

A COHERENT COUPLING BETWEEN GRAPHENE PLASMON AND MOLECULAR VIBRATION IN STRONG COUPLING REGIME

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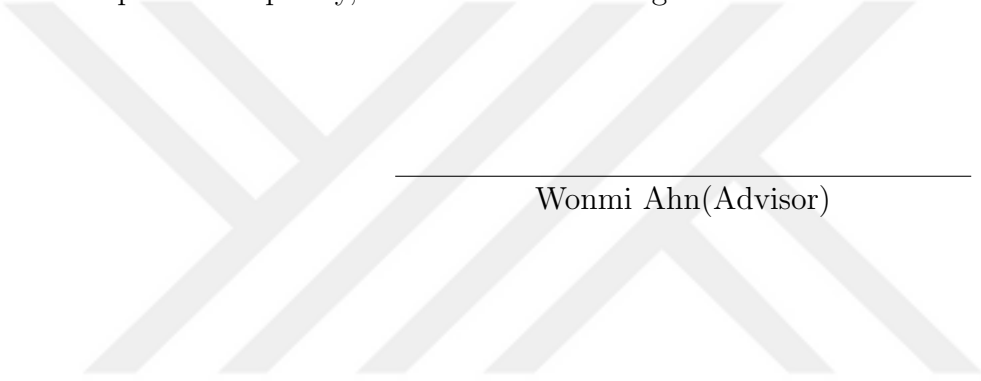
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August 2024

A coherent coupling between graphene plasmon and molecular vibration in strong coupling regime

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August 2024

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



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ABSTRACT

A COHERENT COUPLING BETWEEN GRAPHENE PLASMON AND MOLECULAR VIBRATION IN STRONG COUPLING REGIME

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M.S. in Materials Science And Nanotechnology

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Manipulating the energy states of atoms or molecules is of great interest due to its unlimited potential in spectroscopy, analytical chemistry, atomic structural analysis, imaging, chemical and biological sensing, and many other fields of micro-nanotechnology. Various ways of atomic or molecular energy modulation have been employed to date, such as electric or magnetic field excitation, molecular vibrational or rotational excitation, quantum tunneling, and laser excitation. When electromagnetic wave interacts with materials, it may fall into either a weak, i.e., Fano resonance and Purcell effect, or strong coupling regime depending on the coupling strength. The formation of hybridized polaritonic states in the strong coupling regime opens up a new way to modify materials' physical and chemical properties by altering energy levels of the material excitation. While the formation of polaritonic states has been demonstrated for excitonic transitions, the same phenomenon can also take place with molecular vibrations. In general, a Fabry-Pérot (FP) cavity having two parallel metal or dielectric mirrors is used to induce strong coupling as a cavity optical mode interacts with molecular vibrations of a material placed in the cavity. However, a planar optical cavity has a limited spatial resolution for monitoring polaritonic states. Moreover, strong coupling in the FP cavity represents an ensemble-average due to spatially-varied optical fields inside the FP cavity.

To address some of the limitations of the FP cavity, I used a deep metal grating as a new optical resonator to demonstrate vibrational strong coupling (VSC). First, I simulated the optical properties of the deep metal grating and found that the hybridization between localized surface plasmon resonances and magnetic polaritons is responsible for generating strong mid-infrared optical resonances.

When single-layer graphene was integrated into the grating, the grating resonances showed Fano line shapes as a result of a weak coupling between discrete graphene plasmon modes and continuum grating resonances. In addition, with the addition of a molecular absorber to the deep metal grating, VSC was achieved with tunability in polaritonic energy states by changing the system parameters including the grating height and widths, as well as the chemical potential applied to the graphene. In parallel with simulations, I generated a large area of double-layer graphene by chemical vapor deposition and fabricated deep metal grating structures by electron-beam lithography and inductively-coupled plasma etching.

Keywords: light-matter interaction, strong coupling, deep metal grating, mode hybridization, graphene plasmons, molecular vibrations, nanofabrication, simulation.

