of EF in the first beating volume: $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \mu m \leq$
$z \leq 0.5 \mu m + \text{one beating period}$ is reported in Figure 3-29. Here, note that the beating period changes with the wavelength and the geometrical parameters. So, the first beating volume is different for every $EF$ value in the graphs below. The upper three graphs present the maximum $EF$ values in these 1st beating volumes while the lower three graphs show the averaging $EF$ values. The $EF$ maxima always appear near the slot corners due to the sharp feature, particularly near the bottom corners. Most $EF$ curves below have some fluctuation when the wavelength changes. This is caused by some weak guidable modes in the hybrid waveguide except for the supermodes discussed before. The fluctuations can be seen clearly on the $|E|$ distribution along the propagating direction, particularly in the strip, as shown in Figure 3-30. Except for the $|E|$ beating, there are some interferometric fringes that modulate the field distribution. In Figure 3-29-(a), a big slot has a big enhancement

![Graphs showing maximum and average of $EF$ in the first beating volume of the infinite gold slot.](image)

Figure 3-29 Maximum and average of $EF$ in the first beating volume of the infinite gold slot in Figure 3-28-(a): $-S_m/2 \leq x \leq S_m/2$, $0 \leq y \leq S_m$, $0.5 \mu m \leq z \leq 0.5 \mu m + \text{one beating period}$. The $EF$ curves are reported as a function of (a, d) the slot size $S_m$, (b, e) the strip size $S_D$ and (c, f) the spacing $Sp$.

![Figure 3-30 showing fluctuations of the field beating.](image)

Figure 3-30 Fluctuations of the field beating in the structure in Figure 3-28-(a) with $S_D = 200$ nm, $S_m = 30$ nm and $Sp = 20$ nm: (a) $|E|$ distribution on an x-normal plane with $x = 15$ nm. (b) Regional magnification of $|E|$ distribution in the Si$_3$N$_4$ strip area.
factor for the wavelength shorter than 750 nm while it is the reverse for the wavelength longer than 750 nm. A bigger EF average is always obtained with a small slot size in Figure 3-29-(d). In Figure 3-29-(b) and -(e), the EF maximum and average decrease in the wavelength range shorter than 700 nm. In the long wavelength range, the strip size $S_D = 240$ nm is the best choice for the enhancement. This is because $S_D = 160$ or 200 nm is smaller than the diffraction limit of $\lambda = 900$ nm and the strip size $S_D = 240$ nm has the best confinement of field. When the spacing $Sp$ becomes smaller, the enhancement always increases in Figure 3-29-(c). A smaller $Sp$ strengthens the coupling between the slot and the strip, so the EF average increases. However, if $Sp$ equals 0 nm, the EF average decreases dramatically.

When the gold slot is finite in Figure 3-28-(b), the geometrical dependence of EF in the volume: $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \mu m \leq z \leq 1.1 \mu m]$ is reported in Figure 3-31. Compared to Figure 3-29, the enhancement factors in the slot volume are raised dramatically by the interferences of the in-slot plasmonic field. The EF maximum can reach the order of $10^3$-$10^4$. With the slot size $S_m$ increases, the EF peak shifts to the blue in Figure 3-31-(a) and -(d). This is because the propagating constant of the slot mode becomes smaller. When the strip size $S_D$ changes, the EF peaks do not show any shift. Like that in Figure 3-29-(b) and -(e), when the strip size $S_D$ increases, the EF maximum and average decrease in the wavelength range smaller than 700 nm. For the longer wavelength (>700 nm), the highest value is achieved with $S_D = 320$ nm. The spacing $Sp$ also influences the propagation of the slot mode, so there is a peak shift when $Sp$ changes, but not so obvious as the case of $S_m$.

![Figure 3-31 Maximum and average of EF in the finite gold slot in Figure 3-28-(b): $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \mu m \leq z \leq 1.1 \mu m]$. The EF curves are reported as a function of (a, d) the slot size $S_m$, (b, e) the strip size $S_D$ and (c, f) the spacing $Sp$.](image)

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When the aluminum slot is infinite in Figure 3-28-(a), the geometrical dependence of EF in the 1st beating volume: $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \mu m \leq z$
≤ 0.5 µm + one beating period] is reported in Figure 3-32. Here, note that the beating period changes with the wavelength and the geometrical parameters. So the first beating volume is different for every EF value in the graphs below. The upper three graphs present the maximum EF values in these 1st beating volumes while the lower three graphs show the averaging EF values. The EF maxima always appear near the slot corners due to the sharp feature, particularly near the bottom corners. The EF curves below are smooth when the wavelength changes, which is not like the case of the infinitely-long gold slot in Figure 3-29. Another difference with the gold case is that all the EF curves of aluminum drop when the wavelength goes close to 800 nm. This is because the interband transition of aluminum is at 800 nm and there are strong ohmic losses. In Figure 3-32-(a) and -(b), the enhancement factor firstly increases and then decreases when the slot size Sm increases. The biggest EF maximum is obtained with Sm = 80 nm and the biggest EF average is obtained with Sm = 30 nm and 40 nm. When the strip size Sp increases, the EF peak shifts to the red with a higher value. In Figure 3-32-(c), the EF maximum increases when the spacing Sp decreases. However, the largest EF average is obtained with Sp = 20 nm in Figure 3-32-(d).

Figure 3-32 Maximum and average of EF in the first beating volume of the infinite aluminum slot in Figure 3-28-(a): [-Sm/2 ≤ x ≤ Sm/2, 0 ≤ y ≤ Sm, 0.5 µm ≤ z ≤ 0.5 µm + one beating period]. The EF curves are reported as a function of (a, d) the slot size Sm, (b, e) the strip size Sp and (c, f) the spacing Sp.

When the aluminum slot is finite in Figure 3-28-(b), the geometrical dependence of EF in the volume: [-Sm/2 ≤ x ≤ Sm/2, 0 ≤ y ≤ Sm, 0.5 µm ≤ z ≤ 1.804 µm] is reported in Figure 3-33. The EF curves below are modulated by the in-slot field interferences caused by the slot’s facet reflection, which is not so obvious as the gold case in Figure 3-31. In Figure 3-33-(a) and -(d), the decrease of Sm always brings up an increase of enhancement factor and a small redshift of the interference peaks. In Figure 3-33-(b) and -(e), the increase of Sp shifts the peaks of the EF maximum and the EF average to
the red side with a higher value when \( \lambda > 480 \text{ nm} \). In the short wavelength range (\( \lambda < 480 \text{ nm} \)), the EF maximum curve decreases when \( S_D \) increases. When \( S_p \) changes, the EF maximum curves are almost the same in Figure 3-33-(c). But the averaging EF curves show an obvious dependence on \( S_p \) and the largest value is obtained with \( S_p = 30 \text{ nm} \).

![Figure 3-33](image)

Figure 3-33 Maximum and average of EF in the finite aluminum slot in Figure 3-28-(b): [-\( S_m/2 \leq x \leq S_m/2 \), 0 \( \leq y \leq S_m \), 0.5 \( \mu \text{m} \leq z \leq 1.804 \mu \text{m} \)]. The EF curves are reported as a function of (a, d) the slot size \( S_m \), (b, e) the strip size \( S_D \) and (c, f) the spacing \( S_p \).

### 3.3.4 SERS-detection capacity

In SERS detections of the sensor, the metallic slot can be easily filled up by a small droplet of analyte solution due to its nanoscale size. So the EF average of the sensor is used to estimate the SERS-detection capacity of the sensor. According to the equations (1-8) and (1-9), the Raman signals radiated by a single Raman-active molecule can be expressed as:

\[
P_R = \frac{4\pi}{3} \varepsilon_0 c n_m \left( 1 + \frac{2\rho_R d\sigma_R}{1 + \rho_R} \right) |E_{inc}|^2 \tag{3-11}
\]

where \( \varepsilon_0 \) is the permittivity of vacuum, \( c \) is the light speed in vacuum, \( n_m \) is the refractive index of the medium in the metallic slot, \( \rho_R \) is the depolarization ratio of the Raman tensor \( \sigma_R \), and \( E_{inc} \) is the incident electric field. Here, \( \rho_R \) is set as 0 for simplicity. \( E_{inc} \) is the maximum value of the incident electric field in the Si\(_3\)N\(_4\) strip. Then, the total Raman signals collected by the strip waveguide from the analyte molecules in the sensor’s metallic slot can be expressed as:

\[
P_R^t = N\overline{EF} P_R = \frac{4\pi}{3} \varepsilon_0 c n_m N\overline{EF} \frac{d\sigma_R}{d\Omega} |E_{inc}|^2 \tag{3-12}
\]

where \( N \) is the total molecule number in the slot and \( \overline{EF} \) is the EF average in the slot. It is worth noting that the equation above is based on an assumption that the molecules distribute uniformly in the slot. But the analyte molecules preferably approach the metallic slot walls due to the physisorption or chemisorption. So the
experimental output of Raman signals by the sensor may be stronger than the estimation of the equation (3-12).

To estimate the SERS-detection capacity quantitatively, a sensor with a gold slot is chosen as an example, in which $S_D = 320 \text{ nm}$, $S_m = 30 \text{ nm}$, $S_p = 20 \text{ nm}$ and $L = 600 \text{ nm}$. According to Figure 3-31-(e), the EF average in the gold slot is 60 at $\lambda = 830 \text{ nm}$. The dyes, rhodamine 6G (RH6G) and benzotriazole dye 2 (BTZ), are taken as the probe molecules. When the excitation wavelength is 830 nm, the Raman peak 1510 cm$^{-1}$ ($\lambda = 949 \text{ nm}$) of RH6G has a differential Raman cross-section $2.4 \times 10^{-27} \text{ cm}^2/\text{sr}$, and the Raman peak 1412 cm$^{-1}$ ($\lambda = 940 \text{ nm}$) of BTZ has a differential Raman cross-section $2.5 \times 10^{-28} \text{ cm}^2/\text{sr}$. The excitation power is 10 mW. The lowest detectable power of the detector refers to the Ocean Optics QE65 Pro spectrometer. Its quantum efficiency is about 40% at $\lambda = 940 \text{ nm}$ and the dark current is 4000 e/pixel/sec at 25 °C or 200 e/pixel/sec at 0 °C. The electron number per second excited by the Raman signals of RH6G and BTZ on the detector is shown in Figure 3-34. It is seen that the RH6G solution of $1.4 \times 10^{-3} \text{ mole/L}$ is detectable by the sensor at room temperature. If the detector is cooled, RH6G can be detected at the lowest concentration of $7.27 \times 10^{-5} \text{ mole/L}$ and BTZ can be detected at the lowest concentration of $6.72 \times 10^{-4} \text{ mole/L}$.

Figure 3-34 Electron numbers per second excited by the Raman signals of RH6G and BTZ on the detector of an Ocean Optics QE65 Pro spectrometer. The SERS sensor with a gold slot has the geometrical parameters: $S_D = 320 \text{ nm}$, $S_m = 30 \text{ nm}$, $S_p = 20 \text{ nm}$ and $L = 600 \text{ nm}$. The incident light is the fundamental $TE$ mode of the strip with power 10 mW and wavelength $\lambda = 830 \text{ nm}$. The two black lines are the dark currents of the spectrometer.

3.4 Summary

In this chapter, the theoretical investigation of the SERS sensor based on the hybrid waveguide made of metallic slots (Au or Al) and dielectric strips ($\text{Si}_3\text{N}_4$) is conducted by using the 3D-FDTD method.

Based on the coupling theory, the analyses show that the photonic-plasmonic coupling can be strengthened when the evanescent overlap increases between the modes in metallic slots and dielectric strips. Particularly, the increase of the slot size
\(W_m\) or \(H_m\) is beneficial to couple more energy into the metallic slot and to contain more analyte molecules. But it weakens the confinement of the electric field in the slot and reduces the enhancement factor of Raman scattering.

The SERS processes, excitation of the intense local plasmonic field in slots and radiation of induced Raman dipoles, are simulated to demonstrate the working procedure of the sensor. Based on the enhancement factors in the two individual processes, the \(|E|^4\)-approximation is proved to be valid in estimating the enhancement factor of the SERS sensor. The numerical results show that a SERS sensor based on the hybrid waveguide made of gold/aluminum slots and Si\(_3\)N\(_4\) strips with an enhancement factor of \(10^2 - 10^3/10 - 10^2\) can be realized.

The \(EF\) of the SERS sensor can not show directly the SERS-detection capacity. In the last part, a specific sensor with an Au slot is chosen as an example to show the capacity. It can detect the RH6G solution of \(1.4 \times 10^{-3}\) mole/L is at room temperature with the Ocean Optics QE65 Pro spectrometer. If the detector is cooled, RH6G can be detected at the lowest concentration of \(7.27 \times 10^{-5}\) mole/L and BTZ can be detected at the lowest concentration of \(6.72 \times 10^{-4}\) mole/L.
4. Effects of in-slot metallic nanoparticles on the sensor’s SERS detection

Under SERS conditions, the enhancement factor depends directly on the electrical field intensity of surface plasmons in the position of Raman-active molecules. Due to this dependence, the SERS detection is much more sensitive with molecules in a small metallic gap than near a single metallic surface because of the intense local electrical field resulting from the interaction between metallic objects.

This chapter mainly introduces the theoretical investigation of the effect of in-slot metallic nanoparticles on improving the detection capacity of the SERS sensor. Using 3D-FDTD simulations, the electromagnetic field and charge distributions of the metallic sphere-slot junction are obtained and subsequently the electromagnetic interaction between the in-sphere LSP and the in-slot SPP is discussed. The $EF$ dependence of the metallic particle-slot junction on the particle’s position, size, shape, and material is demonstrated to show the strategy of optimizing the sensor’s detection capacity. On the other hand, the metallic particle-slot junction may lead to loss of Raman signals and the related discussion is presented with the case of two nanoparticles in the slot. The results show that the averaging SERS enhancement factor around the in-slot particle can be increased dramatically, compared to the enhancement factor in the slot without metallic nanoparticles. At some single points in the particle-slot junction, the enhancement factor even reaches $10^{10}$, which is enough to detect a single molecule.

4.1 SPP-LSP coupling

Compared to surface plasmon polaritons (SPP), localized surface plasmons (LSP) are more commonly exploited in SERS substrates. Particularly, colloidal solutions of aggregated metallic nanoparticles always have very strong enhancement effects due to the strongly confined electric field in the gaps between metallic particles (noted as hotspot effect). It has been demonstrated that the LSP in metallic nanoparticles can be excited by the SPP propagating on a metallic surface or in a metallic wire. If the gap in the particle-surface/wire junction is small enough, the plasmonic field inside is so intense that Raman scattering in the gap will be enhanced. In this section, a gold slot and a gold nanosphere are used as an example to demonstrate the SPP-LSP coupling between metallic nanoparticles and the sensor’s metallic slot. The enhancement improvement resulting from the in-slot particle in the sensor is also discussed.

4.1.1 Local surface plasmons of metallic nanoparticles above an embedded Si$_3$N$_4$ waveguide

To demonstrate the electromagnetic interaction between metallic nanoparticles
and the metallic slot of the SERS sensor, the interaction of metallic nanoparticles and the Si$_3$N$_4$ strip waveguide should be known firstly. As shown in Figure 4-1, a gold sphere with diameter 44 nm is located above an embedded strip with a spacing $S_p = 10$ nm. The LSP of the sphere can be excited by the evanescent field of the Si$_3$N$_4$ strip waveguide. According to the field distributions, the LSP is excited in a dipole mode and the maximum electric field appears on the two spherical crowns along the x-axis direction. The maximum value of the local field around the sphere is about 3, which is 3 times stronger than the maximum field of the incident light. Compared to the absorption spectrum of the sphere in free space, as shown in Figure 4-2, the spectrum

Figure 4-1 Field distributions ($\lambda = 720$ nm) of the LSP in a gold sphere with diameter 44 nm above the Si$_3$N$_4$ strip embedded in SiO$_2$ when the strip’s fundamental TE mode is injected as the incident light: (a) Structure frame, where the gold sphere is located with the center coordinates (0 nm, 22 nm, 805 nm). (b) $|E|$ distribution on a z-normal plane with $z = 805$ nm. (c) $|E|$ distribution on an x-normal plane with $x = 0$ nm. (d) $|E|$ distribution on a y-normal plane with $y = 22$ nm.

Figure 4-2 Absorption of the gold sphere with diameter 44 nm above the embedded Si$_3$N$_4$ strip in Figure 4-1-(a) and in free space. The excitation source of the red curve is the strip’s fundamental TE mode while the green curve has the excitation of a 7 $\mu$m x 7 $\mu$m plane wave light. The blue dot curve is the averaging evanescent field intensity at the sphere position (a cuboid volume: [-40 nm < $x$ < 40 nm, -10 nm < $y$ < 10 nm, 766 nm < $z$ < 846 nm]) before the sphere is added above the embedded Si$_3$N$_4$ strip and note that its unit is arbitrary.
of the sphere above the strip does not have the climbing trending when the wavelength decreases from 480 nm. This is because the evanescent interaction between the sphere and the strip becomes weaker due to a shorter evanescent decay length when the wavelength becomes shorter. This is seen in the blue dot curve, which shows the averaging evanescent field intensity at the sphere position before the sphere is added above the Si$_3$N$_4$ strip. It is worth noting that the unit of the blue curve is arbitrary, not the absorption percentage. The peak of the red curve has a small blue shift, compared to that in free space, due to the sphere is surrounded by water.

4.1.2 SPP-LSP coupling between a gold nanosphere and the sensor’s gold slot

To demonstrate the SPP-LSP coupling between a gold nanoparticle and the sensor’s gold slot, the attention is placed on the case of an infinitely long slot firstly, which avoids the interferences of the plasmonic field in the sensor’s slot. As shown in Figure 4-3-(a), a gold sphere with diameter 44 nm is assumed to be located in the slot with the center coordinates (0 nm, 22 nm, 805 nm). Then, two 2nm-wide gaps are created in the sphere-slot junction, as shown in Figure 4-3-(b). With the fundamental $TE$ mode of the Si$_3$N$_4$ strip as the incident light, the in-slot SPP is excited and then induces the LSP of the gold sphere. As shown in Figure 4-3-(c) and -(d), the intense local electric field appears in the gaps of the sphere-slot junction. Since the sphere size is close to the slot width, some energy of the in-slot SPP with $\lambda = 720$ nm cannot pass the sphere and the electric field in the left side of the sphere is stronger than that in the right side in Figure 4-3-(c).

Figure 4-3 SPP-LSP coupling between a gold sphere and an infinitely long gold slot above an embedded Si$_3$N$_4$ strip in SiO$_2$: (a) 3D view of the structure with $W_m = 48$ nm, $H_m = 50$ nm, $W_D = H_D = 200$ nm, and $S_D = 10$ nm. The gold sphere with diameter 44 nm is located with the center coordinates (0 nm, 22 nm, 805 nm). (b) Z-normal cross-section of the sphere in the slot with $z = 0.805$ $\mu$m. (c)-(d) Local field $|E|$ distributions ($\lambda = 720$ nm), which are normalized with the maximum value of the incident electric field, (c) on a $y$-normal plane with $y = 22$ nm and (d) on a $z$-normal plane with $z = 0.805$ $\mu$m. The image in (c) is stretched in the x-axis direction.
The absorption curves of the gold spheres located in the infinite slot are reported in Figure 4-4. The absorption of the gold sphere above the strip without the gold slot is also included. It is seen that the absorption peak 546 nm does not appear in the curves of the in-slot spheres. This peak is suppressed in the hybridization of the in-slot SPP and the in-sphere LSP. It is seen that the highest absorption peak of the in-slot sphere shifts from 690 nm to 732 nm when the z-axis position of the sphere changes from $z = 0.805 \, \mu m$ to $1.0 \, \mu m$. This is reasonable because the in-slot SPP fields along the z-axis direction distribute in beatings and the strongest electromagnetic fields at different z-axis positions appear at different wavelengths. The charge distributions of the sphere-slot junction at the two highest absorption peaks of 690 nm and 732 nm are shown in Figure 4-5. It is obvious that the electron oscillations of the sphere-slot junction are much stronger than those on the slot walls.

Figure 4-4 Absorptions of the gold sphere above the strip as that in Figure 4-1-(a) and the in-slot sphere in an infinite long slot as that in Figure 4-3-(a) with the center coordinate $z = 0.805 \, \mu m$ or $z = 1.0 \, \mu m$.