ÖZET

GÜÇLÜ BAĞLANTI REJİMİNDE GRAFEN PLAZMONU VE MOLEKÜLER TİTREŞİM ARASINDAKİ TUTARLI BAĞLANTI

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Atomların veya moleküllerin enerji durumlarını manipüle etmek, spektroskopi, analitik kimya, atomik yapı analizi, görüntüleme, kimyasal ve biyolojik algılama gibi mikro-nanoteknolojinin pek çok alanında sınırsız bir potansiyel taşıdığı için büyük ilgi çekmektedir. Elektrik veya manyetik alan uyarımı, moleküler titreşim veya dönme uyarımı, kuantum tünelleme ve lazer uyarımı gibi çeşitli yöntemler, atomik veya moleküler enerji modülasyonu için kullanılmaktadır. Elektromanyetik dalgaların malzemelerle etkileşimi, bağlanma gücüne bağlı olarak, Fano rezonansı ve Purcell etkisi gibi zayıf veya kuvvetli bağlanma rejimlerine girebilir. Kuvvetli bağlanma rejiminde hibritleşmiş polaritonik durumların oluşumu, malzeme uyarımının enerji seviyelerini değiştirerek malzemelerin fiziksel ve kimyasal özelliklerini değiştirmek için yeni bir yol sunar. Polaritonik durumların oluşumu eksitonik geçişler için gösterilmişken, aynı fenomen moleküler titreşimlerde de gerçekleşebilir. Genellikle, iki paralel metal veya dielektrik aynanın bulunduğu bir Fabry-Pérot (FP) boşluğu, boşlukta yer alan malzemenin moleküler titreşimleri ile boşluk optik modunun etkileşimi yoluyla kuvvetli bağlanmayı indüklemek için kullanılır. Bununla birlikte, düzlemsel bir optik boşluk, polaritonik durumların izlenmesinde sınırlı bir mekansal çözünürlüğe sahiptir. Ayrıca, FP boşluğundaki kuvvetli bağlanma, FP boşluğundaki optik alanların mekansal olarak değişmesi nedeniyle bir topluluk ortalamasını temsil eder.

FP boşluğunun bazı sınırlamalarını ele almak için, titreşimsel güçlü ku-plajı (VSC) göstermek için yeni bir optik rezonatör olarak derin bir metal kafes kullandım. Öncelikle, derin metal kafesin optik özelliklerini simüle ettim ve yerleştirilmiş yüzey plazmon rezonansları ile manyetik polaritonlar

arasındaki hibridizasyonun güçlü orta kızılötesi optik rezonanslar üretmekten sorumlu olduğunu buldum. Tek katmanlı grafen kafese entegre edildiğinde, kafes rezonansları, ayrık grafen plazmon modları ile sürekli kafes rezonansları arasındaki zayıf kuplajın bir sonucu olarak Fano çizgi şekilleri gösterdi. Ek olarak, derin metal kafese bir moleküler soğurucu eklenerek, kafes yüksekliği ve genişlikleri ile grafene uygulanan kimyasal potansiyel dahil olmak üzere sistem parametrelerini değiştirerek polaritonik enerji durumlarında ayarlanabilirlikle VSC elde edildi. Simülasyonlara paralel olarak, kimyasal buhar biriktirme yöntemiyle geniş bir çift katmanlı grafen alanı oluşturdum ve elektron demeti litografisi ve endüktif olarak eşlenmiş plazma aşındırma yöntemiyle derin metal kafes yapıları ürettim.

Anahtar sözcükler: ışık-madde etkileşimi, güçlü bağlantı, derin metal ızgara, mod hibridizasyonu, grafen plazmonları, moleküler titreşimler, nanofabrikasyon, simülasyon.

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To Those who Sacrificed Their Life to Make My Country
Free from Tyranny

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Chapter 1

Light-Matter Interaction In Strong Coupling Regime

1.1 Introduction

Materials possess different types of energy levels based on their atomic, molecular, and solid-state structures, and manipulating these energy levels offers advantages in various fields of micro-nano technology. The energy levels can be electronic, vibrational, spin, rotational, or magnetic in nature. There are many examples of utilizing the control over energy levels. Electronic energy alteration facilitates the operation of semiconductor devices [1]; manipulating vibrational energy levels allows spectroscopic measurement, such as Raman, impacts chemical reactions, and catalysis [2]. Altering the excitonic energy level was also found to be advantageous in photovoltaics [3], quantum dots [4], and excitonic polaritonic devices [5]. One of the promising ways to control energy levels is utilizing light, which is well-known as light-matter interaction. I am going to describe the classical and quantum aspects of this interaction, the types of light-matter interactions, and how they can be utilized. At the end of this chapter, I will describe the simulation methodology followed in this thesis as well.

1.2 Light-Matter Interaction

The effects of light-matter interaction can be understood from the absorption, emission, reflection, scattering, and fluorescence effects. When the light is absorbed by any media, it excites the electrons of the atoms and changes its energy level from lower to higher if the energy gap between the levels matches the incident light energy. When the electrons return back to a lower energy state, they emit the absorbed energy, which is known as emission. Sometimes, light just changes its direction while passing through a media, which is called scattering. Depending on the elasticity of the scattering, it can be elastic or Rayleigh scattering and inelastic or Raman scattering.