Figure 4-5 Charge distributions of the sphere-slot junction at the absorption peaks of (a)-(b) the green curve at $\lambda = 690 \, nm$ and (c)-(d) the blue curve at $\lambda = 732 \, nm$ in Figure 4-4. (a) and (c) are a z-normal plane with $z = 0.805 \, \mu m$ while (b) and (d) are a y-normal plane with $y = 22 \, nm$. 
If the slot part of the sphere-slot junction is taken as a pseudo-nanoparticle, the charge distributions are the typical light mode in the hybridization of two particles. Besides that, to some degree, the slot part from the left end to the in-slot sphere can be seen as a half-open cavity due to that the sphere size is close to the slot width. This is the reason for the small fluctuations of the green and blue absorption curves. The field interferences in the cavity are also seen by the plasmonic field in Figure 4-3-(c).

When replacing the infinite slot by a finite one, as shown in Figure 4-6-(a), the slot’s facet reflection is introduced and subsequently the in-slot plasmonic field interferes. If not specified otherwise, the sensor frame is kept the same in the following discussion. A gold sphere with diameter 44 nm is assumed to be located at the center of the slot bottom with the center coordinates (0 nm, 22 nm, 805 nm), the same as that in Figure 4-3-(a). Then, two 2nm-wide gaps are created in the sphere-slot junction, as shown in Figure 4-6-(b). With the fundamental \( TE \) mode of the \( \text{Si}_3\text{N}_4 \) strip as the incident light, the in-slot SPP is excited and then induces the LSP of the gold sphere. As shown in Figure 4-6-(c) and -(d), the intense local electric field appears in the gaps of the sphere-slot junction. If analyte molecules are present in the gaps, their Raman scatterings will be strongly enhanced.

![Figure 4-6 SPP-LSP coupling between a gold sphere and the sensor’s gold slot](https://example.com/figure4-6.png)

The absorption curves of the gold spheres in the infinite and finite slots in Figure 4-3-(a) and in Figure 4-6-(a) are reported in Figure 4-7. Compared to the case of the infinite slot, the sphere in the sensor’s finite slot has a new peak at 846 nm. The electromagnetic fields in the slot are modulated constructively or destructively by the interferences, as shown in Figure 4-6-(c). The sphere is excited by the in-slot interfered SSP and the in-sphere plasmons are also shaped by the interferences. This leads to the appearance of the new absorption peak. The charge distributions of the
sphere-slot (finite) junction at the two highest peaks of 690 nm and 846 nm are shown in Figure 4-8. It seems that two peaks can be taken as the light mode in the hybridization of the sphere and the pseudo-particle (a finite slot). For convenience, the oscillation modes of the electrons in the sphere-slot junction are noted as localized SPP-LSP modes, which result from the interaction of the SPP in the finite slot and the LSP of the sphere.

Figure 4-7 Absorptions of the 44nm-diameter gold spheres in the infinite and finite slots in Figure 4-3-(a) and in Figure 4-6-(a).

Figure 4-8 Charge distributions of the sphere-slot junction at the absorption peaks of the sphere within the sensor’s finite slot (a)-(b) at $\lambda = 690$ nm and (c)-(d) at $\lambda = 846$ nm. (a) and (c) are a z-normal plane with $z = 0.805 \, \mu m$ while (b) and (d) are a y-normal plane with $y = 22 \, \mu m$.

4.1.3 Enhancement in the gold sphere-slot junction

To discuss the SERS enhancement of the sphere-slot junction, an example point is chosen at the coordinates (23 nm, 22 nm, 0.805 $\mu m$). The point is the center of the right sphere-slot wall gap marked by a red star in Figure 4-6-(b). The $EF$ of the example point is reported with the red curve in Figure 4-9. The $EF$ curves of the same point are also included for comparison when only the gold sphere or the gold slot exists, as shown in Figure 4-1-(a) and in Figure 4-6-(a). In the sphere-slot junction,
the $EF$ curve of the example point is raised to a level of $10^6$ at 693 nm, 4 orders of magnitude higher than that when only the slot or the sphere exists. A shoulder (639 nm) and two peaks (693 nm, 847 nm) appear in the red solid $EF$ curve. They represent three localized SPP-LSP modes of the sphere-slot junction, the charge distributions of which are reported in Figure 4-10. If grouping these modes by the sphere charge, we can see that the shoulder at 639 nm comes from one quadrupole mode and the two peaks (693 nm, 847 nm) come from two dipole modes. Here, note that there are two peaks at 654 nm and 781 nm in the $EF$ curve of the example point when only the gold slot exists. They are caused by the constructive interferences of the SPP trapped in the gold slot. The finitely long slot can be seen as a resonant cavity and the constructive interferences can be seen as the SPP modes of the slot cavity.

![Figure 4-9](image)

Figure 4-9 Enhancement factors based on the $|E|^4$-approximation of the example point, which is marked by a red star at (23 nm, 22 nm, 805 nm) in Figure 4-6-(a), involving three cases: the gold sphere, the gold slot, and the gold sphere-slot junction.

![Figure 4-10](image)

Figure 4-10 Charge distributions on a z-normal cross-section with $z = 0.805 \mu$m in (a)-(c) and on a y-normal cross sections with $y = 22$ nm in (d)-(f) for the shoulder and peaks of the local field $|E|^4$ i.e. $EF$ of the example point in the sphere-slot junction, as shown by the red curve in Figure 4-9.
Since the local field in the sphere-slot junction is much stronger than other places, the hotspot volume around the particle can be regarded as the probe volume of the sensor. Here, the probe volume is defined as a cuboid: \(-W_m/2 \leq x \leq W_m/2, 0 \leq y \leq H_m, Z_{csphere} - R_{sphere} \leq z \leq Z_{csphere} + R_{sphere}\), where \(Z_{csphere}\) is the z-axis coordinate of the sphere center and \(R_{sphere}\) is the sphere radius. If not specified otherwise, the probe volume is kept the same in the following discussion.

4.2 Influences of multi-factors on the EF around the in-slot metallic nanoparticle

Around the in-slot metallic nanoparticle, the local electrical field intensity is the direct factor in determining the SERS enhancement factor. The local electrical field in the particle-slot junction depends greatly on the size of the particle-slot wall gaps. Besides that, the local electric field is also affected by many other factors, such as the particle’s position, size, material, and number. The section mainly discusses the multi-factor dependence of the enhancement factor in the probe volume around the in-slot metallic nanoparticle.

4.2.1 Particle position and size

The sphere-slot coupling discussed before is based on the assumption that a gold sphere is located at the bottom center of the gold slot in Figure 4-6-(a). However, it is a difficult task to accurately place a nanosphere a desired position in a nanoscale slot in experiments. The sphere’s position is directly related to the sphere-slot wall gap size (transverse position) and the local intensity of the SPP that excites the sphere (longitudinal position). Subsequently, the enhancement of Raman scattering around the sphere is affected by the sphere’s position. To show the influence of the sphere’s transverse (x-axis) position on the enhancement, a transverse offset of +1nm or +2nm is added to the sphere in Figure 4-6-(a). With the two offsets, four sphere-slot wall gaps are created with width = 1nm, 2nm and 4 nm, 0 nm (wedge gap) respectively. The averaging enhancement factors of the probe volume around the sphere are reported in Figure 4-11. The case with no transverse offset is included too for comparison. A transverse offset of the sphere position narrows one of the sphere-slot wall gaps and a narrower gap confines the electric field further. This increases the enhancement factor around the sphere. Comparing the red curve and the green curve below, the \(EF\) peaks show a redshift when increasing the transverse offset. When the offset is +2nm, the sphere touches one slot wall and the sphere-slot wall gap becomes a wedge gap. It has the sharpest nanostructure, leading to the highest enhancement factor of the probe volume within a spectrally broad range. Since there are no localized SPP-LSP modes when the sphere touches the slot wall, the \(EF\) curve is different from the other two cases. The insert graph presents the maximum enhancement factors in the probe volume. The maximum \(EF\) curves are about \(10^4\) times higher than the corresponding averaging \(EF\) curves. The \(EF\) curves of the
maximum value and the corresponding averaging value have the similar curve profiles because the maximum \( EF \) values have more weight in calculating the averaging values.

![Figure 4-11 Averaging enhancement factors of the cuboid probe volume when the in-slot sphere position has a transverse offset 0 nm, 1 nm and 2 nm respectively with the center coordinates \( x = 0, 1, 2 \text{ nm}, y =22 \text{ nm}, \) and \( z = 0.805 \mu\text{m} \). The inset graph is the maximum enhancement factors in the probe volume.](image)

Along the longitudinal (\( z \)-axis) direction, the SPP electric field distributes in a beating and it is also affected by the constructive or destructive interferences due to the slot facet reflection. So, the in-slot SPP (that excites the sphere) changes if the sphere is moved in the longitudinal direction. Meanwhile, the existence of the sphere can modify the field interferences in the slot. When the sphere has the longitudinal position \( z = 0.6 \mu\text{m}, z = 0.7 \mu\text{m} \) and \( 0.805 \mu\text{m} \) respectively with \( x = 0 \text{ nm} \) and \( y =22 \text{ nm} \), the enhancement factors of the probe volume are reported in Figure 4-12. Due to the symmetry, the \( EFs \) of the two half ranges of the slot from \( z = 0.5\mu\text{m} \) to \( z = 0.805 \mu\text{m} \) and \( z = 0.805 \mu\text{m} \) to \( z = 1.11 \mu\text{m} \) are the same. In Figure 4-12, the \( EF \) peaks show an obvious change when the sphere’s longitudinal position changes. This is because the in-slot electric field interferes constructively or destructively along the longitudinal direction. Taking the wavelength 680 nm as an example, the in-slot electric field interferes constructively at \( z = 0.805 \mu\text{m} \), leading to a peak (or a resonant SPP-LSP mode) in the red \( EF \) curve, while the field is interfered destructively at \( z = 0.6 \mu\text{m} \), leading to a deep valley (or an antiresonant SPP-LSP mode) in the blue \( EF \) curve. The electric field distributions of all the peaks in Figure 4-12 are shown in Figure A1 of Appendix.

When the sphere diameter changes, the enhancement in the probe volume is modified due to the size change of the sphere-slot wall gaps. This is similar to the sphere’s transverse position change that has been discussed before. The averaging and maximum enhancement factors of the probe volume around the sphere with different diameters are presented in Figure 4-13. A larger sphere diameter increases the enhancement factor and results in a redshift of the three SPP-LSP modes in the sphere-slot junction. Although increasing the sphere diameter can increase the
enhancement factor, putting the sphere into the slot would become more difficult. It also impedes the analyte molecules from entering into the gaps if the sphere-slot wall gaps are too small.

Figure 4-12 Averaging enhancement factors of the cuboid probe volume when the in-slot sphere has the longitudinal position $z = 0.6 \, \mu m$, $z = 0.7 \, \mu m$ and $0.805 \, \mu m$ respectively with $x = 0 \, nm$ and $y = 22 \, nm$. The inset graph is the maximum enhancement factors in the probe volume.

Figure 4-13 Averaging enhancement factors of the cuboid probe volume when the in-slot sphere diameter is $D = 42 \, nm$, $44 \, nm$, and $46 \, nm$ respectively with the center coordinates $x = 0 \, nm$, $y = 21$, $22$ and $26 \, nm$ respectively and $z = 0.805 \, \mu m$. The inset graph is the maximum enhancement factors in the probe volume.

4.2.2 Particle material and shape

When the material of the in-slot metallic sphere is aluminum, the enhancement factors around the in-slot particle are presented in Figure 4-14. The $EF$ curves of the in-slot gold and aluminum spheres are very similar in profile. Like the gold case, the Al sphere is also excited by the SPP trapped in the gold slot and the peaks result from the interaction of the in-sphere LSP and the in-slot SPP. The excitation wavelength of Al surface plasmons lies in the UV range, which is shown in the left insert image. So, the aluminum sphere shows a weaker Raman enhancement compared to a gold sphere in the wavelength range from 600 nm to 900 nm.
Figure 4-14 Averaging enhancement factors in the cuboid probe volume when the in-slot particle is an Al sphere with diameter 44 nm with the coordinates x = 0 nm, y = 22 nm, and z = 0.805 μm. The left inset image is the absorption spectrum of the Al sphere in free space. The right inset graph is the maximum enhancement factors in the probe volume.

Except for the sphere, the particle that is placed into the slot can have other shapes, such as cube and cylinder. The enhancement factors of the probe volume around these particles are presented in Figure 4-15. The enhancement factors of the in-slot sphere are also included for comparison. All the particles have the same size of 44 nm and are located at the center of the slot bottom with the same center coordinates x = 0 nm, y = 22 nm, and z = 0.805 μm. All the gaps in the particle-slot junctions are 2 nm wide, so the averaging enhancement factors around these particles are on the similar order of magnitude of $10^2$ - $10^4$. Compared to the others, the cube has one more peak in the red curve. This is because the cube has more LSP modes due to its shape. The electric field distributions of the peaks and shoulders in Figure 4-15 are presented in Figure A2 of Appendix.

Figure 4-15 Averaging enhancement factors of the cuboid probe volume when the in-slot particle has different shapes with the same center coordinates x = 0 nm, y = 22 nm and z = 0.805 μm. The cube side is 44 nm. The height and the diameter of the cylinder are both 44 nm. When the axis of the cylinder is along the z-direction / the y-direction, it is marked with “H” / “V”. The sphere diameter is 44 nm. The inset graph is the maximum enhancement factors in the probe volume.

When the in-slot particle has a size close to the slot width, the particle-slot wall
gaps can be very small. However, it is a difficult task to put the particle into the slot in experiments. An intuitive way to solve this problem is decreasing the particle size. If some surface functional technologies are used, the particle can be immobilized near the slot walls and a small particle-slot wall gap can be created. Thus, the strong enhancement of Raman scattering can still be obtained in the particle-slot junction.

The enhancement factors of the probe volume are shown in Figure 4-16 when the in-slot particle has different shapes with the same size of 10 nm. Note that the probe volume here is redefined as the cuboid volume: \([10 \text{ nm} < x < 24 \text{ nm}; 0 < y < 12 \text{ nm}; 798 \text{ nm} < z < 812 \text{ nm}].\) All the particle-slot wall gaps are 2 nm wide. All the curves have two \(EF\) peaks around 650 nm and 770 nm. At all these peaks, the on-particle charges oscillate in a dipole mode, knowing from the electric field distributions in Figure A3 of Appendix. The two wavelength positions are similar with the peak positions at 654 nm and 781 nm of the blue dash curve in Figure 4-9, which is for the case without the in-slot metallic nanoparticle. This means that the influence of the in-slot particles on the interfered SPP is almost negligible when the particle size is 10 nm. So the peak positions are mainly determined by the interfered SPP of the slot and they appear at the same positions. In Figure 4-16, the sphere has the highest \(EF\) curve while the cube has the lowest one. In experiments, the small metallic particles can be synthesized chemically and be placed in the slot easily.

Figure 4-16 Averaging enhancement factors of the cuboid probe volume when the in-slot particle has different shapes with the same center coordinates \(x = 17 \text{ nm}, y = 5 \text{ nm}\) and \(z = 0.805 \mu\text{m}\). The cube side is 10 nm. The height and the diameter of the cylinder are both 10 nm. When the axis of the cylinder is along the z-direction / the y-direction, it is marked with “H” / “V”. The sphere diameter is 10 nm. The inset graph is the maximum enhancement factors in the probe volume. Here, note that the probe volume is defined as: \([10 \text{ nm} < x < 24 \text{ nm}; 0 < y < 12 \text{ nm}; 798 \text{ nm} < z < 812 \text{ nm}].\)

4.2.3 Particle number and signal loss caused by the in-slot particles

To obtain more hotspots or probe volumes in the sensor, a method is to put more metallic nanoparticles into the slot. To demonstrate it, the output of the Raman signals scattered by an x-polarized dipole near the 1\textsuperscript{st} gold sphere is analyzed before and after the 2\textsuperscript{nd} gold sphere is added inside the slot. Two cases with the diameters 44 nm and
10 nm are considered for examples. The radiation enhancement factor $E_{\text{Rad}}$ curves are reported in Figure 4-17. The radiation enhancement factors are calculated on the basis of the Raman dipole radiation which can propagate stably in the form of the guided $TE$ mode of the $\text{Si}_3\text{N}_4$ strip. It is seen that half of the signals radiated by the Raman dipole is lost due to the 2$^{\text{nd}}$ sphere when the sphere diameter is 44 nm. However, the signals have almost no loss when the sphere diameter is 10 nm. This is because the big in-slot particle blocks the propagation of the in-slot SPP excited by Raman signals and impedes the coupling between the slot and the strip. On the other hand, the enhancement factor of the sphere-slot wall gaps becomes smaller when the in-slot sphere is small. So, if the particle size is big, it is not recommended to put many metallic particles into the sensor slot. If the particles are small, more than two particles can be employed in the slot to obtain more hotspots and more Raman signals.

Figure 4-17 Radiation enhancement factors of the Raman dipole radiation with/without the 2$^{\text{nd}}$ gold sphere in the slot. The 1$^{\text{st}}$ gold sphere with diameter 44 nm is located at the bottom center of the slot like that in Figure 4-6-(a) with the center coordinates $x = 0$ nm, $y = 22$ nm and $z = 0.805$ $\mu$m. The 2$^{\text{nd}}$ one is placed with $x = 0$ nm, $y = 22$ nm and $z = 1.0$ $\mu$m. The 1$^{\text{st}}$ gold sphere with diameter 10 nm is located with the center coordinates $x = 17$ nm, $y = 22$ nm and $z = 0.805$ $\mu$m. The 2$^{\text{nd}}$ one is placed with $x = 17$ nm, $y = 22$ nm and $z = 1.0$ $\mu$m. The Raman dipole is $x$-polarized and at the center of a 1$^{\text{st}}$ sphere-slot wall gap with the coordinates $x = 23$ nm, $y = 22$ nm for the big sphere and $y = 5$ nm for the small sphere and $z = 0.805$ $\mu$m. The white dash line marks the output plane where the dipole radiation energy is detected.

4.3 SPP-LSP coupling in the aluminum particle-slot junction and $E_{\text{F}}$ dependence on in-slot metallic nanoparticles

Although the Al slot exhibits a weaker enhancement for Raman scattering than the Au slot, as shown in the part 3.3.3, the fabrication cost can be very low if the sensor’s slot is aluminum. Aluminum is compatible with CMOS foundries, so it is convenient to integrate the sensor with other photoelectric circuits. Besides that, the sensor with an Al slot can work with an excitation wavelength shorter than 600 nm
and the cross-section of Raman scattering can be bigger due to the $1/\lambda^4$ dependence in the equation (1-6). This section mainly shows the SPP-LSP coupling in the aluminum particle-slot junction and the enhancement improvement introduced by the in-slot particle in the SERS sensor with an Al slot. Particularly, the factors, which influence the enhancement factor in the probe volume around the in-slot particle, are discussed to indicate the strategy for optimizing the SERS-detection capacity of the sensor with an Al slot.

4.3.1 SPP-LSP coupling between Al nanoparticles and the sensor’s Al slot

Here, the SERS sensor with an Al slot is taken as an example to demonstrate the SPP-LSP coupling in an aluminum particle-slot junction, as shown in Figure 4-18-(a) and -(b). If not specified otherwise, the sensor frame is kept the same in the following discussion. An Al sphere with diameter 26 nm is assumed to be located at the center of the slot bottom with the center coordinates (0 nm, 13 nm, 1.124 µm). Then, two 2nm-wide gaps are created in the sphere-slot junction, as shown in Figure 4-18-(a). The sphere-slot wall gaps can confine the electromagnetic fields and introduce the hotspot effect of SERS for molecules in the sphere-slot junction. The z-normal plane with $z = 1.124 \mu$m is the symmetrical plane of the Al slot in the longitudinal (z-axis) direction.

![Figure 4-18](image)

Figure 4-18 Schematics of the SERS sensor with an Al slot and an Al sphere inside: (a) Cross section of the hybrid waveguide, where an Al sphere is located at the center of the slot bottom. (b) Side view of the sensor.

The excitation wavelength of aluminum surface plasmons is shorter than that of gold, so the wavelength is set as 200 nm - 800 nm in analyzing the aluminum particle-slot junction. An impulse of the fundamental $TE$ mode ($\lambda = 530$ nm) of the Si$_3$N$_4$ strip is injected as the incident light of the SERS sensor. As shown in Figure 4-19, the electric field intensity around the in-slot Al sphere, particularly in the sphere-slot wall gaps, is raised dramatically, compared to the field $|E|$ before the sphere is added. If Raman-active molecules are present in the gaps, Raman scattering will be strongly enhanced. It is worth noting that the field $|E|$ in the slot has fluctuations along the $z$-axis direction due to the interferences caused by the slot’s facet reflection.
Figure 4-19 Electric field $|E|$ distributions ($\lambda = 530$ nm) in the aluminum slot before and after the Al sphere is added: (a)-(b) shows the in-slot field $|E|$ without the sphere on a z-normal plane with $z = 1.124 \, \mu m$ and a y-normal plane with $y = 13 \, nm$ respectively. (c)-(d) show the in-slot field $|E|$ on the two same planes after the Al sphere with diameter 26 nm is added into the slot with the center coordinates (0 nm, 13 nm, 1.124 $\mu m$). The incident light is the fundamental TE mode of the Si$_3$N$_4$ strip. To show the distributions clearly, the images in (b) and (d) are stretched in the x-axis direction.

The absorption curves of the Al sphere with/without the Al slot are reported in Figure 4-20-(a). When the Al slot in Figure 4-18 is removed and only the Al sphere exists above the Si$_3$N$_4$ strip, the absorption peak of the sphere is at $\lambda = 210$ nm in the UV range. The absorbance is very small because the sphere only interacts with the evanescent field of the photonic mode guided in the strip. When the Al slot exists, the absorption of the sphere increases. This is because the energy in the strip is coupled into the slot and interacts with the in-slot sphere. Being similar to the gold sphere-slot junction, the LSP of the in-slot Al sphere is hybridized with the SPP of a finitely long Al slot that can be seen as a cavity. The sphere is excited directly by the in-slot SPP, which are modulated constructively or destructively by the interferences, as shown in Figure 4-19-(d). Meanwhile, the sphere also influences the in-slot SPP. Thus, several peaks appear in the absorption curve of the in-slot sphere, which results from the localized SPP-LSP modes of the sphere-slot junction.

To discuss the SERS enhancement in the sphere-slot wall gaps, one example point is chosen at the coordinates (14 nm, 13 nm, 1.124 $\mu m$), which is marked by a red star in Figure 4-18-(a). The EF curve of the example point is reported in Figure 4-20-(b). The EF curves of the same point are also included for comparison when only the Al sphere or the Al slot exists. When the sphere-slot junction exists, the EF of the example point is at the level of $10^5$ at 494 nm, 5-6 orders of magnitude higher than the isolated slot or sphere. The hotspots around the Al particle can be defined as the probe volume of the sensor by a cuboid: $[-W_m/2 \leq x \leq W_m/2, 0 \leq y \leq H_m, Z_{sphere} - R_{sphere} \leq z \leq Z_{sphere} + R_{sphere}]$, where $Z_{sphere}$ is the Z coordinate of the sphere center and $R_{sphere}$ is the sphere radius. If not specified otherwise, the probe volume is kept the same in the following discussion.
Figure 4-20 Absorptions of the Al sphere and enhancement factors of the example point: (a) Absorptions of the Al sphere in the sensor’s slot in Figure 4-18 and the same sphere when the slot is removed. (b) Enhancement factors of the example point, which is marked by a red star at (14 nm, 13 nm, 1.124 µm) in Figure 4-18-(a), involving three cases: the Al sphere, the Al slot and the Al sphere-slot junction.

To show the SPP-LSP coupling more clearly, the charge distributions of two representative localized SPP-LSP modes in the sphere-slot junction are shown in Figure 4-21. It is seen that the electron density in the sphere-slot junction is evidently higher than the other place on the slot walls. Before and after the Al sphere is added into the slot, the charge distributions on the slot walls are very similar. It means that the in-slot sphere does not obviously influence the charge distribution (SPP) on the slot walls and the SPP dominates in the SPP-LSP coupling. That is the reason why the $EF$ curve profile and the peak positions of the sphere-slot junction are very similar to those of the isolated slot in Figure 4-20-(b).

Figure 4-21 Charge distributions of two representative localized peaks around 500 nm in Figure 4-20-(b): (a)-(b) are for the isolated slot and (c)-(d) are obtained after the sphere is added into the slot. To show the distributions clearly, the images in (b) and (d) are stretched in the x-axis direction.

4.3.2 Influences of multi-factors on the $EF$ around the in-slot metallic nanoparticle

Like the gold case, the enhancement factor for Raman scattering in the Al
The particle-slot junction depends greatly on the size of the particle-slot wall gaps. Besides that, the local electric field is also affected by many other factors, such as the particle’s position, size, material, and number. The section mainly discusses the multi-factor dependence of the enhancement factor in the probe volume around the in-slot particle. It demonstrates the strategy to optimize the SERS-detection capacity of the sensor with an Al slot.

**Position and size**

The in-slot sphere’s position is related to the sphere-slot wall gap size (transverse position) and the intensity of the SPP that excites the sphere (longitudinal position). So, the enhancement of Raman scattering in the sphere-slot junction is affected greatly by the sphere’s position. To demonstrate the influence of the sphere’s transverse (x-axis) position, a transverse offset of +1 nm or +2 nm is added to the sphere in Figure 4-18. With the two offsets, four sphere-slot wall gaps are created with width = 1nm, 2nm and 4 nm, 0 nm (wedge gap) respectively. The averaging enhancement factors of the probe volume around the sphere are reported in Figure 4-22. The case with no transverse offset is included too for comparison. The averaging enhancement factor of the probe volume increases when the sphere has a transverse offset. This is because the offset narrows one of the sphere-slot wall gaps and a narrower gap confines the electric field further. When the transverse offset exists, the peaks of the $EF$ curves do not have an obvious shift. This is because the in-slot Al sphere does not obviously influence the in-slot SPP and the SPP dominates in the SPP-LSP coupling in the sphere-slot junction. Even when the sphere with an offset of 2 nm touches a slot wall, the profile and peak positions of the $EF$ curve is still similar to those of the two other offsets. The insert graph presents the maximum $EF$ values in the probe volume. They are higher $10^3$ times than the corresponding averaging $EF$ values.

![Figure 4-22 Averaging enhancement factors of the cuboid probe volume when the in-slot sphere position has a transverse offset 0 nm, 1 nm and 2 nm respectively with the center coordinates $x = 0, 1, 2$ nm, $y =13$ nm, and $z = 1.124 \mu$m. The inset graph is the maximum enhancement factors in the probe volume.](image-url)
The sphere’s longitudinal (z-axis) position does not change the gap size in the sphere-slot junction but it changes the intensity of the local SPP field that excites the sphere. Meanwhile, the sphere’s longitudinal position can influence the field interferences in the slot. When the sphere has the longitudinal position $z = 0.55 \, \mu m$, $z = 0.75 \, \mu m$, $0.95 \, \mu m$ and $1.124 \, \mu m$ respectively with $x = 0 \, nm$ and $y = 13 \, nm$, the enhancement factors of the probe volume are reported in Figure 4-23. When the sphere’s longitudinal position changes from $z = 0.55 \, \mu m$ to $z = 1.124 \, \mu m$, the $EF$ of the probe volume increases. This is because more energy is coupled into the slot from the strip when the position becomes closer to the longitudinal middle plane with $z = 1.124 \, \mu m$, as shown in Figure 4-19-(b). The $EF$ peaks show an obvious change when the sphere’s longitudinal position changes. This is because the in-slot electric field interferes constructively or destructively along the longitudinal direction. The insert graph presents the maximum $EF$ values in the probe volume.

When the sphere diameter changes, the enhancement in the probe volume is modified due to the size change of the sphere-slot wall gaps. This is similar to the sphere’s transverse position change that has been discussed before. The averaging and maximum enhancement factors of the probe volume around the sphere with different diameters are presented in Figure 4-24. When the sphere diameter changes from 26 nm to 10 nm, the sizes of the two sphere-slot wall gaps increases from 2 nm to 10 nm and subsequently the enhancement factors decrease rapidly. When the diameter becomes smaller, it is easier to place the sphere into the sensor’s slot but the enhancement factor is smaller. If the sphere is small, some surface functional technologies should be used to immobilize it near the slot walls for creating a small particle-slot wall gap.
Material and shape

When the material of the in-slot sphere is gold and silver, the enhancement factors of the probe volume are presented in Figure 4-25. The Al sphere has the highest enhancement factor in the wavelength range 200 nm - 400 nm because the excitation wavelength of Al surface plasmons lies in the UV range. The gold and silver spheres are resonantly excited by visible light, so the $EF$ curves of the two spheres are higher than that of the Al sphere in the long wavelength range. Gold has strong absorption for a wavelength smaller than 600 nm, so the highest enhancement factor in the wavelength range 400 nm - 600 nm is achieved by the Ag sphere.

Apart from the sphere, the in-slot particle can have some other shapes, such as cube and cylinder. The enhancement factors of the probe volume around these particles are presented in Figure 4-26. The enhancement factors of the sphere are also
included for comparison. All the particles have the same size 26 nm and they are located at the center of the slot bottom with the same center coordinates \( x = 0 \) nm, \( y = 13 \) nm, and \( z = 1.124 \) µm. All the gaps in the particle-slot junctions are 2 nm wide, so the averaging enhancement factors around these particles are on the similar order of magnitude of \( 10^2 \) - \( 10^3 \) while the maximum values are about \( 10^4 \) - \( 10^5 \).

![Graph showing the effect of particle shapes on averaging enhancement factors.]

Figure 4-26 Averaging enhancement factors of the cuboid probe volume when the in-slot particle has different shapes with the same center coordinates \( x = 0 \) nm, \( y = 13 \) nm and \( z = 1.124 \) µm. The cube side is 26 nm. The height and the diameter of the cylinder are both 26 nm. When the axis of the cylinder is along the z-direction / the y-direction, it is marked with “H” / “V”. The sphere diameter is 26 nm. The inset graph is the maximum enhancement factors in the probe volume.

◆ Number and signal loss caused by the in-slot particles

To obtain more hotspots or probe volumes in the SERS sensor, a method is to place more metallic nanoparticles into the slot. To demonstrate it, the output of the Raman signals scattered by an x-polarized dipole near the 1st Al sphere is analyzed before and after the 2nd Al sphere is added into the slot. Two cases with the diameters 26 nm and 10 nm are considered for the examples and the radiation enhancement factor (\( EF_{\text{Rad}} \)) curves are reported in Figure 4-27. The radiation enhancement factors are calculated on the basis of the Raman dipole radiation which can propagate stably in the form of the fundamental \( TE \) mode of the Si\(_3\)N\(_4\) strip waveguide. It is seen in Figure 4-27 that the 1/3 signals radiated by the Raman dipole are lost due to the existence of the 2nd sphere when the sphere diameter is 26 nm. However, there is almost no signal loss caused by the 2nd sphere when the sphere diameter is 10 nm. This is because the big in-slot particle blocks the propagation of the in-slot SPP excited by Raman signals and impedes the coupling between the slot and the strip. On the other hand, the enhancement factor of the sphere-slot wall gaps becomes smaller when the in-slot sphere is small. So, if the particle size is big, it is not recommended to place many metallic particles into the sensor’s slot. If the particles are small, more than two particles could be employed in the slot to obtain more hotspots and more Raman signals.
Chapter IV

4.4 SERS-detection capacity of the sensor with metallic nanoparticles

According to the equation (3-12) and the two assumptions (the analyte molecules distribute uniformly in the slot and the Raman depolarization ratio $\rho_R = 0$), the SERS-detection capacity of the sensor with metallic nanoparticles can be estimated quantitatively. The SERS sensor described in Figure 4-6 is taken as an example to show the SERS-detection capacity of the sensor with a gold slot and a gold sphere. The averaging enhancement factor of the probe volume is $3.052 \times 10^4$ when the excitation wavelength is 693.5 nm, as shown by the red curve in Figure 4-11. The excitation power is 10 mW and the excitation wavelength is 693.5 nm. The lowest detectable power of the detector refers to the Ocean Optics QE65 Spectrometer. The dyes, rhodamine 6G (RH6G) and benzotriazole dye 2 (BTZ), are taken as the probe molecules. It is seen in Figure 4-28-(a) that the RH6G solution of $1.36 \times 10^{-5}$ mole/L and the BTZ solution of $1.13 \times 10^{-4}$ mole/L are detectable by the sensor at room temperature. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-6}$ mole/L. If the gold sphere has a transverse offset 2 nm, the averaging $EF$ value of the probe volume will increase to $9.10 \times 10^5$ at $\lambda = 693.5$ nm, as shown by the blue curve in Figure 4-11. Then the lowest detectable concentrations in Figure 4-28-(a) can be decreased by 30 times.

If the sensor has an Al sphere in its Al slot, as shown in Figure 4-18, the electron number per second excited by Raman signals of the sensor is presented in Figure...
4-28-(b). The averaging $EF$ value of the probe volume is 495 when the excitation wavelength is 494 nm, as shown by the red curve in Figure 4-22. It is seen that the lowest detectable concentrations of the RH6G and BTZ dyes are higher than those of the Au case. The RH6G solution of $1.21 \times 10^{-3}$ mole/L and the BTZ solution of $1.15 \times 10^{-2}$ mole/L are detectable by the sensor at room temperature. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-4}$ mole/L. If the Al sphere has a transverse offset 2 nm, the averaging $EF$ value of the probe volume will increase to $1.97 \times 10^{4}$ at $\lambda = 494$ nm, as shown by the blue curve in Figure 4-22. Then the lowest detectable concentration in Figure 4-28-(b) can be decreased by 40 times.

Figure 4-28 Electron numbers per second excited by the Raman signals of RH6G and BTZ on the detector of an Ocean Optics QE65 Pro spectrometer. (a) The SERS sensor has a gold sphere in the gold slot, as shown in Figure 4-6. The averaging $EF$ value of the probe volume is $3.052 \times 10^{5}$ when the excitation wavelength is 693.5 nm, as shown by the red curve in Figure 4-11. (b) The SERS sensor has an Al sphere in the Al slot, as shown in Figure 4-18. The averaging $EF$ value of the probe volume is 495 when the excitation wavelength is 494 nm, as shown by the red curve in Figure 4-22. The two black lines are the dark currents of the spectrometer.

4.5 Summary

In this chapter, the theoretical investigation of the effect of in-slot metallic nanoparticles on improving the SERS-detection capacity of the sensor is conducted by using 3D-FDTD simulations.

By the electric field and charge distributions, it is known that the localized SPP-LSP modes appear in the metallic sphere-slot junction due to the electromagnetic interaction between the in-slot metallic nanoparticle and the finitely long slot (a half-open cavity). The metallic nanoparticles in the sensor’s Au slot can make several molecule detections possible by providing some averaging $EF$ values as high as $10^{6}$ in the probe volume around the in-slot particle. The metallic nanoparticles in the sensor’s Al slot provide some smaller averaging $EF$ values in the probe volume, reaching $10^{5}$. The influences of the particle position, size, shape and number on the enhancement in the probe volume have been investigated adequately to point out the strategy to optimize the sensing performance.
To characterize quantitatively the sensor’s SERS-detection capacity, two specific sensors with an Au sphere-slot junction and an Al sphere-slot junction are chosen as the examples. It is seen that the RH6G solution of $1.36 \times 10^{-5}$ mole/L and the BTZ solution of $1.13 \times 10^{-4}$ mole/L are detectable at room temperature with the sensor with the Au sphere-slot junction. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-6}$ mole/L. For the sensor with the Al sphere-slot junction, the RH6G solution of $1.21 \times 10^{-3}$ mole/L and the BTZ solution of $1.15 \times 10^{-2}$ mole/L are detectable at room temperature. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-4}$ mole/L.
5. Experiments and preliminary results

The theoretical and numerical investigations have predicted that a SERS sensor can be achieved based on the hybrid waveguide made of metallic slots and dielectric strips. The SERS sensor can give out detectable Raman signals with a high enhancement factor. However, the feasibility of the sensor still needs to be verified by experiments.

This chapter mainly introduces the experimental verification of the feasibility of the SERS sensor in reality. The sensor prototypes are obtained by fabricating some arrays of gold slots on the Si$_3$N$_4$ waveguides. The Raman probing molecules, methylene blue (MB) dissolved in distilled water, are dropped and dried on the arrays of gold slots. The SERS-detection capacity of the sensor prototypes is characterized by a Raman microscope *LabRAM 800HR*. The preliminary experimental results show that the Raman signals of the sensor prototypes are detectable.

5.1 Samples of Si$_3$N$_4$ waveguides

The Si$_3$N$_4$ strip waveguides were fabricated by our collaborators in the laboratory LETI, at CEA in Grenoble. The frame and parameters of the waveguides are presented in Figure 5-1. The waveguides are embedded in a SiO$_2$ cladding on a Si substrate. The cross-section is semi-elliptic (not rectangular) with width 320 nm and height 200 nm. During the fabrication process of the Si$_3$N$_4$ waveguides in Figure 2-5-(e), the etching was not enough anisotropic, leading to the semi-elliptic shape. The thickness of the upper SiO$_2$ cladding on the waveguides is 700 nm and the evanescent fields of the waveguides are totally confined in this thick cladding. Before fabricating the metallic slot waveguides, the SiO$_2$ cladding should be etched to let the evanescent fields of the Si$_3$N$_4$ waveguides extend out. If not, the thick cladding will prevent the electromagnetic interaction between the Si$_3$N$_4$ strip waveguides and the metallic slot waveguides.

![Figure 5-1 Frame and parameters of the Si$_3$N$_4$ waveguides. (a) Cross-section of the waveguides, which is semi-elliptic with width 320 nm and height 200 nm. (b) Regional side view of the waveguides to show the thicknesses of the different layers.](image)

The length of the Si$_3$N$_4$ waveguides is about 8 mm and there are 47 Si$_3$N$_4$ waveguides distributed parallelly in an area with size 8 mm × 5 mm on the sample. A grating is fabricated at the end of every waveguide, as shown in Figure 5-2. The
gratings act as the light input/output of the waveguides. The best coupling angle $\theta$ between the incident light in free space and the fundamental $TE$ mode in the waveguides ($\lambda = 633 \text{ nm}$) is $25^\circ$, according to the coupling equation $\beta = k_0 \sin \theta \pm n\Lambda$, where $\beta$ is the wave vector of the mode in the $Si_3N_4$ waveguides, $k_0$ is the wave vector of the incident light, $\Lambda$ is the reciprocal vector of the gratings, and $n = 1, 2, 3, \ldots$. To strengthen the coupling with the incident light, the waveguide is widened at the end. If the incident light is injected via an optical fiber, the widening can match the guided mode of the waveguides and the fiber mode. If the incident light is injected by an objective, it can increase the area for receiving the light.

![Figure 5-2 Input/output grating of the $Si_3N_4$ waveguides. (a) Side view of the grating at a waveguide end. The coupling of the incident light ($\lambda = 633 \text{ nm}$) into the $Si_3N_4$ waveguide is the strongest when the injection angle is $25^\circ$. (b) Optical image of a waveguide end with a grating. The waveguide is widened at the end to receive more incident energy.](image)

**5.2 Fabrication of gold slots on $Si_3N_4$ waveguides**

The sample of $Si_3N_4$ waveguides is etched by reactive-ion etching (RIE) until the evanescent fields of the $Si_3N_4$ waveguides extend out of the cladding. However, the RIE process is difficult to control accurately and the exact remnant $SiO_2$ thickness is always unknown after etching. Besides that, the $SiO_2$ cladding cannot be imaged clearly under scanning electron microscopes (SEM) and the thickness is difficult to measure. To solve this problem, the stair etching technique is used, as shown in Figure 5-3. The $Si_3N_4$ waveguides on the sample are divided into four areas and the difference of etching time between two neighboring areas is 0.5 min. Firstly, the area “A” is etched for 0.5 min while the other three areas are covered by a glass slide. Secondly, the areas “A” and “B” are etched for 0.5 min while the other two areas are covered by a glass slide. Thirdly, the areas “A”, “B” and “C” are etched for 0.5 min while the area “D” is covered by a glass slide. Then, the four areas have a stair difference of etching time 0.5 min. After that, the sample is etched several times with step 0.5 min without the glass covering. After every etching, the light ($\lambda = 633 \text{ nm}$) propagation is checked in the waveguides of the area “A”. If the light can not propagate in the waveguides, it is approximately believed that all the upper $SiO_2$ cladding is removed in the area “A”. This is because the modal effective index changes when the upper cladding is removed, leading to the too weak coupling between the incident light and the $Si_3N_4$ waveguides. As shown in Figure 5-3, the 700 nm $SiO_2$ cladding is etched totally in the area “A” when the total etching time is 9.5
min. According to that, the averaging etching speed is about 74 nm/sec. So, the SiO₂ cladding of the area “B” is estimated to be 36 nm and that of the area “C” is 72 nm. The upper SiO₂ thickness of the area “D” is 108 nm, which is too thick and not concerned in the following discussion. It is worth noting that this is not an exact method to control the remnant SiO₂ thickness but it is a practical method in experiments.