One important resonator to utilize light-matter interaction is the optical cavity. Fabry-Pérot (FP) cavity is a simple form of the optical cavity where two mirrors are placed parallel to each other. When light enters through one mirror, it reflects back and forth inside the cavity. There will be constructive interference between the reflected waves for a certain cavity thickness, t_c that allows the phase matching.

$$t_c = \frac{m\lambda}{2} \tag{1.1}$$

Here, m is the positive integer, and λ is the wavelength. The phase matching condition for an FP cavity is obtained when the length that light travels for one reflection is an integer multiple of the wavelength. A standing wave is formed by the superposition of the reflected beam inside the cavity creating a resonant condition in the cavity. Based on the cavity thickness, there can be multiple wavelengths that can form the standing wave. For lower wavelengths, the number of nodes and anti-nodes will be increased [6].

The cavity decay rate is a very important parameter of an optical cavity. In the late 60s, Drexhage explained the concept of the decay rate for a quantum emitter [7]. Through the demonstration of the change of decay rate of the fluorescence

molecules as a function of the distance of a reflective surface, he explained the rate at which a weak perturbation causes a quantum system to go from one energy eigenstate to a set of energy eigenstates in a continuum. For an optical cavity, the decay rate is a measure of the rate of reduction of light intensity inside the cavity. The cavity decay rate is denoted by κ and expressed as [8]

$$\kappa = \frac{\omega}{2Q} \quad (1.2)$$

When any material is placed inside an optical cavity, if the transitional energy levels of this material match with the cavity resonance energy, an interaction happens between these two resonances. Based on the strength of this interaction, it can be weak coupling or strong coupling.

1.2.1 Weak Coupling Regime

Weak coupling happens when the coupling strength is less than the decay rates of molecular transition and cavity modes. This phenomenon is often called the Purcell effect. The Purcell effect explains the spontaneous emission of a quantum emitter modified inside an optical cavity. E.M. Purcell first demonstrated it for a nuclear magnetic resonator [9]. It has also been demonstrated to quench the emission rate [10], as monomeric optical microscopy [11], and photoluminescence quantum yield enhancement [12].

The emission rate enhancement often quantified by the so-called Purcell factor is expressed as follows [13],

$$F = \frac{\gamma}{\gamma_0} = 1 + \frac{6\pi\epsilon_0^2}{|\mathbf{d}|^2} \frac{1}{k^3} \text{Im} [\mathbf{d}^* \cdot \mathbf{E}_s(\mathbf{r}_d)] \quad (1.3)$$

Here, γ is the free space emitter decay rate, γ_0 is the emitter decay rate inside an optical cavity, $\mathbf{d}$ is the dipole moment, k is the wavenumber at free space,

and $\mathbf{E}_s(\mathbf{r}_d)$ is the net scattered field. This expression can be applied not only to quantum systems but also to classical systems [14].

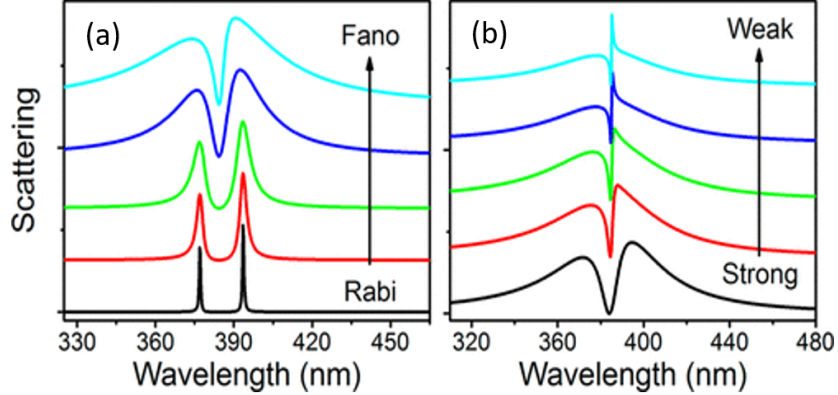


Figure 1.1: A coupled oscillator model was demonstrated to show the transformation from (a) Rabi splitting, e.g., strong coupling regime to Fano resonance, which belongs to weak coupling regime, and (b) strong Fano to weak Fano based on the oscillators' coupling strength. (Reprinted with permission from “J. Phys. Chem. C 2014, 118, 5, 2710–2717”. Copyright © 2014, American Chemical Society)