![Figure 5-3 Stair etching of the upper SiO₂ cladding of the Si₃N₄ waveguides. The purple semi-ellipses are the cross sections of the Si₃N₄ waveguides. The waveguides on the sample are divided into four areas and the difference of the etching time between two neighboring areas is 0.5 min.](image)

After etching the SiO₂ cladding, the next step is fabricating the gold slots above the Si₃N₄ waveguides. The related techniques of fabricating metallic nanostructures have been introduced in the part 2.2.2. The main challenge of the slot fabrication is the axle-wire alignment of the gold slots and the Si₃N₄ waveguides. To solve the alignment problem, the EBL’s writing pattern is designed as a slot array with 39 columns × 40 rows, as shown in Figure 5-4. The elements of the array are composed of two 350 nm × 500 nm slabs and the slot width between the two slabs is 70 nm. The array’s vertical period is 1.2 µm and the transverse period is 1 µm. The total area of the array is about 40 µm × 50 µm. In every column, there is another slot with width 100 nm appearing between two neighboring elements. In every row, the axle wires of two neighboring elements have a vertical shift 30 nm. So, 11 (320 nm / 30 nm ≈ 11) slots will be located on the Si₃N₄ waveguide, which goes across the array along the array’s transverse direction.

When writing the pattern of slot arrays into the PMMA deposited on the waveguide sample, the first task is to calibrate the waveguides’ propagation direction via the positioning markers on the sample. The waveguides’ propagation direction is set as the slot array’s transverse direction. Then, the focused e-beam is moved to the middle part of waveguides and the slot arrays are written into the PMMA on the waveguides. From the markers (in the area “A” of Figure 5-3) to tens of the Si₃N₄ waveguides (in the area “A”, “B” and “C” of Figure 5-3), the travel spinning is several millimeters and a position deviation may happen. Once the position deviation is smaller than 50 µm, the waveguides can be always covered by the slot arrays. Here,
it is worth mentioning that the EBL writing of slot arrays was conducted by the collaborator Mr. Feifei Zhang in our lab. After development, gold deposition, and lift-off, the gold slot arrays are fabricated on the Si$_3$N$_4$ waveguides, as shown in Figure 5-5. It is seen that the waveguide does not go across the center of the slot array, which is caused by the position deviation. However, there are still some gold slots on the waveguide. The thickness of the gold slabs is 40 nm and the other geometrical parameters can be found in the SEM images of the gold slots. Because of the size (about 30 nm) of the EBL’s focused e-beam, the gold slot width is smaller than the designed value.

Figure 5-4 Designed pattern of a slot array with 39 columns × 40 rows. Every element is composed of two 350 nm × 500 nm slabs (black blocks) with slot width 70 nm. The vertical period is 1.2 µm and the transverse period is 1 µm in the array. In every row, the axle wires of two neighboring elements have a vertical shift 30 nm. A 320nm-wide Si$_3$N$_4$ waveguide is assumed to go across the array along the array’s transverse direction.

Figure 5-5 Morphology of the sensor prototypes (one in the area “B” for example). (a) Optical image of a gold slot array on a Si$_3$N$_4$ waveguide. (b) SEM image of the overlap area of the slot array and the Si$_3$N$_4$ waveguide. (c) SEM image of the gold slots.
5.3 Characterization of SERS-detection capacity

To characterize the SERS-detection capacity of the sensor, the methylene blue (MB) molecules are chosen as the probe analyte. The applied MB analyte is dissolved in distilled water with concentration $10^{-4}$ mole/L. A small droplet of 4 µL MB solution is dropped and dried on the gold slot arrays, as shown in Figure 5-6. It is worth noting that the slot array is so far (several millimeters) from the waveguide ends that the waveguide’s gratings are not covered by MB molecules. The Raman measurements are conducted by a commercial Raman microscope Labram 800HR. In the figure below, the symbols “×” mark the four positions where Raman signals are measured, which will be discussed in the following.

![Diagram of characterization setup](image)

Figure 5-6 Schematic for characterizing the SERS-detection capacity of the sensor prototypes. A droplet of 4 µL MB solution is dropped and dried on the slot array. The symbols “×” mark the four positions where Raman signals are measured in the following discussion.

To discuss the output signals of the sensor prototypes, the reference Raman spectra of MB molecules should be measured firstly. As shown in Figure 5-7, the classic Raman signals and SERS signals (enhanced by the gold slot arrays directly) of the dried MB droplet in Figure 5-6 are presented. Here, the Si$_3$N$_4$ waveguide under the slot array is in the area “B”, which is noted as $N2T5$ and shown in Figure 5-5. The SiO$_2$ spacing between the Si$_3$N$_4$ strip and the gold slot array is 36nm. The spectra are measured by focusing the excitation laser (633 nm, 8.3 mW) from the Labram objective (10×, NA 0.3) directly on the positions marked by the blue and black symbols “×” in the insert image. It is seen that the black curve is obviously higher than the blue one due to the enhancement of the gold slot array. Here, the peaks 1625 cm$^{-1}$ and 1391 cm$^{-1}$ are mainly concerned in the Raman spectra of MB molecules. The peak 1625 cm$^{-1}$ comes from the stretching of the C-C rings in MB molecules while the peak 1396 cm$^{-1}$ is caused by the symmetrical stretching of the C-N bands[138]. Note that the highest Raman peak at 520 cm$^{-1}$ comes from the Si substrate, not from the MB molecules.
Figure 5-7 Classic Raman signals and SERS signals (enhanced by gold slot arrays directly) of the dried MB droplet in Figure 5-6. Here, the Si$_3$N$_4$ waveguide under the slot array is in the area “B”, which is noted as N2T5 and shown in Figure 5-5. In the inserted optical image of Labram 800HR (Note that there are two slot arrays in the image), the blue and black symbols “×” mark the focusing positions of the excitation laser from the Labram objective (10×, NA 0.3). The integration time of measurements is 10 s.

The output signals of the sensor prototypes are measured at the position marked by the red symbol “×” in Figure 5-6. Two detection configurations (direct and indirect) are used to test the sensors, which have been described in Figure 2-7. In the direct detection configuration, the excitation laser is directly injected in the sensor’s gratings by the Labram objective. In the indirect detection configuration, the excitation laser of Labram 800HR enters the gratings via a fiber.

**Direct detection configuration**

The output signals of two representative sensor prototypes (noted as N2T5 and N2T6) in the area “B” with a 36-nm-thick upper SiO$_2$ cladding are shown in Figure 5-8-(a) and -(b). The Raman signals of MB molecules are measured by injecting the excitation laser into the gratings of the SERS sensors by the Labram objective and the Raman signals of the backward Raman scattering are collected by the same objective, as shown in Figure 5-8-(c). The signals are noted as “In grating” for convenience. The Raman spectra of the positions out of the gratings are also measured, which are noted as “Out of grating”, to remove the possibility that the area of gratings is polluted by MB molecules. The red and green symbols “×” in Figure 5-8-(d) mark the focusing positions of the excitation laser from the Labram objective. As the reference, the Raman spectrum “Slot” in Figure 5-7 is also included in the figures below. In the green curve “Out of grating”, except for the Raman peak 520 cm$^{-1}$ of Si and the fluorescence of SiO$_2$, there are no Raman peaks of MB molecules. It is proved that there are no MB molecules in the area of gratings. So, the Raman peaks of MB molecules in the spectra “In grating” come only from the gold slot arrays on the Si$_3$N$_4$ waveguides. In the blue and pink boxes below, it is seen that the spectra “In grating” have two peaks 1625 cm$^{-1}$ and 1391 cm$^{-1}$, which also appear in the reference spectrum.
“Slot” of MB molecules. It means that the SERS sensor made of Si₃N₄ strips and gold slot arrays can detect the SERS signals of MB molecules deposited on the gold slot arrays. The strong backgrounds in the red curves mainly come from the enhanced fluorescence of MB molecules and Si₃N₄.

Figure 5-8 SERS signals of MB molecules measured at the sensor prototypes’ gratings. (a)-(b) Output signals of two representative sensor prototypes (noted as N2T5 and N2T6) in the area “B”. (c) Optical paths of excitation and collection of SERS signals in the sensor prototypes in the direct detection configuration. (d) The red and green symbols “×” mark the focusing positions of the excitation laser from the Labram objective.

To analyze quantitatively the enhancement factor (EF) of Raman scattering, the fluorescence backgrounds in Figure 5-8 are removed. Then, the SERS spectra in the blue and pink boxes are shown in Figure 5-9. The Raman peaks of the MB spectra are fitted with Lorentz model. The enhancement factors are calculated by normalizing the peak intensity of the SERS spectra to the intensity of the classic Raman spectrum. Note that this EF definition is different from the EF definition in the theoretical investigations of Chapter 3 and 4. The positions, intensities, and widths of the two fitted Raman peaks 1625 cm⁻¹ and 1391 cm⁻¹ are shown in Table 5-1. It is seen that the Raman signals given out by the SERS sensors are stronger than the classic Raman signals in the same conditions (i.e. EF_N2T5 > 1 and EF_N2T6 > 1). The slot’s SERS intensity is stronger than the two sensors at the peak 1625 cm⁻¹ while the EF of the sensor N2T6 is bigger than the slot at the peak 1391 cm⁻¹.
After discussing the sensor prototypes in the area “B” in Figure 5-3, a glimpse is given on the sensor prototypes in the areas “A” and “C”, which have a thinner or thicker SiO$_2$ spacing between the Si$_3$N$_4$ waveguides and the gold slot arrays.

It has been mentioned before that the light (633 nm) cannot propagate in the Si$_3$N$_4$ waveguides in the area “A” due to the change of the modal effective index after the 9.5 min etching. The output signals of a sensor prototype in the area “A” are reported in Figure 5-10-(a) and it is accompanied with the SERS signals of MB molecules measured directly on the sensor’s slot array. In the waveguide’s grating, only the fluorescence of Si$_3$N$_4$ and the Raman peak 520 cm$^{-1}$ of Si are observed, and no SERS signals of MB molecules are detected. This is because the Raman signals cannot propagate from the slot array to the grating.

The area “C” is etched for 8.5 min and the SiO$_2$ spacing between the Si$_3$N$_4$ waveguides and the gold slot arrays is about 72 nm. In Figure 5-10-(b), the output signals of a sensor prototype in the area “C” is reported. Because of the thick SiO$_2$ spacing, the electromagnetic interaction between the Si$_3$N$_4$ waveguide and the gold slot array is weak, leading to the decrease of the SERS-detection capacity of the sensor. So, the Raman peak 1625 cm$^{-1}$ of MB molecules in the red curve below is almost unobservable and it becomes a very small thorn. Its intensity is close to the
noise. On the other hand, the fluorescence background is still observable since the fluorescence effect is much stronger than Raman scattering.

Figure 5-10 Signals given out by the sensor prototypes’ gratings and the slot arrays on the Si₃N₄ waveguides (a) in the area “A” (noted as N2T2) and (b) in the area “C” (noted as N2P1).

◆ Indirect detection configuration

When the prototype sensors are tested with the indirect detection configuration in Figure 5-11-(a), the SERS signals of MB molecules are not observed by Labram 800HR in the gratings. The reason is that the Raman spectrum of the fiber is so strong that the MB signals from the sensors’ gratings are overwhelmed totally, as shown in Figure 5-11.

Figure 5-11 Indirect detection configuration for measuring the output signals of the sensor prototypes. (a) Indirect detection configuration. The excitation laser of Labram 800HR enters the sensor’s grating via a fiber. (b) Comparison of the MB spectrum obtained on the gold slot array directly and the Raman spectrum of the fiber.

5.4 Summary

In this chapter, the in-reality feasibility of the SERS sensor is verified by experiments. The sensor prototypes are obtained by fabricating some arrays of gold slots on the Si₃N₄ waveguides. The Raman signals of MB molecules given out by the sensor prototypes are detected experimentally.

To control the SiO₂ thickness above the Si₃N₄ waveguides, the stair etching technique is used. The etching-time difference 0.5 min between two neighboring areas
on the sample leads to a SiO$_2$ thickness difference 36 nm. This assures that a thin (about 36 nm) SiO$_2$ cladding above the Si$_3$N$_4$ waveguides is obtained in one of the etched areas on the sample. The arrays of gold slots of the sensor prototypes are fabricated by the e-beam lithography techniques. The pattern of slot arrays solves the problem of the axle-wire alignment between the gold slots and the Si$_3$N$_4$ waveguides.

Methylene blue (MB) molecules are chosen as the Raman probe molecules, which are dissolved in distilled water and dropped on the arrays of gold slots. The Raman measurements are conducted by a commercial Raman microscope Labram 800HR. The Raman peaks of MB molecules are observed in the output signals of two representative sensor prototypes. The enhancement factors of the two prototypes are 1.70 and 2.65 (4.15 and 7.54) respectively, by comparing to the peak 1625 cm$^{-1}$ (1391 cm$^{-1}$) intensity of the classic MB Raman spectrum.
Conclusions and Perspectives

This thesis presents a SERS sensor based on the hybrid waveguide made of metallic (Au/Al) slots and dielectric (Si$_3$N$_4$) strips and a method to improve the SERS-detection capacity by placing metallic nanoparticles into the sensor’s slot. It has been proven theoretically that the Raman scattering of molecules in the sensor’s metallic slot can be enhanced by the in-slot plasmonic field and the Raman signals can be enhanced more dramatically if metallic nanoparticles are placed into the slot. Finally, the in-reality feasibility of the sensor is proved in experiments.

The main mathematical tool in the thesis is the 3D-FDTD method, which can solve Maxwell’s equations within specific boundaries. The result of one FDTD simulation can provide a broadband electromagnetic response of metallic nanostructures covering a wide wavelength range. Based on the $|E|^4$-approximation and the electric field information obtained by FDTD simulations, the enhancement factors ($EF$) of SERS substrates can be estimated. Another mathematical tool is the strong coupling model, which is used to analyze the photonic-plasmonic coupling between metallic slots and dielectric strips. The experiments in the thesis mainly contain the fabrication of the sensor prototypes and the characterization of the SERS-detection capacity. The fabrication work is mainly about the metallic slot waveguides, which is conducted by the standard process of the electron beam lithography (EBL). The SERS-detection capacity of the sensor prototypes is characterized by two detection configurations based on a commercial Raman microscope Labram HR800.

The numerical simulations demonstrate that the hybrid waveguide can effectively transform light between in-strip photonic modes and in-slot plasmonic modes, solving the main challenge of exciting and extracting Raman signals in the sensor. The SERS processes, excitation and radiation of induced Raman dipoles, are simulated to demonstrate the working procedure of the sensor. The influence of the geometrical parameters on the coupling efficiency in the hybrid waveguide is investigated to show the strategy to optimize the electric field intensity in the metallic slot and the enhancement there. The numerical results show that a SERS sensor based on the hybrid waveguide made of gold slots and Si$_3$N$_4$ strips with an enhancement factor $10^2$ - $10^3$ can be realized. The enhancement factor of the sensor with an Al slot is much smaller, which is less than 10. A specific sensor with an Au slot is chosen as the example to show the SERS-detection capacity. The RH6G solution of $1.4 \times 10^{-3}$ mole/L is detectable with the Ocean Optics QE65 Pro spectrometer at room temperature. If the detector is cooled, RH6G can be detected at the lowest concentration of $7.27 \times 10^{-5}$ mole/L and BTZ can be detected at the lowest concentration of $6.72 \times 10^{-4}$ mole/L.
To improve the SERS-detection capacity of the sensor, a method is to place metallic nanoparticles into the slot. The theoretical investigation of the effect of in-slot metallic nanoparticles on improving the SERS-detection capacity of the sensor with an Au slot or an Al slot is conducted. Based on the electromagnetic fields and charge distributions of the metallic particle-slot junction, it is known that the localized SPP-LSP modes appear in the junction, due to the electromagnetic interaction between the in-slot metallic particle and the finitely long slot (a half-open cavity). The gold particle-slot junction can make several molecule detections possible in the sensor by providing some averaging EF values as high as $10^6$ in the probe volume around the in-slot particle. The aluminum particle-slot junction provides some smaller averaging EF values, reaching $10^5$. The influences of the particle position, size, shape and number on the enhancement in the probe volume have been investigated adequately to point out the strategy to optimize the sensing performance. To characterize quantitatively the sensor’s SERS-detection capacity, two specific sensors with a gold sphere-slot junction and an aluminum sphere-slot junction are chosen as the examples and the detector is the Ocean Optics QE65 Pro spectrometer. It is seen that the RH6G solution of $1.36 \times 10^{-5}$ mole/L and the BTZ solution of $1.13 \times 10^{-4}$ mole/L are detectable at room temperature by the sensor with the gold sphere-slot junction. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-6}$ mole/L. For the sensor with the aluminum sphere-slot junction, the RH6G solution of $1.21 \times 10^{-3}$ mole/L and the BTZ solution of $1.15 \times 10^{-2}$ mole/L are detectable at room temperature. If the detector is cooled, BTZ can be detected at the lowest concentration of $6.06 \times 10^{-4}$ mole/L.

The in-reality feasibility of the SERS sensor is verified by experiments. The sensor prototypes are obtained by fabricating some arrays of gold slots on the Si$_3$N$_4$ waveguides after the upper SiO$_2$ cladding of the Si$_3$N$_4$ waveguides is etched by stairs. Methylene blue (MB) molecules are chosen as the Raman probe molecules, which are dissolved in distilled water and dropped on the arrays of gold slots. The Raman peaks of MB molecules are observed in the output gratings of two Si$_3$N$_4$ waveguides covered by the gold slot arrays with a Si$_2$O spacing 36 nm. The enhancement factors of the two prototypes are 1.70 and 2.65 (4.15 and 7.54) respectively, by comparing to the peak 1625 cm$^{-1}$ (1391 cm$^{-1}$) intensity of the classic MB Raman spectrum. Here, note that this EF definition is different from the EF definition in the theoretical investigations.

In the following research on the SERS sensor, the work should focus on the fabrication and characterization of the SERS sensor. The experimental results until now just verify the feasibility of the SERS sensor in reality. There is still much work to do for optimizing the SERS-detection capacity. For example, the SiO$_2$ layer between slot arrays and Si$_3$N$_4$ strip waveguides is still thick, about 36 nm while the optimal value obtained by numerical investigations is about 10 nm. At present, the
metallic slots of the sensor prototypes are 50 - 70 nm wide. If the slots are narrowed, a stronger SERS-detection capacity is expected in the sensor. Another important experimental work is placing some metallic nanoparticles into the sensor’s slot to verify the particle effect that obtained in theoretical investigations.

In future, the sensor can be integrated with other micro-spectroscopic-components, like lasers, micro dispersion components AWG and CCD detectors. Then, a fully integrated SERS-detection system is achieved on chips for low-cost, portable and situ SERS detections. Even the micro SERS-detection system can be implanted into smart cell phones as hands-on labs for our daily life.
6. French summary

La spectroscopie Raman exaltée de surface (SERS) est une technique largement utilisée pour exalter la diffusion intrinsèquement inélastique de vibrations ou de rotations moléculaires. La spectroscopie Raman est un outil non intrusif et sans marquage pour identifier les empreintes spectrales moléculaires, même pour les molécules mélangées à d'autres substances. Cependant, la plupart des détections SERS sont mises en œuvre dans des configurations en espace libre, ce qui conduit à des systèmes assez volumineux et coûteux. Cela limite ses applications potentielles, comme le test de drogue, l'investigation environnementale, etc. Récemment, l'avènement de l'optique intégrée a facilité l’apparition d’un certain nombre de capteurs ou de composants sur les micro-circuits photoniques. Cela fournit une approche possible pour miniaturiser les systèmes SERS à l'échelle microscopique avec des composants spectroscopiques intégrés, tels que les AWGs (grilles de guide d'onde en réseau), les PCGs (réseaux échelle concave) et les EDGs (réseaux de diffraction gravé), qui sont utilisés dans la spectroscopie Raman pour disperer les signaux. Les systèmes intégrés sur puces pour les détections SERS avec des sensibilités élevées sont l'un des outils les plus souhaitables à l'avenir. Ils peuvent même être implantés dans des téléphones intelligents et faciliter le développement de laboratoires portables.

Cette thèse présente un capteur SERS basé sur un guide d'onde hybride constitué d'une fente métallique et d'un ruban diélectrique. Les études théoriques montrent qu'un capteur SERS très sensible peut être réalisé sur la base du guide d'onde hybride et de nanoparticules métalliques. Ensuite, la faisabilité en réalité du capteur est prouvée par des résultats expérimentaux.

6.1 Introduction

Bénéficiant d’un caractère non intrusif et sans marquage la spectroscopie Raman est une technique bien établie pour analyser les structures moléculaires dans des applications comme la pharmacologie, la salubrité des aliments, etc[1]–[4]. Son défaut est la faiblesse du signal dans des conditions normales. La spectroscopie Raman exaltée de surface (SERS) est l'une des techniques développées pour exalter et détecter les signaux Raman faibles. Cependant, les configurations conventionnelles sont des systèmes complexes et coûteux. Les progrès récents de l'optique intégrée offrent une approche pour miniaturiser les systèmes SERS dans des micro-circuits photoniques qui sont économiques, fiables et portables.

6.1.1 La spectroscopie Raman et la spectroscopie Raman exaltée de surface (SERS)

La diffusion Raman, une diffusion inélastique de lumière, a d'abord été
découverte dans des expériences sur des liquides en 1928 par les scientifiques indiens C. V. Raman et K. S. Krishnan[5], et indépendamment dans les cristaux par les scientifiques soviétiques G. Landsberg et L. Mandelstam[6], après avoir été prédit en 1923 par A. Smekal[7]. La diffusion inélastique signifie qu'il y a un échange d'énergie entre les photons incidents et les molécules Raman lors du processus. Lorsque les photons incidents interagissent avec des molécules, la plupart des photons sont dispersés en diffusion élastique Rayleigh, en conservant la fréquence de l'onde incidente. Néanmoins, une petite quantité de photons est dispersée sous forme de diffusion Raman, avec des fréquences inférieures (processus Stokes) ou plus élevées (processus anti-Stokes), correspondant à la perte ou au gain d'énergie des photons incidents par interaction avec des vibrations (ou des rotations) moléculaires. La section efficace différentielle de la diffusion Raman est très inférieure à $10^{-30}$ cm$^2$/sr typiquement. Ceci est beaucoup plus faible que la fluorescence. Pour exploiter la spectroscopie Raman, il est nécessaire d'exalter ce signal faible lorsque les détecteurs ne sont pas assez sensibles ou trop coûteux. Au cours des dernières décennies, la spectroscopie Raman exaltée est le sujet le plus étudié parmi les recherches effectuées en diffusion Raman.

Le SERS est l'une des techniques de spectroscopie Raman les plus célèbres parmi celles développées au cours des dernières décennies. Il a d'abord été observé en 1974 par Fleischmann sur une électrode d'argent[9]. Trois ans plus tard, les chercheurs ont commencé à révéler l'origine de l'effet d'exaltation de surface[10]. Par rapport à la diffusion Raman normale, cet effet d'exaltation peut facilement exalter le signal Raman de plusieurs ordres de grandeur, facteur appelé facteur d'exaltation (EF), lorsque les molécules Raman sont proches des objets métalliques. Le facteur d'exaltation par des solutions colloïdales de nanoparticules métalliques peut être supérieur à $10^{10}$, permettant même de détecter une seule molécule[11].

Un mécanisme largement reconnu d'exaltation est l'amplification du champ local due à l'interaction photon-métal par le plasmon de surface. La diffusion Raman est considérablement exaltée par le champ électrique des plasmons, qui est une oscillation collective des électrons à l'interface entre des matériaux ayant une permittivité opposée. Un autre mécanisme d'exaltation largement discuté est l'exaltation chimique. Elle est liée au fait que la section efficace Raman peut être modifiée lorsque les molécules sont adsorbées sur une surface métallique. Le mécanisme électromagnétique est la principale contribution de l'exaltation SERS, alors que le facteur d'exaltation chimique est d'environ 2 ordres de grandeur dans la littérature[13]. Par conséquent, résoudre les équations électromagnétiques ou mesurer les champs électromagnétiques réels, permet de prédire le facteur d'exaltation Raman pour un cas spécifique.

L'exaltation SERS peut être séparée en deux parties: l'exaltation du champ local $M_{Loc}$ pendant le processus d'excitation des dipôles Raman par des plasmons de
surface et $M_{\text{Rad}}$ l'exaltation du rayonnement des dipôles Raman par les plasmons des objets métalliques. Ainsi, le facteur d'exaltation ($EF$) est exprimé comme:

$$EF = EF_{\text{Loc}}(\omega_L)EF_{\text{Rad}}(\omega_R)$$  \hspace{1cm} (6-1)

L'approximation $|E|^4$ a été largement utilisée dans la littérature SERS pour estimer le facteur d'exaltation. On suppose souvent que $EF_{\text{Rad}}(\omega) \approx EF_{\text{Loc}}(\omega)$ et $\omega_R \approx \omega_L$. Dans ce cas, le facteur $EF$ est exprimé simplement comme:

$$EF = EF_{\text{Loc}}EF_{\text{Rad}} = EF_{\text{Loc}}^2 = \frac{|E_{\text{Loc}}(\omega)|^4}{|E_{\text{inc}}|^4}$$  \hspace{1cm} (6-2)

Cette approximation évite une estimation du terme $EF_{\text{Rad}}$ pour chaque position possible (et pour au moins trois orientations orthogonales) du dipôle, ainsi que les problèmes potentiels causés par les singularités dipolaires.

6.1.2 Contexte de l'étude

Le capteur SERS de l'étude est basé sur le couplage photonique-plasmonique entre une fente métallique et un ruban diélectrique. Il a été démontré qu'il existe un couplage direct entre un guide d'onde diélectrique et un guide d'onde métallique sous forme de fils[88], [90], [98]–[102] ou de fentes[103]–[106]. La fente métallique est choisie de préférence dans l'étude car elle peut confiner les champs plasmoniques dans un petit volume, en particulier autour des coins de la fente[107]–[113]. Cette structure exalte considérablement l'émission spontanée de dipôles Raman de molécules d'analyte[114]–[116]. La Figure 6-1 représente un coupleur photonique-plasmonique créé par un ruban en silicium et une fente en cuivre.

Figure 6-1 Le couplage photonique-plasmonique entre un ruban en silicium et une fente en cuivre[103]: (a) Vue 3D du coupleur hybride métal-oxyde-silicium. (B) Distribution de champ $|E|^2$ dans un plan y-normal du guide d'onde hybride avec le mode TE fondamental guidé dans le ruban en silicium comme champ incident. Ici, $2L_c = 2,5 \mu m$. Les barres d'échelle horizontale et verticale sont respectivement de 1 \( \mu m \) et 0,1 \( \mu m \).

6.2 Méthodes mathématiques et techniques expérimentales

Selon l'approximation $|E|^4$ dans l'équation (6-2), on sait que l'exaltation des substrats SERS peut être estimée par le champ électrique des plasmons métalliques. Les propriétés plasmoniques des objets métalliques peuvent être obtenues en résolvant les équations de Maxwell avec des conditions aux limites spécifiques, qui peuvent être effectuées par de nombreuses méthodes mathématiques. Les techniques de
nanofabrication dans cette thèse sont la lithographie à faisceau d'électrons (EBL) pour
la fabrication des guides d'ondes métalliques sur les guides d'ondes diélectriques
(Si₃N₄) fournis par nos collaborateurs. Après la fabrication, la capacité de détection
SERS des capteurs est caractérisée par un microscope Raman LabRAM 800HR.

6.2.1 Méthodes mathématiques

Les méthodes mathématiques pour la résolution des équations de Maxwell
peuvent être classées en deux groupes: analytiques (problèmes simples) et numériques
(problèmes complexes). Parmi les méthodes numériques, la méthode des différences
finies dans le domaine temporel (FDTD) peut fournir une réponse électromagnétique
des nanostructures métalliques couvrant une large gamme de longueurs d'onde pour
une seule simulation. Nous choisissons donc d'analyser numériquement le capteur
SERS. Le modèle analytique du couplage entre une fente métallique et un ruban
diélectrique est également introduit ici.

◆ La méthode des différences finies dans le le domaine temporel (FDTD)

Les simulations 3D-FDTD dans cette thèse sont menées par un logiciel
commercial, FDTD solutions, de Lumerical Inc. La méthode FDTD, également
appelée méthode de Yee, est d'abord proposée en 1966 par le mathématicien appliqué
Kane S. Yee[125]. De manière simple, cette méthode résout les équations
rotationnelles de Maxwell par itération au fil du temps dans des frontières artificielles
après que les équations différentielles soient transformées en des différences finies
dans le domaine temporel sur une grille de l'espace. Les discrétisations de l'espace et
du temps des équations de Maxwell sont fondamentales. Les champs discrétisés sont

![Figure 6-2 Champs électromagnétiques discrétisés dans une cellule de Yee: (a) la cellule
3D de Yee. (B) la cellule 1D de Yee, qui est développée sur l'axe temporel.](image)

répartis dans la cellule de Yee, comme sur la Figure 6-2-(a). Pour simplifier, le cas de
1D-FDTD est discuté ici, comme sur la Figure 6-2-(b). Les champs électromagnétiques \( E_x \) et \( H_y \) sont alternativement situés sur l'axe \( z \) avec les
numéros de position \( i \) et \( i + 0.5 \). Selon la différence centrale et la valeur moyenne, les
équations ci-dessus peuvent être discrétisées comme suit
\[
\begin{aligned}
H_y^{n+0.5}(i + 0.5) &= H_y^{n-0.5}(i + 0.5) + \frac{2\Delta t}{2\mu\Delta z}(E_x^n(i + 1) - E_x^n(i)) \\
E_x^{n+1}(i) &= \frac{2\varepsilon - \sigma\Delta t}{2\varepsilon + \sigma\Delta t} E_x^n(i) + \frac{2\Delta t}{(2\varepsilon + \sigma\Delta t)\Delta z}(H_y^{n+0.5}(i + 0.5) - H_y^{n-0.5}(i + 0.5))
\end{aligned}
\]

où \(\Delta z\) et \(\Delta t\) sont les variations d'espace et de temps. \(\mu\), \(\varepsilon\) et \(\sigma\) sont la perméabilité magnétique, la permittivité et la conductivité électrique respectivement. Avec l'itération temporelle les champs électromagnétiques aux points discrétisés sont obtenus tels que \(E_x^n(i) \Rightarrow H_y^{0.5}(i + 0.5) \Rightarrow E_x^1(i) \Rightarrow H_y^{1.5}(i + 0.5) \Rightarrow \cdots\).

**Théories de couplage**

Selon l'interaction électromagnétique, le processus de couplage entre deux guides d'ondes peut être modélisé analytiquement, comme sur la Figure 6-3. Dans la littérature, le couplage plasmonique-photonique entre la fente métallique et le ruban diélectrique est analysé par un modèle de couplage fort[99], [102]–[104]. Avec la condition initiale: \(a(0) = 1\) et \(b(0) = 0\), les fractions des modes individuels dans le guide d'onde hybride peuvent être obtenues comme:

\[
\begin{aligned}
a(z) &= \left[\cos(\varphi z) + i\frac{\Delta}{\varphi}\sin(\varphi z)\right]e^{i\phi z} \\
b(z) &= \frac{iK_{ba}}{\varphi}\sin(\varphi z)e^{i\phi z}
\end{aligned}
\]

où \(\Delta = (\gamma_q - \gamma_p)/2\), \(\varphi = \sqrt{\Delta^2 + K_{pq}K_{qp}}\) et \(\phi = (\gamma_q + \gamma_p)/2\). Les constantes corrées de propagation \(\gamma_{p,q}\) sont définies comme \(\gamma_{p,q} = \beta_{p,q} + (K_{pp,qq} - \overline{C}K_{qq,pp})/(1 - \overline{C}^2)\) et les coefficients corrégés de couplage sont définis comme \(K_{pq,qp} = (K_{pq,qp} - \overline{C}K_{qq,pp})/(1 - \overline{C}^2)\). Ici, \(\overline{K}_{mn} = 0.25\omega \int\int (\varepsilon^t - \varepsilon^n)[E_t^m \cdot E_t^n - (\varepsilon^m/\varepsilon^t)E_z^m E_z^n]dxdy\), \(\overline{C} = 0.5(C_{mn} + C_{nm})\) et \(C_{mn} = 0.5 \int\int (E_t^m \times H_t^n) \cdot 2dxdy\). La fraction de l’énergie dans le guide d’onde \(q\) couplé au guide d’onde \(p\) peut être calculée comme:

\[
\eta_{p\rightarrow q} = Re[(C_{qp}a + b)(C_{pq}^*a^* + b^*)]
\]

Figure 6-3 Diagrammes schématiques pour le modèle de couplage fort entre deux guides d'ondes: (a) le guide d'onde unique \(p\), (b) le guide d'onde unique \(q\) et (c) le guide d'onde hybride \(p+q\).
6.2.2 Techniques expérimentales

Les expériences dans cette thèse contiennent la fabrication du capteur SERS et le test de détection SERS.

◆ Fabrication des fentes métalliques

En raison de la taille de quelques dizaines de nanomètres, la fabrication des fentes métalliques est effectuée par EBL. Le processus de fabrication est illustré sur la Figure 6-4, et détaillé ci-dessous:

**La gravure ionique réactive (RIE):** Les guides d'ondes de Si₃N₄ sont recouverts d'une gaine épaisse de SiO₂ (quelques centaines de nanomètres) qui empêche l'interaction évanouissante entre le guide d'onde de Si₃N₄ et le guide d'onde métallique. Ainsi, la RIE de SiO₂ doit être une étape préliminaire avant de fabriquer des guides d'ondes métalliques. La gravure est effectuée par la machine RIE *MU 400 PLASSYS*. Les gaz sont SF₆ et O₂ avec des vitesses d'écoulement de 17 sccm et 6 sccm respectivement. La puissance RIE est de 90 W et la pression est de 4 mTorr dans la chambre.

**Le dépôt du méthacrylate de poly-méthyle (PMMA) et de Espacer 300z est fait par centrifugation:** le PMMA et l'Espacer 300z sont déposés sur la gaine du ruban de Si₃N₄ gravé et nettoyé. Le PMMA est une résine positive pour le faisceau électronique et il est dissous dans le méthyl isobutylcétone (MIBK) avec une concentration de 30 g/L. Une couche de PMMA de 150 nm est déposée sur des échantillons, qui peuvent être utilisés comme masque pour fabriquer des nanostructures de hauteur inférieure à 50 nm (un rapport de 3:1 entre l'épaisseur de PMMA et la hauteur de nanostructure est recommandé). Pour étaler la couche de PMMA, la résine est recuite à 180 °C pendant 10 min. L'Espacer 300Z est un polymère conducteur qui est recuit à 70 °C pendant 10 min. Les paramètres RIE sont choisis comme: accélération 4 000 tr/min, vitesse 3000 tr/min et time 30 sec.

**La lithographie à faisceau d'électrons (EBL):** Les motifs des guides d'ondes métalliques sont écrits dans le masque PMMA par la machine EBL *Raith E-line*. Le filament fonctionne par émission de champ thermique et l'étage est positionné par des interféromètres avec une précision de déplacement de 2 nm. Les paramètres principaux sont choisis comme: tension de colonne 10 kV, ouverture 10 µm (contrôler le courant de faisceau d'électrons), dose 150 µc/cm² et champ d'écriture 50 × 50 µm².

**Le développement:** Pour développer les patterns écrits dans la résine PMMA, le revêtement Espacer 300Z et le revêtement PMMA exposés sont supprimés. D'abord, l'échantillon est immergé dans de l'eau distillée pendant 1 min et l'Espacer 300Z est dissous. Par la suite, l'échantillon est immergé dans un solvant de MIBK et d'IPA avec une proportion volumique de 1:3 pendant 1 min pour éliminer le revêtement de PMMA exposé. Pour nettoyer les résidus, l'échantillon est immergé dans l'IPA pendant 30 sec et séché avec de l'air.
Figure 6-4 Fabrication de fentes métalliques par l’EBL: (a) Revêtement de PMMA et Espacer 300z par centrifugation sur le revêtement des rubans de Si\textsubscript{3}N\textsubscript{4} gravés. (B) EBL. (C) Développement. (D) Dépôt de métaux. (E) Décollage.

**Le dépôt de métaux**: Le dépôt physique en phase vapeur (PVD) des métaux est effectué par la machine PVD MEB 400 PLASSYS. Pour augmenter l’adhérence des nanostructures métalliques sur l’échantillon, une couche (3nm) de chrome (Cr) est déposée. Le Cr est évaporé par faisceau électronique et la vitesse de dépôt est de 0,18 nm/sec. Le métal (Au) est évaporé par effet thermique et la vitesse de dépôt est de 0,3 nm/sec. La pression est $1 \times 10^{-6}$ Torr dans la chambre.

**Le décollage**: Après le dépôt de métaux, l’échantillon est immergé dans l’acétone pendant 24 heures pour éliminer le PMMA non exposé et le métal sur le dessus. L’échantillon est lavé par IPA et séché avec de l’air pour éliminer les résidus.

◆ **Caractérisation du capteur**

La caractérisation concerne principalement la topographie et la détection SERS du capteur.

**Microscopes électroniques à balayage (SEM)**: la machine SEM Hitachi SU 8030 est utilisée pour obtenir les informations morphologiques du capteur. Son filament fonctionne par émission de champ froid et le faisceau d’électrons est accéléré par une tension de colonne (1-30 kV). Un ensemble de lentilles électromagnétiques concentre et scanne le faisceau d’électrons sur la surface de l’échantillon et la résolution spatiale est de 1,0 nm à 15 kV et 1,3 nm à 1 kV. Les signaux détectés proviennent principalement de deux types d’électrons: les électrons secondaires (SE) et les électrons rétrodiffusés (ESB). Les électrons secondaires sont émis par des atomes de l’échantillon excités par le faisceau d’électrons et le nombre d’électrons dépend de la topographie de l’échantillon. Par contre il ne peut pas aller profondément dans la gaine de SiO\textsubscript{2} des rubans de Si\textsubscript{3}N\textsubscript{4}. Les électrons rétrodiffusés ont des énergies plus élevées pour passer la gaine de SiO\textsubscript{2} et interagissent avec les guides d’ondes de Si\textsubscript{3}N\textsubscript{4}.
**Microscope Raman:** Pour caractériser la capacité de détection SERS du capteur, on utilise le microscope Raman, *LabRAM 800HR*, de Horiba, Ltd. Il est équipé d'un laser à l'hélium-néon (632,8 nm, 8,3 mW) et d'un détecteur CCD Peltier (1024 × 256 pixels). Trois objectifs sont disponibles avec les paramètres 10× NA0,3, 50× NA0,8 et 100× NA0,9. Le blocage du filtre pour la diffusion Rayleigh est de 60 dB et le réseau de dispersion est de 600 lignes/mm. La résolution du spectre est de 3 cm⁻¹ et la précision de déplacement de l'étage est de 1 µm. Dans les expériences, les signaux de diffusion Raman rétrodiffusés sont détectés et deux configurations différentes de détection sont présentées sur la Figure 6-5.

![Figure 6-5 Configurations pour la mesure des signaux Raman du capteur SERS intégré sur la puce: (a) Configuration indirecte, où une fibre est utilisée pour connecter le capteur SERS et l'objectif du microscope Raman. (B) Configuration directe, où l'objectif du microscope Raman et le réseau du capteur sont couplés directement en espace libre.](image)

### 6.3 Capteurs SERS basés sur un guide d'onde hybride constitué d'une fente métallique et d'un ruban diélectrique

Cette section présente l'étude théorique du capteur SERS basé sur le guide d'onde hybride constitué d'une fente métallique et d'un ruban diélectrique avec la méthode 3D-FDTD. Il commence par le design du capteur et le couplage photonique-plasmonique entre une fente métallique et un ruban de Si₃N₄. En utilisant l'approximation $|E|^4$, le facteur d'exaltation dans la fente métallique est obtenu. La capacité de détection SERS du capteur est caractérisée sur des molécules de colorants. Les résultats montrent que le capteur SERS peut atteindre un facteur d'exaltation de 10⁻¹⁰² pour la diffusion Raman dans la fente métallique.

#### 6.3.1 Design du capteur

Le schéma du capteur est présenté sur la Figure 6-6 où une fente métallique est située sur le substrat de silice alors qu'un guide ruban de nitrure de silicium (Si₃N₄) est incorporé verticalement avec une distance $Sp$. Le Si₃N₄ est presque transparent pour le régime spectral qui est visible ou proche IR, avec une constante diélectrique élevée $\varepsilon = 4$, ce qui assure un bon confinement des champs électromagnétiques. Le matériau de la fente est choisi en or (Au) ou en aluminium (Al). L'or est l'un des métaux les plus prometteurs pour la plasmonique dans le domaine spectral qui va du rouge au proche infrarouge, avec également une bonne stabilité chimique. L'aluminium est un autre choix pour la fente. Même si une fente d'aluminium a des résonances
plasmoniques plus faibles, son coût peut être très inférieur aux fentes d'or. Les formes des guides d'ondes (fente et ruban) sont toujours rectangulaires. $W_D$, $H_D$, $W_m$ et $H_m$ sont la largeur et la hauteur, de la fente et de la bande respectivement. $Sp$ est la distance entre la fente et la bande. Le matériau de superstrat est l’eau ($\epsilon = 1,33$), qui est le milieu pour l'excitation et le rayonnement des dipôles Raman dans les molécules existantes en solution. Dans le logiciel commercial FDTD solutions, un modèle analytique de permittivité basé sur les données expérimentales est généré automatiquement. Les propriétés optiques de l'or et de l'aluminium qui sont présentées sur la Figure 6-7, sont référencées dans le manuel de E. D. Palik[136] alors que le nitrure de silicium est référencé dans le papier de H. R. Philipp[139].