Apart from the Purcell effect, there is another phenomenon that belongs to the weak coupling regime known as Fano resonance. The primary indicator of Fano resonance is the asymmetric spectral line shape in any type of spectroscopy. Fano resonance happens due to the interference between the discrete energy state with a continuum mode [15][16]. To describe the asymmetry of the line shape the following formula is applied [17],

$$I_i(\omega) = I_{i0} \times \frac{\left(1 + \frac{\omega - \omega_i}{q_i \Gamma_i}\right)^2}{1 + \left(\frac{\omega - \omega_i}{\Gamma_i}\right)^2} \quad (1.4)$$

Where I_{i0} is the intensity of the peak, q_i is the asymmetric factor of the Fano peak, Γ_i is the peak width indicator, and ω_i is the central wavelength. If there are multiple asymmetric peaks that interfere together, the multiple Fano fitting simply involves the summation of all the Fano curves.

$$I(\omega) = \sum_{i=1}^k I_i(\omega) \quad (1.5)$$

In this formula, the coupling strength is indicated by the characteristic Fano parameter, q_i . Fano resonance has been utilized in many fields, for example, in refractive index sensing [18], optical switching [19], and broadband light manipulation [20].

1.2.2 Strong Coupling Regime

Due to the strong coupling between material transition and optical resonance, different energy eigenstates are formed that are distinctive in nature from the original resonance modes. These energy states are called polaritonic energy states [21]. Polaritons can be formed due to phononic [22], excitonic [23], or plasmonic [24] interaction of materials with light. The strong coupling phenomena are most widely studied for the excitonic transition of various materials. When the material with excitonic transition is located inside an optical cavity, the excitonic mode strongly couples with the cavity mode, which is evident from the peak splitting in the transmission spectra or from the avoided crossing of the dispersion diagram [25].

A classical mechanical representation of strong coupling is illustrated in Figure 1.2. the eigenfrequency of the uncoupled system can be represented as $\omega_A^o = \sqrt{\frac{k_A}{m_A}}$ and $\omega_B^o = \sqrt{\frac{k_B}{m_B}}$. At the time of coupling between the two systems, the equation of motion can be expressed as [26]

$$m_A \ddot{x}_A + k_A x_A + \kappa(x_A - x_B) = 0 \quad (1.6)$$

$$m_B \ddot{x}_B + k_B x_B - \kappa(x_A - x_B) = 0 \quad (1.7)$$

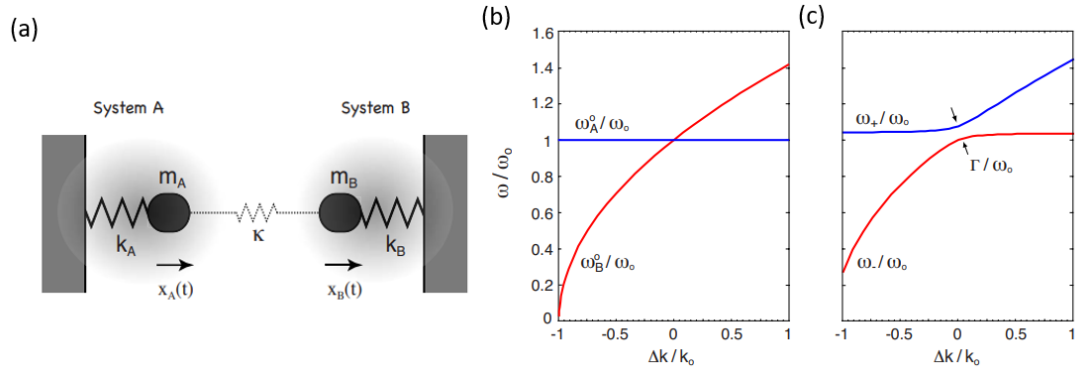


Figure 1.2: Classical mechanical description of strong light-matter coupling. (a) Two classical mechanical oscillators, A and B, with mass m_A, m_B , and spring constant k_A, k_B , are coupled by coupling strength g . (b) Two uncoupled oscillators with frequency ω_A and ω_B . (c) Anticrossing and frequency splitting $[\omega_+ - \omega_-]$ due to strong coupling. (Reprinted with permission from “Am. J. Phys. 78, 1199–1202 (2010)”. Copyright © 2010, AIP Publishing)