L’illumination est injectée dans le ruban de Si$_3$N$_4$. Ensuite, la lumière se couple à la fente métallique et y excite des champs plasmoniques. Les champs peuvent induire des dipôles Raman dans les molécules d'analyte, dont le rayonnement excitera les modes plasmoniques guidés par la fente. Les signaux rayonnés sont couplés ensuite dans le ruban de Si$_3$N$_4$, qui est relié à des éléments dispersifs tels qu'un spectromètre. Les spectres Raman des analytes sont obtenus enfin par le détecteur photoélectrique des éléments dispersifs.

Figure 6-6 Schéma du capteur: (a) Section transversale du guide d'onde hybride, où un ruban de nitrure de silicium (Si$_3$N$_4$) rectangulaire avec des côtés $W_D$ et $H_D$ est située sous une fente métallique rectangulaire (Au/Al) avec les côtés $W_m$ et $H_m$ sur le substrat de silice. La distance entre la fente et le ruban est $Sp$. (B) Vue 3D, où la fente métallique de longueur $L$ est placée au-dessus du ruban de Si$_3$N$_4$.

Figure 6-7 Les modèles analytiques de permittivité (a) de l'or, (b) de l'aluminium et (c) de nitrure de silicium, qui sont disponibles dans le logiciel FDTD solutions.

6.3.2 Couplage photonique-plasmonique entre la fente métallique et le ruban de Si$_3$N$_4$

Le couplage photonique-plasmonique entre la fente métallique et le ruban de Si$_3$N$_4$ est le mécanisme de l'excitation du plasmon et de la collection des signaux Raman dans le capteur SERS. Les principes du couplage et de l'efficacité de celui-ci
sont analysés sur la base des simulations FDTD et du modèle de couplage fort.

**Supermodes et battements de champ**

Pour démontrer le couplage photonique-plasmonique, un guide d'onde hybride est choisi comme exemple avec les paramètres: \( W_m = H_m = 30 \text{ nm} \), \( S_p = 10 \text{ nm} \) et \( W_D = H_D = 200 \text{ nm} \). La source incidente est le mode TE \((E_x > E_y, E_z)\) du ruban de Si\(_3\)N\(_4\) et elle est injectée à la position \( z = 0,25 \mu \text{m} \). La distribution de champ électrique \(|E|\) et l'efficacité de couplage sont reportés sur la Figure 6-8. Notez que le champ \(|E|\) dans cette thèse est normalisé avec la valeur maximale du champ électrique de la source incidente. Le processus de couplage est décrit par deux supermodes TE de la superstructure, quasi-pair et impair, dont la dénomination est basée sur les profils de phase. Lorsque deux modes \( k_1, k_2 \) se propagent dans la direction \( z \), leur superposition d'amplitude de champ \( E \) est exprimée comme:

\[
E = \cos(k_1z-\omega t) + \cos(k_2z-\omega t) = 2\cos[0.5(k_1-k_2)z]\cos[0.5(k_1+k_2)z-\omega t].
\]

Il est évident que le champ \( E \) est modulé avec une variation périodique par le terme \( \cos[0.5(k_1-k_2)z] \). Considérant que \( k_1, 2 = (2\pi/\lambda)\text{neff}_{\text{pair}}, \text{impair} \), la période de battement \( L_{\text{beat}} \) peut être exprimée comme:

\[
L_{\text{beat}} = \lambda/\text{Re}(\text{neff}_{\text{pair}} - \text{neff}_{\text{impair}})
\]

où \( \text{neff}_{\text{pair}}, \text{impair} \) est l'indice de réfraction effectif des supermodes, \( \text{Re} \) est la partie réelle d'un nombre complexe et \( \lambda \) est la longueur d'onde dans le vide. Sur la base du modèle de couplage fort, l'efficacité de couplage de l'énergie couplée dans la fente est reportée sur la Figure 6-8-(d). Les champs modaux des deux guides isolés dans les inserts sont obtenus par expansion de mode propre (EME) dans le logiciel FDTD solutions.

![Figure 6-8](image)

Figure 6-8 Couplage photonique-plasmonique dans le guide d'onde hybride constitué d'une fente d'or d'un ruban de Si\(_3\)N\(_4\): (a) Champ électrique \(|E|\) sur un plan x-normal. (b) Champ électrique \(|E|\) de supermode pair avec \( \text{neff}_{\text{pair}} = 3.0141 + 0.1149i \). (c) Champ électrique \(|E|\) du supermode impair avec \( \text{neff}_{\text{impair}} = 1.3780 + 0.0022i \). Les inserts présentent les profils de phase. (d) L'efficacité de couplage \((\lambda = 720 \text{ nm})\) de l'énergie couplée dans la fente du ruban. Les inserts montrent les profils modaux du ruban de Si\(_3\)N\(_4\) isolé et de la fente d'or isolée respectivement.

**Dépendance géométrique de l'efficacité de couplage**

Par souci de simplicité et de clarté, le ruban diélectrique et la fente métallique du capteur SERS sont définis comme carrés, \( W_D = H_D \) et \( W_m = H_m \) (pour plus de commodité, la taille du ruban/de la fente est notée comme \( S_D/S_m \)). La longueur d'onde...
est définie comme 720 nm par exemple. L'efficacité de couplage entre un ruban de Si$_3$N$_4$ et une fente d'or est reportée sur la Figure 6-9. On voit sur la Figure 6-9-(a) que les valeurs maximales de l'efficacité de couplage sont obtenues pour $S_D = 220$ nm alors que $S_m = 40$ nm. L'efficacité du couplage augmente lorsque $Sp$ devient plus petit sauf pour $Sp = 0$ nm. Lorsque la surface inférieure de la fente métallique touche le ruban, la frontière Si$_3$N$_4$-SiO$_2$ du ruban devient une frontière Si$_3$N$_4$-Au. Cela conduit à la modification soudaine du profil modal dans le ruban et ensuite à la diminution de l'efficacité de couplage. Cette diminution d'efficacité avec $Sp = 0$ nm est également observée sur la Figure 6-9-(b). L'espacement $Sp = 10$ nm est la distance optimale entre la fente et le ruban. Sur la Figure 6-9-(b), l'efficacité du couplage augmente avec l'augmentation de la taille de la fente $S_m$, provoquée par l'augmentation du recouvrement évanescant.

Bien que l'augmentation de $W_m$ ou $H_m$ soit bénéfique pour coupler plus d'énergie dans la fente métallique et pour contenir plus de molécules, elle affaiblit le confinement du plasmon dans la fente et réduit le champ plasmonique. Compte tenu de l'objectif d'exalter la diffusion Raman dans la fente métallique, l’intensité du champ est le facteur pertinent, et non l'efficacité du couplage. Ainsi, la taille de la fente d’or est limitée à moins de 70 nm. D'autre part, l'augmentation de $W_D$, $H_D$ peut diminuer la densité d'énergie dans le recouvrement évanescant et ensuite affaiblir le couplage. Ici, la largeur du ruban est limitée à moins de 350 nm.

De même, la dépendance géométrique de l'efficacité de couplage ($\lambda = 530$ nm) entre un ruban de Si$_3$N$_4$ et une fente d'aluminium est indiquée sur la Figure 6-10. L'efficacité du couplage diminue de manière monotone lorsque la taille du ruban $S_D$ diminue et $S_m = 30$ nm. L'efficacité du couplage augmente lorsque $Sp$ devient plus petit sauf pour $Sp = 0$ nm Cette diminution de l'efficacité avec $Sp = 0$ nm est également observée sur la Figure 6-10-(b). L'espacement $Sp = 10$ nm est la distance optimisée entre la fente et le ruban. Dans la Figure 6-10-(b), l'efficacité de couplage augmente d'abord, puis diminue avec l'augmentation de la taille de la fente $S_m$. 

![Figure 6-9 Efficacité de couplage ($\lambda = 720$ nm) entre un ruban de Si$_3$N$_4$ et une fente d'or: (a) en fonction de la taille du ruban $S_D$ pour plusieurs espacements quand $S_m = 40$ nm. (b) en fonction de la taille de la fente $S_m$ pour plusieurs espacements quand $S_D = 200$ nm.](image)
6.3.3 Diffusion Raman exaltée dans le capteur SERS

Étant donné que la diffusion Raman est comprise comme étant deux étapes de processus virtuels, l'excitation des dipôles Raman et le rayonnement des dipôles, l'exaltation électromagnétique du capteur SERS est obtenue en simulant ces deux processus avec la méthode 3D-FDTD. Les résultats permettent de vérifier la validité de l'approximation $|E|^4$ dans le capteur SERS. Ensuite, la dépendance géométrique de l'exaltation est démontrée.

◆ Excitation et rayonnement des dipôles Raman

Pour démontrer l'excitation et le rayonnement des dipôles Raman, un capteur SERS est choisi comme exemple avec les paramètres: $W_m = H_m = 48$ nm, $W_D = H_D = 200$ nm, $S_p = 10$ nm, et $L = 0,61\mu m$, qui est indiqué sur la Figure 6-11-(a).

Pour l'excitation des dipôles Raman, la source est le mode $TE$ du ruban de Si$_3$N$_4$ et il est injecté à la position $z = 0,25\mu m$. La distribution du champ $|E|$ ($\lambda = 720$ nm) sur un plan y-normal avec $y = 22$ nm est présentée sur la Figure 6-11-(b). On voit que le champ électrique dans la fente est plus fort que celui dans le ruban. Le champ amplifié peut exciter des dipôles Raman si des molécules Raman sont dans la fente et donc la diffusion Raman est exaltée. Le champ plasmonique dans la fente a des fluctuations le long de l'axe z. La fente d'or étant de longueur finie, les réflexions sur les facettes de la fente conduisent à des 'interférences du champ plasmonique dans la fente. La fente d'or finie peut être considérée comme une cavité qui piège le champ plasmonique. Le champ piégé se distribue dans la fente selon les règles d'interférence. Le couplage photonique-plasmonique est une voie d'échange d'énergie entre la cavité (la fente) et l'extérieur (le ruban).

Pour le rayonnement des dipôles Raman, un dipôle polarisé le long de l'axe x est situé dans la fente avec les coordonnées (23 nm, 22 nm, 805 nm), sur la Figure 6-11-(c), ce qui est le lieu d'un dipôle Raman excité par le champ local $|E|$ sur la Figure 6-11-(b). Le rayonnement, collecté par le capteur sur le plan de sortie en $z =$
1,3 µm, est reporté sur la Figure 6-11-(d). Le champ total est la somme complexe de nombreux modes guidants ou de fuite. Le rayonnement détectable des dipôles peut se propager dans le mode du ruban de Si₃N₄, comme pour le mode TE sur la Figure 6-11-(e) tandis que le reste du rayonnement échappe au guide d'onde pendant son trajet vers les détecteurs photoélectriques. Le rayonnement détectable est calculé par le recouvrement des profils du champ sur le plan de sortie et du mode TE du ruban.

En tenant compte l'excitation et le rayonnement des dipôles Raman ensemble, les facteurs d'exaltation (EF) de la position (23nm, 22nm, 805nm) sont reportés sur la Figure 6-12. En considérant que le capteur est symétrique par rapport au plan z-normal en z = 805 nm, le trajet de rayonnement d'un dipôle au point (x, y, z) est l'inverse du chemin d'excitation au point (x, y, 1,61µm-z). Ainsi, le terme EFₚₚₚₚ peut s'exprimer comme EFₚₚₚₚₓᵧₜₑₚₑ ≈ |Eₓᵧₜₑₚₑ(z)²|. D'autre part, le rayonnement dipolaire a deux directions opposées de propagation, de sorte que la moitié des signaux Raman sont collectés à la sortie du capteur. De plus, l'approximation |E|⁴ pour estimer le facteur d'exaltation globale doit être modifiée comme:

EFₓᵧₜₑₚₑ = 0.5EF₀ₑₓᵧₜₑₚₑ EFₓᵧₜₑₚₑ = 0.5|Eₓᵧₜₑₚₑ(z)²|Eₓᵧₜₑₚₑ(1,61µm-z)² (6-8)

On voit ci-dessous que EF = EF₀ₑₓᵧₜₑₚₑ ≈ 0.5EF₀ₑₓᵧₜₑₚₑ ⁴, ce qui prouve que l'équation ci-dessus avec cette approximation est valable pour l'analyse du capteur.

Notez que le champ plasmonique dans la fente métallique du capteur est facilement obtenu par une simulation FDTD en résolvant les formules électromagnétiques avec des conditions spécifiques et des sources incidentes. Ensuite, l'estimation du facteur pour chaque position est effectuée simplement, en évitant la simulation complexe du dipôle dans la fente du capteur.

Figure 6-11 Excitation et rayonnement des dipôles Raman dans le capteur SERS. (a) Vue 3D du capteur, où une fente d'or est placée au-dessus du ruban de Si₃N₄. (b) Distribution de champ |E| (λ = 720 nm) dans un plan y-normal avec y = 22 nm lorsque le mode TE du ruban de Si₃N₄ est injecté comme excitation. L'image intercalée montre le profil de champ |E| en (b). (c) Un dipôle polarisé le long de l'axe x est situé avec des coordonnées (23 nm, 22 nm, 805 nm), qui est le lieu d'un dipôle Raman excité par le champ |E| en (b). (d) Distribution de champ |E| (λ = 720 nm) dans le plan z-normal avec z = 1,3 µm lorsque le dipôle est l’excitation. (e) Distribution de champ |E| (λ = 720 nm) du mode TE du ruban de Si₃N₄, qui est identique à l'image intercalée de (b).
Figure 6-12 Approximation $|E|^2$ lorsqu'une molécule est située au point (23nm, 22nm, 805nm) dans le capteur de la Figure 6-11.

**Dépendance géométrique du facteur $EF$**

Lorsque la fente d'or a une longueur de $L = 0,6 \, \mu m$, la dépendance géométrique de l'exaltation dans la fente: $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0,5 \, \mu m \leq z \leq 1,1 \, \mu m]$ est représentée sur la Figure 6-13. Il est évident que $EF$ dans le volume est modulé par l'interférence causée par la réflexion sur les facettes de la fente. Le maximum $EF$ peut atteindre une valeur de l'ordre de $10^3$-$10^4$. Lorsque la taille de la fente $S_m$ augmente, le pic d'exaltation est décalé vers le bleu sur la Figure 6-13-(a) et -(d), parce que la constante de propagation du mode de fente devient plus petite. Lorsque la taille du ruban $S_D$ change, les pics des interférences ne montrent pas de décalage. Lorsque la taille du ruban $S_D$ augmente, le maximum de $EF$ diminue dans le domaine de longueur d'onde inférieur à 700 nm. Pour des longueurs d'onde plus grandes (> 700 nm), la valeur la plus élevée est obtenue pour $S_D = 240 \, \text{nm}$. L'espacement $Sp$ affecte également la propagation du mode, donc il y a des changements des pics lorsque $Sp$ change, mais pas de manière aussi évidente que pour le cas de $S_m$.

Figure 6-13 Maximum et moyenne de l'EF dans une fente d'or du capteur SERS: $[-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0,5 \, \mu m \leq z \leq 1,1 \, \mu m]$. Les courbes $EF$ sont signalées en fonction de la taille de la fente $S_m$ dans (a) et (d), la taille du ruban $S_D$ dans (b) et (e) et l'espacement $Sp$ dans (c) et (f).
Lorsque la fente d'aluminium a une longueur finie \( L = 1,304 \, \mu m \), la dépendance géométrique de l'exaltation dans la fente: \([-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \, \mu m \leq z \leq 1,804 \, \mu m\] est reportée sur la Figure 6-14. Les courbes de \( EF \) ci-dessous sont affectées par les interférences du champ plasmonique dans la fente. Dans la Figure 6-14-(a) et -(d), la diminution de \( S_m \) augmente toujours et produit un léger décalage vers le rouge des pics. Lorsque \( S_m = 30 \, nm \) et \( Sp = 10 \, nm \) sur la Figure 6-14-(b) et -(e), l'augmentation de \( S_D \) déplace les pics du maximum de \( EF \) (\( \lambda > 480 \, nm \)) et de la moyenne de \( EF \) vers le rouge avec des valeurs plus élevées. Pour des longueurs d'onde \( \lambda < 480 \, nm \), la courbe maximale diminue quand \( S_D \) augmente. Lorsque \( S_m \) et \( S_D \) sont constants, les courbes des maxima sont presque identiques sur la Figure 6-14-(c). Par contre les courbes des moyennes montrent une dépendance évidente de \( Sp \) et la plus grande valeur est obtenue pour \( Sp = 30 \, nm \).

Figure 6-14 Maximum et moyenne de \( EF \) dans une fente d'aluminium du capteur SERS: \([-S_m/2 \leq x \leq S_m/2, 0 \leq y \leq S_m, 0.5 \, \mu m \leq z \leq 1,804 \, \mu m\]. Les courbes de \( EF \) sont évaluées en fonction de la taille de la fente \( S_m \) dans (a), (d), la taille du ruban \( S_D \) dans (b), (e), et de l'espacement \( Sp \) dans (c), (f).

6.3.4 Capacité de détection du capteur SERS

Pour les détections effectuées par le capteur SERS, la fente métallique peut facilement être remplie par une petite gouttelette de solution de molécules. Ainsi, la moyenne du facteur \( EF \) de la fente métallique est plus adaptée pour estimer la capacité de détection du capteur que le maximum de \( EF \). Les signaux Raman totaux qui ont été recueillis par le ruban de Si\(_3\)N\(_4\) sont exprimés comme:

\[
P_{Rad} = \frac{4\pi}{3} \varepsilon_0 c n_m N \overline{EF} \left[1 + \frac{2 \rho_R d\sigma_R}{d\Omega} \right] |\overline{E_{inc}}|^2
\]

où \( N \) est le nombre de molécules dans la fente et \( \overline{EF} \) est la moyenne de \( EF \) de la fente. Notez que l'équation ci-dessus se base sur l'hypothèse que les molécules se répartissent uniformément dans la fente. En fait les molécules s'adsorbent de
préférence sur les surfaces de la fente métallique en raison de la physisorption ou de la chimiisorption. Ainsi, les signaux Raman expérimentaux du capteur seront plus forts que l’estimation donnée par l’équation ci-dessus. Pour simplifier, on suppose que le rapport de dépolarisation du tenseur Raman \( \rho_R \) est de 0.

Pour analyser quantitativement la capacité de détection, un capteur avec une fente d’or est choisi comme exemple, dans lequel \( S_D = 320 \text{ nm} \), \( S_m = 30 \text{ nm} \), \( S_p = 20 \text{ nm} \) et \( L = 600 \text{ nm} \). Selon la Figure 6-13-(e), la moyenne de \( EF \) dans la fente d’or est de 60 quand \( \lambda = 830 \text{ nm} \). Les colorants choisis, la rhodamine 6G (RH6G) et le benzotriazole 2 (BTZ) sont considérés comme les molécules Raman. Lorsque la longueur d'onde d'excitation est de 830 nm, le pic de diffusion Raman à 1510 cm\(^{-1} \) (\( \lambda = 949 \text{ nm} \)) de RH6G a une section efficace différentielle de diffusion Raman de \( 2.4 \times 10^{-27} \text{ cm}^2/\text{sr} \) et le pic Raman à 1412 cm\(^{-1} \) (\( \lambda = 940 \text{ nm} \)) de BTZ a une section efficace \( 2.5 \times 10^{-28} \text{ cm}^2/\text{sr} \). La puissance de l'excitation est de 10 mW et la longueur d'onde est de 830 nm. La puissance détectable la plus basse du détecteur se réfère au spectromètre Ocean Optics QE65 Pro. Son efficacité quantique est d'environ 40% à \( \lambda = 940 \text{ nm} \) et le courant d’obscurité est de 4000 e/pixel/sec à 25 °C ou 200 e/pixel/sec à 0 °C. Le nombre d'électrons par seconde, excités par les signaux Raman de RH6G et BTZ sur le détecteur, est représenté sur la Figure 6-15. On voit que la solution de RH6G avec la concentration de \( 1.4 \times 10^{-3} \text{ mole/L} \) est détectable à température ambiante. Si le détecteur est refroidi, RH6G peut être détecté avec la concentration de \( 7.27 \times 10^{-5} \text{ mole/L} \) et BTZ peut être détecté avec la concentration de \( 6.72 \times 10^{-4} \text{ mole/L} \).

![Figure 6-15](image)

Figure 6-15 Nombre d'électrons par seconde excités par les signaux Raman de RH6G et BTZ sur le détecteur d'un spectromètre Ocean Optics QE65 Pro. Le capteur SERS a une fente d'or avec les paramètres: \( S_D = 320 \text{ nm} \), \( S_m = 30 \text{ nm} \), \( S_p = 20 \text{ nm} \) et \( L = 600 \text{ nm} \). L'excitation est le mode \( TE \) du ruban de Si\(_3\)N\(_4\) avec une puissance 10 mW et \( \lambda = 830 \text{ nm} \). Les deux lignes noires sont les courants d’obscurité du spectromètre.

### 6.4 Effet des nanoparticules métalliques sur les détections SERS du capteur

Dans les condition SERS, les détections du signal Raman sont beaucoup plus
sensibles pour les molécules situées dans un petit espace métallique qu’autour d’une seule surface métallique, en raison du champ électrique confiné entre des objets métalliques. Cette section présente l’étude théorique de l’effet de nanoparticules métalliques pour obtenir une amélioration de la capacité de détection du capteur SERS.

6.4.1 Nanoparticules métalliques dans une fente d’or du capteur SERS

Une fente d’or et une nanosphère d’or servent d’exemple pour démontrer le couplage SPP-LSP entre la nanoparticule métallique et la fente métallique du capteur SERS. Le champ local dans la jonction entre les surfaces de la fente et de la particule est en forte relation avec de nombreux facteurs, tels que la position, la taille et le matériau de la particule. La dépendance de EF autour de la nanoparticule dans la fente métallique est discutée.

◆ Couplage SPP-LSP dans une jonction sphère-fente d’or

Ici, le capteur SERS avec une fente d’or est choisi comme exemple pour démontrer le couplage SPP-LSP sur la Figure 6-16-(a). Une sphère d’or avec un diamètre de 44 nm est située au centre du fond de la fente avec les coordonnées centrales suivantes (0 nm, 22 nm, 805 nm). Ensuite, deux espaces de 2nm sont créés dans la jonction sphère-fente sur la Figure 6-16-(b). Avec le mode TE du ruban de Si₃N₄ comme excitation, le SPP dans la fente est excité puis excite le LSP de la sphère d’or. Sur la Figure 6-16-(c) et -(d), un champ intense apparaît dans les gaps de 2nm pour la largeur de la jonction sphère-fente. Notons que le champ électrique sur la Figure 6-16-(c) a des fluctuations le long de l’axe z en raison des interférences dans la fente.

Figure 6-16 Couplage SPP-LSP entre la sphère d’or et la fente d’or du capteur: (a) Vue 3D du capteur avec les paramètres \( W_m = 48 \text{ nm}, H_m = 50 \text{ nm}, W_D = H_D = 200 \text{ nm}, \) \( Sp = 10 \text{ nm}, \) and \( L = 0,61 \text{ µm}. \) (b) Section transversale Z-normale de la sphère avec une diamètre de 44 nm située au centre du fond de la fente. (c) - (d) Distributions du champ |\( E | (\lambda = 720 \text{ nm}), qui sont normalisées avec la valeur maximale du champ électrique de l’excitation, (c) dans un plan y-normal avec \( y = 22 \text{ nm} \) et (d) dans un plan z-normal avec \( z = 0,805 \text{ µm}. \)
Les courbes d'absorption de la sphère au-dessus du ruban sans la fente d'or et de la même sphère dans la fente du capteur sont reportées sur la Figure 6-17. La résonance LSP de la sphère à 546 nm n'apparaît pas sur la courbe d'absorption de la sphère dans la fente, de sorte que l'interaction électromagnétique directe entre le ruban et la sphère est très faible. Les champs électromagnétiques dans la fente sont modulés de manière constructive ou destructive par les interférences. La sphère est excitée par le SPP modulé dans la fente. Donc, le plasmon de la sphère est également modifié par les interférences. L'épaulement à 624 nm et les deux pics à 587 nm et 846 nm sont les modes LSP excités par l'interférence constructive des SPP dans la fente autour de la sphère. Ils sont désignés comme modes SPP-LSP, qui résultent de l'interaction du SPP dans la fente fini et du LSP dans la sphère.

Pour discuter de l'exaltation SERS dans les gaps de la jonction sphère-fente, un point est choisi avec les coordonnées (23 nm, 22 nm, 0.805 µm), qui est le centre du gap droit. Le facteur $EF$ en ce point est représenté par la courbe rouge sur la Figure 6-17. Les $EF$s du même point sont également inclus pour la comparaison lorsque la sphère d'or ou la fente d'or est seulement présente. Avec la jonction sphère-fente, la courbe de $EF$ atteint un niveau de $10^6$ à 693 nm, soit 4 ordres de grandeur supérieurs par rapport au cas de la fente ou de la sphère seule.

**Figure 6-17 Absorption d’une sphère d’or et $EF$ en un point comme exemple: (a) Absorptions de la sphère Au dans la fente du capteur et de la même sphère lorsque la fente est enlevée. (b) $EF$ du point avec les coordonnées (23 nm, 22 nm, 805 nm), pour trois cas: la sphère d'or, la fente d'or et la jonction sphère-fente d'or.**

**Influences des facteurs sur l'EF autour le nanoparticule dans la fente d'or**

Étant donné que le champ électrique dans la jonction sphère-fente est beaucoup plus fort qu’ailleurs, le volume autour de la particule est considéré comme le volume de la sonde du capteur. Ici, le volume est défini comme un cuboïde: $[-W_m/2 \leq x \leq W_m/2, 0 \leq y \leq H_m, Z_{sphere} - R_{sphere} \leq z \leq Z_{sphere} + R_{sphere}]$, où $Z_{sphere}$ est la coordonnée Z du centre de la sphère et $R_{sphere}$ est le rayon de la sphère. La dépendance du facteur d'exaltation ($EF$) dans le volume de la sonde autour de la particule métallique dans la fente est illustrée sur la Figure 6-18. Sauf contre-indication, les paramètres de la
particule dans la fente sont les mêmes que ceux de la Figure 6-16.

Figure 6-18 Moyenne de $EF$ dans le volume de la sonde lorsque (a) la sphère a un déplacement transversal de 0 nm, 1 nm ou 2 nm respectivement avec les coordonnées $x = 0$, 1, 2 nm, $y = 22$ nm et $z = 0,805 \mu m$. (b) la sphère a la position longitudinale $z = 0,6 \mu m$, $z = 0,7 \mu m$ et $0,805 \mu m$ respectivement lorsque $x = 0$ nm et $y = 22$ nm. (c) la sphère a un diamètre $D = 42$ nm, 44 nm et 46 nm respectivement avec les coordonnées $x = 0$ nm, $y = 21$, 22 et 26 nm respectivement et $z = 0,805 \mu m$. (d) le matériau de la sphère est l'aluminium. (e) la particule a des formes différentes. Le côté du cube est de 44 nm. La hauteur et le diamètre du cylindre sont de 44 nm. Lorsque l'axe du cylindre est le long de la direction $z$ / la direction $y$, il est marqué par "H" / "V". Le diamètre de la sphère est de 44 nm. (f) la particule a des formes différentes avec le même centre $x = 17$ nm, $y = 5$ nm et $z = 0,805 \mu m$. La taille de toutes les particules est de 10 nm. Notez que le volume de la sonde est défini comme: $[10 \text{ nm} < x < 24 \text{ nm}; 0 < y < 12 \text{ nm}; 798 \text{ nm} < z < 812 \text{ nm}]$. Les graphiques d'insertion dans les figures sont les facteurs maximums d'exaltation dans le volume de la sonde.

Pour obtenir des signaux Raman plus élevés avec le capteur, une méthode consiste à mettre plus de nanoparticules dans la fente. D'autre part, les particules métalliques dans la fente introduisent également des pertes pour les signaux. Pour le démontrer, le signal Raman rayonné par un dipôle polarisé le long de l'axe x près de la 1ère sphère d'or est analysé avant et après l'ajout de la 2ème sphère d'or dans la fente. Deux cas avec les diamètres 44 nm et 10 nm sont choisis comme exemple et les courbes de $EF_{\text{Rad}}$ sont reportées sur la Figure 6-19. La grande sphère peut provoquer la perte des signaux Raman rayonnés par le dipôle autour de la 1ère sphère. Sa taille bloque la propagation des signaux Raman dans la fente.
Figure 6-19 Facteurs d'exaltation du rayonnement \( EF_{\text{rad}} \) du dipôle Raman avec/sans la 2\(^{\text{ème}}\) sphère d'or dans la fente. La 1\(^{\text{ère}}\) sphère d'or avec un diamètre de 44nm est située avec les coordonnées \( x = 0 \) nm, \( y = 22 \) nm et \( z = 0.805 \) µm. La 2\(^{\text{ème}}\) est placée avec \( x = 0 \) nm, \( y = 22 \) nm et \( z = 1,0 \) µm. La 1\(^{\text{ère}}\) sphère d'or avec un diamètre de 10nm est située avec des coordonnées \( x = 17 \) nm, \( y = 22 \) nm et \( z = 0.805 \) µm. La 2\(^{\text{ème}}\) est placé avec \( x = 17 \) nm, \( y = 22 \) nm et \( z = 1,0 \) µm. Le dipôle Raman est polarisé le long de l'axe x et au centre du gap de la jonction sphere-fente avec les coordonnées \( x = 23 \) nm, \( y = 22 \) nm pour la grande sphère ou \( y = 5 \) nm pour la petite sphère et \( z = 0.805 \) µm. La ligne en tirets blancs marque le plan de sortie où l'énergie de rayonnement est obtenue.

6.4.2 Nanoparticules métalliques dans une fente d'aluminium du capteur SERS

Bien que la fente d'aluminium présente une exaltation plus faible que la fente d'or pour la diffusion Raman, le coût de la fabrication du capteur est très faible si le capteur SERS utilise une fente d’aluminium. En outre, la fente d'aluminium peut fonctionner pour une longueur d'onde inférieure à 600 nm, ce qui favorise l'augmentation de la section efficace de la diffusion Raman en raison de la dépendance en \( 1/\lambda^4 \).

\[ \text{Couplage SPP-LSP dans une jonction sphère-fente d’aluminium} \]

Ici, le capteur SERS avec une fente d'aluminium est choisi comme exemple pour démontrer le couplage SPP-LSP, ce qui est montré sur la Figure 6-20. Une sphère d'aluminium avec un diamètre de 26 nm est située au centre du fond de la fente avec les coordonnées (0 nm, 13 nm, 1,124 µm). Ensuite, deux gaps de 2nm sont créés dans la jonction sphere-fente. La longueur d’onde de l’excitation plasmonique de l’aluminium est plus courte que celle de l’or, de sorte que la longueur d’onde concernée ici est définie comme: 200 nm - 800 nm. Une impulsion du mode \( TE (\lambda = 530 \) nm) du ruban de \( \text{Si}_3\text{N}_4 \) est injectée comme excitation. L'intensité du champ autour de la sphère d'aluminium augmente considérablement par rapport au champ \( |E| \) avant que la sphère ne soit ajoutée. Notez que le champ \( |E| \) dans la fente a des fluctuations le long de l'axe z en raison des interférences.
Figure 6-20 Couplage SPP-LSP entre la sphère d'aluminium et la fente d'aluminium du capteur: (a) - (b) Vue 3D du capteur avec $W_m = H_m = 30$ nm, $W_D = H_D = 250$ nm, $S_p = 10$ nm, and $L = 1.248$ µm. Une sphère est située au centre du fond de la fente. (c) - (d) Distributions du champ $|E|$ ($\lambda = 530$ nm) dans la fente sans particules. (e) - (f) Distributions du champ $|E|$ ($\lambda = 530$ nm) dans la fente après que la sphère est ajoutée. Pour montrer clairement les images, les images dans (d) et (f) sont étirées dans la direction de l'axe x. L'excitation est le mode $TE$ du ruban de Si$_3$N$_4$.

Les courbes d'absorption de la sphère d'aluminium sont reportées sur la Figure 6-21-(a). Lorsque la fente d'aluminium est supprimée, le pic d'absorption de la sphère est à 210 nm dans la gamme UV: c'est la résonance LSP de la particule individuelle. Lorsque la fente est ajoutée, l'absorption de la sphère augmente, la jonction sphère-fente ayant un fort couplage électromagnétique avec les champs évanescents du ruban. Étant similaire à la jonction d’or, le LSP de la sphère d'aluminium dans la fente s'hybride avec le SPP de la fente qui est considérée comme une cavité. Un point particulier est choisi comme exemple avec les coordonnées (14 nm, 13 nm, 1,124 µm) pour discuter de l’exaltation SERS dans les gaps de la jonction sphère-fente. L'EF est représenté par la courbe rouge sur la Figure 6-21-(b). Les EFs du même point sont également inclus pour comparaison lorsque seule la sphère ou la fente est présente. Lorsque la sphère est dans la fente, l'EF atteint un niveau de $10^5$ à 494 nm, 5 - 6 ordres de grandeur supérieurs à la fente ou à la sphère isolée.
Figure 6-21 Absorptions de la sphère d’aluminium et EFs du point choisi comme exemple:
(a) Absorptions de la sphère dans la fente du capteur et la même sphère lorsque la fente est enlevée. (b) EFs du point à (14 nm, 13 nm, 1,124 µm), pour trois cas: la sphère d’aluminium, la fente d’aluminium et la jonction d’aluminium sphère-fente.

♦ Influences des facteurs sur l’EF autour le nanoparticule dans la fente d’aluminium

Le volume autour de la particule est défini comme le volume de la sonde du capteur par un volume cuboïde: 

\[-W_m/2 \leq x \leq W_m/2, 0 \leq y \leq H_m, Z_{csphere} - R_{sphere} \leq z \leq Z_{csphere} + R_{sphere}\]

où $Z_{csphere}$ est la coordonnée Z de la sphère et $R_{sphere}$ est le rayon de la sphère. La dépendance du facteur d'exaltation dans le volume de la sonde autour de la particule métallique est illustrée sur la Figure 6-22. Sauf contre-indication, les paramètres de la particule dans la Figure 6-22-(a) - (e) sont les mêmes que ceux de la Figure 6-22-(a) et -(b). La Figure 6-22-(f) montre les facteurs d'exaltation du rayonnement du dipôle Raman avec/sans la 2ème sphere d'aluminium dans la fente. Similaire au cas de l'or, 1/3 des signaux rayonnés par le dipôle Raman sont perdus en raison de la 2ème sphère lorsque le diamètre de la sphère est de 26 nm. Cependant, il n'y a presque aucune perte des signaux Raman causée par la 2ème sphère métallique lorsque le diamètre est de 10 nm.

6.4.3 Capacité de détection SERS du capteur avec des nanoparticules métalliques

Selon l'équation (6-9), qui est basée sur deux hypothèses (les molécules Raman se répartissent uniformément dans la fente et le rapport de dépolarisation Raman $\rho_R = 0$), la capacité de détection SERS du capteur avec des nanoparticules métalliques est estimée quantitativement sur la Figure 6-23-(a), l'intensité des signaux Raman (le nombre d'électrons par seconde) délivré par le capteur SERS avec une sphère d'or étant indiquée. Le capteur SERS sur la Figure 6-16 est choisi comme exemple pour montrer la capacité de detection SERS du capteur avec une fente d'or et une sphère d'or. La moyenne de EF dans le volume de la sonde est de $3,052 \times 10^4$ lorsque la longueur d'onde d'excitation est de 693,5 nm, selon la Figure 6-18-(a). La puissance d'excitation est de 10 mW et la longueur d'onde est de 693.5 nm. La puissance détectable la plus basse du détecteur se réfère au spectromètre Ocean Optics QE65.
Pro. Les colorants, à savoir la rhodamine 6G (RH6G) et le benzotriazole 2 (BTZ), sont considérés comme les molécules Raman. On voit que la solution RH6G avec la concentration de $1,36 \times 10^{-5}$ mole/L, et la solution BTZ avec la concentration de $1,13 \times 10^{-4}$ mole/L sont détectables avec le capteur à température ambiante. Si le détecteur est refroidi, BTZ peut être détecté avec la concentration de $6,06 \times 10^{-6}$ mole.

Figure 6-22 Moyenne de l'EF dans le volume de la sonde lorsque (a) la sphère a un déplacement transversal de 0 nm, 1 nm ou 2 nm respectivement avec les coordonnées $x = 0$, $1, 2$ nm, $y = 13$ nm et $z = 1,124$ µm. (b) la sphère a la position longitudinale $z = 0,55$ µm, $z = 0,95$ µm et $1,124$ µm respectivement tandis que $x = 0$ nm et $y = 13$ nm. (c) la sphère a un diamètre $D = 10$ nm, 18 nm et 26 nm respectivement avec les coordonnées $x = 0$ nm, $y = 5, 9$ et 13 nm respectivement et $z = 1,124$ µm. (d) le matériau de la sphère est Au, Ag et Al respectivement. (e) la particule a des formes différentes avec les mêmes coordonnées $x = 0$ nm, $y = 13$ nm et $z = 1,124$ µm. Le côté du cube est de 26 nm. La hauteur et le diamètre du cylindre sont de 26 nm. Lorsque l’axe du cylindre est le long de la direction $z$ / la direction $y$, il est marqué par "H" / "V". Le diamètre de la sphère est de 26 nm. Les graphismes d’insertion de (a) - (e) sont les facteurs maximum d'exaltation dans le volume de la sonde. (f) Facteurs d'exaltation du rayonnement $EF_{Rad}$ du dipôle Raman avec/sans la 2ème sphère d'aluminium dans la fente. La 1ère sphère d'aluminium avec un diamètre de 26nm est située dans la fente avec les coordonnées $x = 0$nm, $y = 13$nm et $z = 1,124$ µm. La 2ème sphère d'aluminium avec un diamètre de 10nm est située avec les coordonnées $x = 8$nm, $y = 5$nm et $z = 1,124$ µm. Lorsque le capteur contient une sphère d'aluminium dans la fente d'aluminium, comme sur la Figure 6-20, l'intensité des signaux Raman (le nombre d'électrons par seconde) est présentée sur la Figure 6-23-(b). La moyenne de $EF$ dans le volume de la sonde est de 495 lorsque la longueur d'onde d'excitation est 494 nm, selon la Figure 6-22-(a). La concentration la plus faible détectée est plus élevée que celle du capteur.
d’or. La solution RH6G avec la concentration de $1.21 \times 10^{-3}$ mole/L et la solution BTZ avec la concentration de $1.15 \times 10^{-2}$ mole/L sont détectables à température ambiante. Si le détecteur est refroidi, BTZ peut être détecté avec la concentration de $6.06 \times 10^{-4}$ mole/L.

Figure 6-23 Nombre d'électrons par seconde excité par les signaux Raman de RH6G et BTZ sur le détecteur d'un spectromètre Ocean Optics QE65 Pro. (a) Le capteur SERS possède une sphère d'or dans la fente d'or, comme la Figure 6-16. (b) Le capteur SERS possède une sphère d'aluminium dans la fente d'aluminium, comme la Figure 6-20. Les deux lignes noires sont les courants d’obscurité du spectromètre.

6.5 Expériences et résultats préliminaires

Les recherches théoriques et numériques ont prédit qu'un capteur SERS est obtenu avec le guide d'onde hybride constitué d'une fente métallique et d'un ruban diélectrique. D'autre part, la faisabilité du capteur doit être vérifiée expérimentalement. Certains prototypes du capteur sont fabriqués et leur capacité de détection SERS est caractérisée par des molécules de bleu de méthylène (MB) comme molécules de la sonde.

6.5.1 Échantillons de guides rubans de Si$_3$N$_4$

Les guides rubans de Si$_3$N$_4$ ont été fabriqués par nos collaborateurs du LETI, CEA à Grenoble. La structure et les paramètres des guides d'ondes sont présentés sur la Figure 6-24. La section transversale des guides d'ondes est semi-elliptique avec une largeur de 320 nm et une hauteur de 200 nm. L'épaisseur de la gaine de SiO$_2$ sur les guides d'ondes est de 700 nm et le champ évanescents des guides est totalement dans cette gaine épaissie. Avant de fabriquer les guides d'ondes métalliques, la gaine de SiO$_2$ doit donc être gravée.

Figure 6-24 Structure et paramètres des guides rubans d'ondes de Si$_3$N$_4$. (a) Section transversale des guides d'ondes. (b) Vue latérale des guides d'ondes pour montrer les épaisseurs des couches.
Les longueurs des guides d'ondes sont d'environ 8 mm et il y a 47 guides d'ondes répartis parallèlement sur une zone de 8 mm × 5 mm sur l'échantillon. Une grille est fabriquée à chaque extrémité du guide d'onde, comme sur la Figure 6-25. Les grilles agissent comme entrée/sortie de lumière des guides d'ondes et le meilleur angle de couplage (λ = 633 nm) est de 25°. Pour renforcer le couplage avec l'excitation, le guide d'onde est élargi à la fin et la zone de grille augmente.

Figure 6-25 Grille d'entrée/de sortie des guides rubans d'ondes de Si₃N₄. (a) Vue latérale du grille à une extrémité du guide d'onde. (b) Image optique d'une extrémité de guide d'onde avec une grille. Le guide d'onde est élargi à la fin pour renforcer le couplage des guides avec l'excitation.

6.5.2 Fabrication de fentes d'or sur des guides rubans d'ondes de Si₃N₄

Dans le processus RIE, il est difficile de contrôler l'épaisseur de SiO₂ restante exactement. En plus, la gaine de SiO₂ ne peut pas être visualisée clairement sous SEM. Ainsi, l'épaisseur est difficile à mesurer. Pour résoudre ce problème, on utilise une gravure en escaliers qui est présentée sur la Figure 6-26. Les guides d'ondes sur l'échantillon sont divisés en quatre zones et la différence de temps de gravure entre deux zones voisines est de 0,5 min. Après chaque gravure, la propagation de la lumière (λ = 633 nm) est vérifiée dans les guides d'ondes de la zone “A”. Lorsque la lumière commence à fuir les guides de la zone “A”, on pense que la gaine de SiO₂ de 700 nm est enlevée. Ainsi, la vitesse de gravure moyenne est d'environ 74 nm/sec. La gaine de SiO₂ de la zone “B” est estimée à 36 nm et celle de la zone “C” est de 72 nm. Ce n'est pas une méthode exacte pour contrôler la gaine de SiO₂ restante, mais elle est pertinente pour les expériences.

Figure 6-26 Gravure avec les escaliers de la gaine de SiO₂ sur des guides rubans de Si₃N₄. Les demi-ellipses pourpres sont les sections transversales des guides d'ondes de Si₃N₄. Les guides d'ondes sur l'échantillon sont divisés en quatre zones et le temps de gravure différent entre deux zones voisines est de 0,5 min.
Après la gravure, l'étape suivante consiste à fabriquer les fentes d'or au-dessus des guides d'ondes de Si₃N₄. Les techniques connexes de la fabrication ont été introduites sur la Figure 6-4. Pour aligner les fentes d'or et les guides de Si₃N₄, le pattern d'écriture est une matrice de fentes avec une taille 39 × 40, comme la Figure 6-27-(a). Les éléments de la matrice sont composés de deux dalles de 350 nm × 500 nm et le gap entre deux dalles est de 70 nm. La taille de la matrice est d'environ 40 µm × 50 µm. Dans chaque colonne, il existe une fente de 100 nm apparaissant entre deux éléments voisins. Entre deux colonnes, les fentes des éléments ont un changement vertical de 30 nm. Ainsi, 11 (320 nm / 30 nm ≈ 11) fentes seront situés le guide d'onde de Si₃N₄ qui traverse la matrice le long de la direction transversale de la matrice.

Pour l'écriture de la matrice dans le masque PMMA, la première tâche consiste à calibrer la direction des guides d'ondes de Si₃N₄ par les marqueurs de positionnement. La direction de propagation du guide d'onde de Si₃N₄ est définie comme la direction transversale de la matrice. Ensuite, le faisceau électronique focalisé est enlevé de la partie centrale de l'échantillon et les matrices de fentes sont écrites dans le masque PMMA. Après le développement, le dépôt d'or et le décollage, les matrices de fentes d'or sont obtenues sur les guides d'ondes de Si₃N₄, qu'est présentée sur la Figure 6-27-(b) et -(c). On voit que le guide de Si₃N₄ ne dépasse pas le centre de la matrice, ce qui est dû à l'écart de position. Cependant, il existe encore des fentes d'or couvrant le guide. L'épaisseur des dalles d'or est de 40 nm et les autres paramètres géométriques peuvent être trouvés dans l'image SEM ci-dessous.

Figure 6-27 Fabrication de la matrice de fentes d'or. (a) Pattern d'une matrice de fentes avec une taille de 39 × 40. Un guide d'onde de Si₃N₄ traverse la matrice le long de la direction transversale. (b) Image optique d'une matrice de fentes d'or sur un guide d'onde de Si₃N₄ après décollage. (c) Image SEM des éléments de la matrice de fentes d'or.
6.5.3 Caractérisation de la capacité de détection SERS

Pour caractériser la capacité de détection du capteur SERS, les molécules de bleu de méthylène (MB) sont choisies comme les molécules Raman. L'analyte MB est dissous dans de l'eau distillée avec une concentration de $10^{-4}$ mole/L. Une petite gouttelette de solution MB de 4 µL est déposée et séchée sur l'échantillon, comme la Figure 6-28. Il convient de noter que le réseau de fentes est loin (plusieurs millimètres) des extrémités des guides de sorte que les réseaux ne sont pas couverts par des molécules MB. Les mesures Raman sont effectuées par un microscope commercial Raman Labram. Dans la figure ci-dessous, les symboles "×" marquent les quatre positions où les signaux Raman sont mesurés, qui seront discutés dans la discussion suivante.

La configuration directe pour détection SERS décrite sur la Figure 6-5-(b), le laser d'excitation (633 nm, 8,3 mW) est focalisé directement sur les grilles des guides d'ondes de Si$_3$N$_4$ par l'objectif Labram (10×, NA 0.3) et les signaux Raman sont collectés directement par le même objectif. Les signaux Raman des molécules MB sont observés dans les grilles des guides de Si$_3$N$_4$ dans la zone “B” de la Figure 6-26. Les signaux de sortie de deux guides représentatifs (notés comme $N2T5$ et $N2T6$) dans la zone “B” sont reportés sur la Figure 6-29. Le but de la mesure des signaux “Out of Grating” est de supprimer la possibilité que la zone des grilles soit polluée par des molécules MB. Il est prouvé qu'il n'y a pas de molécules MB sur des grilles. Ainsi, les pics Raman ne viennent que des guides d'ondes couverts par les matrice de fentes d'or. Les signaux de diffusion Raman classiques obtenus à la position sans fentes d'or et les signaux SERS obtenus directement sur matrice de fentes sont inclus. On voit que le pic Raman à 1625 cm$^{-1}$ apparaît dans les signaux "In grating" obtenus dans des grilles des guides de Si$_3$N$_4$. Cela signifie que le capteur SERS constitué du ruban de Si$_3$N$_4$ et une matrice de fentes d'or peuvent détecter les signaux SERS des molécules MB.
Figure 6-29 Signaux SERS de molécules MB sur les matrice de fentes d'or couvrant les guides d'ondes de Si₃N₄. Les signaux sont obtenus par la configuration directe décrite sur la Figure 6-5-(b). (a)-(b) montrent les signaux Raman à les quatre positions décrite sur la Figure 6-28. Les deux guides d'ondes représentatifs (notés comme N2T5 et N2T6) sont dans la zone “B” de la Figure 6-26. Dans (c)-(d), les symboles “×” marquent les positions du laser d'excitation focalisé par l'objectif Labram (10×, NA 0.3).

Pour analyser quantitativement le facteur d'exaltation (EF) de la SERS, les segments des spectres dans la boîte bleue dans la Figure 6-29 sont représentés sur la Figure 6-30. Le fond de fluorescence a été supprimé. Les pics de 1625 cm⁻¹ et 1391 cm⁻¹ sont ajustés par le modèle de Lorentz. Les facteurs d'exaltation (EF) sont obtenus en normalisant l'intensité maximale des spectres SERS à l'intensité du spectre de diffusion Raman classique. On voit que le capteur SERS composé de la fente d'or et du ruban de Si₃N₄ peut exalter la diffusion Raman de molécules MB.

Figure 6-30 Ajustement des pics de 1625 cm⁻¹ et 1391 cm⁻¹ des spectres Raman des molécules MB par le modèle Lorentz. Les facteurs d'exaltation (EF) sont obtenus en normalisant l'intensité maximale des spectres SERS à l'intensité du spectre Raman classique.
La zone “A” est gravée pendant 9,5 min par RIE et les guides d'ondes de Si₃N₄ ne peuvent plus guider la lumière. Sur la Figure 6-31-(a), le spectre Raman ou de fluorescence des molécules MB n'apparaît pas à la sortie du guide d'onde de Si₃N₄ alors que la matrice de fentes peut donner un spectre SERS de molécules MB. Les signaux dans la gamme de 1000 cm⁻¹ à 2000 cm⁻¹ sont la fluorescence de Si₃N₄. La zone “C” est gravée pendant 8,5 min et la gaine de SiO₂ est d'environ 72 nm. Sur la Figure 6-31-(b), le pic Raman à 1625 cm⁻¹ est presque inobservable, ce qui apparaît comme un petit pic. Son intensité est proche du niveau de bruit. L'effet de la fluorescence étant plus fort que la diffusion de Raman, le spectre fluorescent est observable.

Figure 6-31 Signaux détectés sur (a) la grille d'un guide d'onde de Si₃N₄ dans la zone “A” (noté comme N2T2) et la matrice de fentes couvrant, (b) la grille d'un guide d'onde de Si₃N₄ dans la zone “C” (noté comme N2P1) et la matrice de fentes recouvrant.

◆ Configuration indirecte pour la detection SERS

Lorsque l'échantillon est testé par la configuration indirecte sur la Figure 6-5-(a), les signaux SERS des molécules MB ne sont pas observés par le Labram. Sur la Figure 6-32, le spectre Raman de la fibre est seulement observé. Le signal de fond de la fibre est si fort que les signaux MB sur les capteurs ne sont pas observés.

Figure 6-32 Configuration indirecte pour caractériser la capacité de détection. (a) Comparaison du spectre MB obtenu directement sur la matrice de fentes d'or et le spectre Raman de la fibre dans la configuration indirecte décrite dans (b). L'objectif Labram (10×, NA 0.3) est utilisé pour focaliser le laser sur la tête de fibre.
6.6 Conclusions et perspectives

Cette thèse présente un capteur SERS basé sur un guide d'onde hybride constitué d'une fente métallique et d'un ruban diélectrique et une méthode pour améliorer la capacité de détection SERS en plaçant des nanoparticules métalliques dans la fente du capteur. Il a été prouvé théoriquement que la diffusion Raman des molécules dans la fente métallique du capteur peut être exaltée par le champ plasmonique dans la fente métallique et les signaux Raman peuvent être augmentés considérablement si une nanoparticule métallique est placée dans la fente. Ensuite, la faisabilité du capteur est prouvée par les expériences.

L'outil mathématique est la méthode 3D-FDTD, qui peut résoudre les équations de Maxwell avec des conditions spécifiques. Le résultat d'une simulation peut fournir une réponse électromagnétique des nanostructures métalliques couvrant un large domaine de longueurs d'onde. Sur la base de l'approximation $|E|^4$ et des informations sur le champ, les facteurs d'exaltation (EF) des substrats SERS sont estimés. Le couplage photonique-plasmonique entre une fente métallique et un ruban diélectrique est analysé par le modèle de couplage fort. Les expériences sont principalement la fabrication des prototypes du capteur et le test de la capacité de détection SERS. La fabrication faite dans la thèse concerne principalement les fentes métalliques, réalisée par le procédé standard de l'EBL. La capacité de détection SERS des prototypes du capteur est caractérisé par deux configurations pour la détection du signal, basées sur un microscope Raman.

Les simulations numériques démontrent que le guide d'onde hybride peut transformer efficacement l'énergie entre le mode photonique et le mode plasmonique. Les processus, l'excitation du champ plasmonique dans la fente, et le rayonnement des dipôles Raman, sont simulés pour démontrer le principe de fonctionnement du capteur. Sur la base de l'analyse modale, l'influence des paramètres géométriques sur le couplage dans le guide d'onde hybride est étudiée pour démontrer la stratégie afin d'optimiser l'intensité du champ électromagnétique dans la fente métallique. Les résultats numériques montrent qu'un capteur SERS basé sur le guide d'onde hybride constitué de la fente d'or et du ruban de Si$_3$N$_4$ peut être réalisé avec un facteur $EF$ de $10^2$-10$^3$ dans la fente. Si la fente est en aluminum, le facteur EF moyen est plus petit, inférieur à 10. Un capteur spécifique avec une fente d'or est choisi comme exemple. Il peut détecter une solution de molécules RH6G avec une concentration de $1,4 \times 10^{-3}$ mole/L à température ambiante avec le spectromètre Ocean Optics QE65 Pro. Si le détecteur est refroidi, la molécule RH6G peut être détectée avec une concentration de $7,27 \times 10^{-5}$ mole/L et BTZ peut être détectée avec une concentration de $6,72 \times 10^{-4}$ mole/L.

Pour améliorer la capacité de détection SERS du capteur, une nanoparticule métallique est placée dans la fente métallique. L'étude théorique de l'effet des nanoparticules métalliques sur l'amélioration de la capacité de détection SERS du
capteur est discutée. Sur la base des champs électromagnétiques et des distributions de charge, on sait que les modes SPP-LSP apparaissent dans la jonction sphérique-fente métallique, en raison de l'interaction électromagnétique entre la particule métallique et la fente finie (une cavité semi-ouverte). La nanoparticule métallique dans une fente d'or peut fournir en moyenne un facteur $EF$ jusqu'à $10^6$ dans le volume autour du particule. La particule métallique dans une fente d'aluminium fournit une moyenne de $EF$ de $10^5$. Les influences de la position, de la taille, et de la forme de la particule sur le facteur $EF$ du volume de la sonde ont été étudiées pour optimiser les performances du capteur. La perte sur les signaux introduite par les particules dans la fente est discutée aussi si plus de deux particules sont placées dans la fente du capteur. Pour caractériser quantitativement la capacité de détection du capteur, deux capteurs spécifiques avec une fente d'or et une fente d'aluminium sont choisis comme exemples, le détecteur étant le spectromètre Ocean Optics QE65 Pro. La solution de RH6G avec une concentration de $1,36 \times 10^{-5}$ mole/L et la solution de BTZ avec une concentration de $1,13 \times 10^{-4}$ mole/L sont détectables à température ambiante par le capteur avec la fente d'or. Si le détecteur est refroidi, BTZ peut être détectée avec une concentration de $6,06 \times 10^{-6}$ mole/L. Pour le capteur avec la fente d'aluminium, la solution RH6G avec une concentration de $1,21 \times 10^{-3}$ mole/L et la solution de BTZ avec une concentration de $1,15 \times 10^{-2}$ mole/L sont détectables à température ambiante. Si le détecteur est refroidi, BTZ peut être détectée avec une concentration de $6,06 \times 10^{-4}$ mole/L.

La faisabilité du capteur SERS est vérifiée aussi par les expériences. Les signaux des prototypes du capteur sont détectés expérimentalement. Les prototypes du capteur sont obtenus en fabriquant les matrices de fentes d'or sur les guides d'ondes de Si$_3$N$_4$. Les molécules de bleu de méthylène (MB) sont choisies, qui sont dissoutes dans de l'eau distillée et déposées sur les matrices de fentes d'or. Les pics Raman des molécules MB sont observés à la sortie de deux guides d'ondes de Si$_3$N$_4$ couverts par des matrices de fentes d'or. À $1625 \text{ cm}^{-1}$, les facteurs d'exaltation ($EF$) des capteurs sont respectivement de 1,70 et 2,65 par rapport à l'intensité de la diffusion Raman classique sur l'échantillon.

Dans les perspectives du capteur SERS, le travail devrait se concentrer sur la fabrication et la caractérisation du capteur SERS. Les résultats expérimentaux jusqu'à maintenant juste vérifient la faisabilité du capteur SERS. Il reste du travail à faire pour optimiser la capacité de détection du capteur. Par exemple, l’espacement entre la fente métallique et le ruban de Si$_3$N$_4$ est encore plus élevé que la valeur optimale de 10 nm obtenue par les investigations numériques. Les fentes d'or des prototypes du capteur ont une largeur de 50 à 70 nm. Si les fentes sont rétrécies, la capacité de détection SERS est meilleure. En résumé, après preuve de sa faisabilité, la fabrication contrôlable et précise du capteur en fonction de la structure du capteur optimisée par des investigations numériques est la prochaine tâche dans les recherches à suivre sur
le capteur SERS. Un autre travail important est le dépôt des nanoparticules métalliques dans la fente du capteur pour vérifier l'effet de la particule observé dans les recherches théoriques.

L'intégration du capteur SERS avec un micro-laser et un micro-spectromètre permet de réaliser un système SERS intégré pour une détection SERS peu coûteuse et portable. L'objectif final de cette recherche est de réaliser des dispositifs SERS à bas coût et compacts et de les implanter dans les téléphones intelligents à l'avenir.
Figure A1 Electric field $|E|$ distributions around an in-slot sphere that has the longitudinal position $z = 0.6 \ \mu m$ (a-c), $z = 0.7 \ \mu m$ (d-g) and $0.805 \ \mu m$ (h-j) respectively while $x = 0 \ \text{nm}$ and $y = 22 \ \text{nm}$. This situation is discussed in Figure 4-12.
Figure A2 Electric field $|E|$ distributions around an in-slot particle that has different shapes: (a-d) cube, (e-g) cylinder “V” and (h-j) cylinder “H”, with the same center coordinates $x = 0$ nm, $y = 22$ nm and $z = 0.805$ µm. The cube side is 44 nm. The height and the diameter of the cylinder are both 44 nm. When the axis of the cylinder is along the z-direction/ the y-direction, it is marked with “H” / “V”. The sphere diameter is 26 nm. These particles are discussed in Figure 4-15.

Figure A3 Electric field $|E|$ distributions around an in-slot particle that has different shapes: (a-b) sphere, (c-e) cylinder “V”, (f-g) cylinder “H” and (h-i) cube, with the same center coordinates $x = 17$ nm, $y = 5$ nm and $z = 0.805$ µm. The cube side is 10 nm. The height and the diameter of the cylinder are both 10 nm. When the axis of the cylinder is along the z-direction/ the y-direction, it is marked with “H” / “V”. The sphere diameter is 10 nm. These particles are discussed in Figure 4-16.
References


References

Micro-capteurs SERS basés sur les circuits photoniques-plasmoniques et les nanoparticules métalliques

La spectroscopie Raman exaltée de surface (SERS) est largement utilisée comme un outil non-intrusif et sans marquage pour identifier les empreintes spectrales moléculaires dans des applications comme la pharmacologie, la salubrité des aliments, etc. Cette thèse présente un micro-capteur SERS basé sur un guide d'ondes hybride constitué de fentes métalliques (Au/AI) et de rubans diélectriques (Si3N4) et sur une méthode pour promouvoir la capacité de détection SERS en plaçant des nanoparticules métalliques dans la fente du capteur.

L'étude théorique du capteur est principalement menée par la méthode des différences finies dans le domaine temps en trois dimensions (3D-FDTD) qui fournit la réponse électromagnétique à large bande des nanostructures métalliques. Les facteurs d'exaltation du capteur sont estimés par l'approximation $\text{E}^{\text{H}}$. Les expériences sont basées principalement sur la fabrication de fentes métalliques, qui est réalisée par la lithographie à faisceau d'électrons (EBL), et sur la caractérisation de la capacité de détection SERS des capteurs.

Les résultats montrent que les signaux Raman donnés par les capteurs SERS sont détectables. Les nanoparticules métalliques, qui sont situées dans le capteur, peuvent améliorer considérablement la capacité de détection SERS. En combinant le capteur SERS avec les éléments photoniques et électro-niques, un système de détection SERS entièrement intégré sur une puce peut être développé dans un proche avenir pour des détections SERS portables et stables.

Mots clés : Raman, effet augmenté en surface - capteurs optiques - plasmons – optique intégrée.

Micro SERS Sensors based on Photonic-plasmonic Circuits and Metallic Nanoparticles

Surface-enhanced Raman spectroscopy (SERS) is widely used as a non-intrusive and label-free tool to identify the molecular spectral fingerprints in pharmacology, biology, etc. This thesis presents a SERS sensor based on the hybrid waveguide made of metallic (Au/AI) slots and dielectric (Si3N4) strips and a method to improve the SERS-detection capacity by placing metallic nanoparticles into the sensor's slot.

The theoretical investigation of the sensor is mainly conducted by the 3D finite-difference time-domain method (3D-FDTD) which provides the broadband electromagnetic response of metallic nanostructures. The enhancement factors in the sensor’s slot are estimated based on the $\text{E}^{\text{H}}$-approximation. The experiments are mainly the fabrication of metallic slots, which is conducted by the electron beam lithography (EBL), and the characterization of the SERS-detection capacity of the sensors.

The results show that the Raman signals given out by the SERS sensors are detectable. Metallic nanoparticles, which are located in the sensor's slot, can improve dramatically the SERS-detection capacity. By combining the SERS sensor with the extended photonic and electronic elements, a fully-integrated on-chip SERS detection system on a chip can be developed in the near future for portable and stable SERS detections.

Keywords: Raman effect, surface enhanced - optical detectors - plasmons (physics) – integrated optics.

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