By solving the equations of motion, we can have the eigenfrequency for the coupled state expressed by

$$\omega_{\pm}^2 = \frac{1}{2} \left[\omega_A^2 + \omega_B^2 \pm \sqrt{(\omega_A^2 - \omega_B^2)^2 + 4\Gamma^2\omega_A\omega_B} \right] \quad (1.8)$$

Here, $\omega_A = \sqrt{\frac{k_A+g}{m_A}}$, $\omega_B = \sqrt{\frac{k_B+g}{m_B}}$ and $\Gamma = \frac{\sqrt{\frac{g}{m_A}}\sqrt{\frac{g}{m_B}}}{\sqrt{\omega_A\omega_B}}$. When coupling happens in between the two oscillators, e.g., when $\kappa \neq 0$, $\Gamma = [\omega_+ - \omega_-]$. For the coupling to be labeled as strong coupling, the frequency splitting should be higher than the linewidth of the oscillators. In other words, the following expression should be satisfied,

$$\frac{\Gamma}{\left(\frac{\gamma_A}{m_A} + \frac{\gamma_B}{m_B}\right)} > 1 \quad (1.9)$$

Where γ_A and γ_B are the damping rates of the systems A and B, respectively. In this case, the Rabi frequency can be given by $\Omega_R = \frac{\Gamma}{\omega_o}$.

Another popular way of explaining strong coupling is Jaynes–Cummings model

where the material transition is considered to be a two-level system which is resonant with an optical cavity mode [27][28].

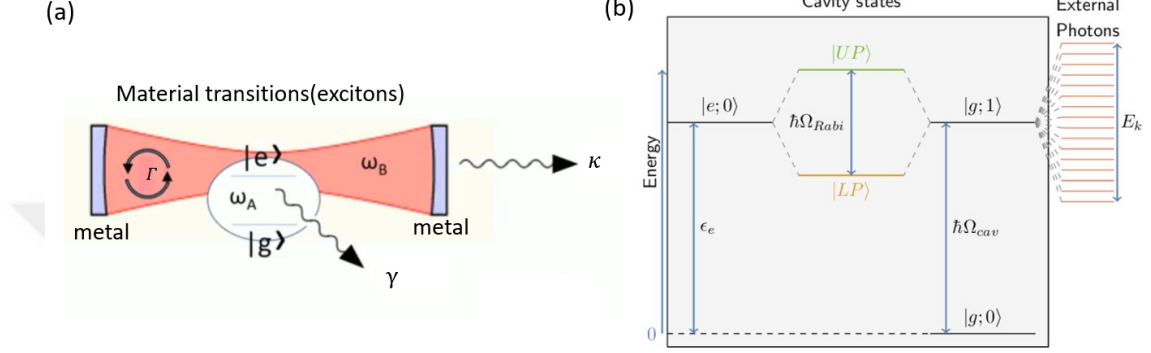


Figure 1.3: (a) Excitonic material inside a cavity. The material transition has a decay rate γ , and the cavity decay rate is κ . $|e\rangle$ and $|g\rangle$ are denoting the ground state and excited state of the molecules. (b) Energy diagram for cavity coupled case. The excitonic materials inside an optical cavity form upper and lower polaritons separated by $\hbar\omega_R$. (Reprinted with permission from “arXiv:2104.09631 [physics.chem-ph]”. CC BY 4.0)

The Hamiltonian for Jaynes–Cummings model expressed as follows,

$$\hat{H} = \frac{\hbar\omega_B}{2}\hat{\sigma}_z + \hbar\omega_A\hat{a}^\dagger\hat{a} + \hbar g (\hat{\sigma}_+\hat{a} + \hat{\sigma}_-\hat{a}^\dagger) \quad (1.10)$$

where $\hbar$ is plank’s constant, ω_A and ω_B are the atomic transition frequency and cavity resonance frequency, respectively, and g is the coupling strength. $\hat{\sigma}_z$ is the operator to represent the atomic state, $\hat{\sigma}_+$ and $\hat{\sigma}_-$ are the operators representing the change of states, $\hat{a}^\dagger$ and $\hat{a}$ are the operators to add and remove the photon in the field mode.

Under the strong coupling condition, by utilizing the above expression, we can get the energy eigenstates of the upper and lower polaritons as follows,

$$|UP_n\rangle = \cos\left(\frac{\theta_n}{2}\right)|e;0\rangle + \sin\left(\frac{\theta_n}{2}\right)|g;1\rangle \quad (1.11)$$

$$|LP_n\rangle = \sin\left(\frac{\theta_n}{2}\right) |e; 0\rangle - \cos\left(\frac{\theta_n}{2}\right) |g; 1\rangle \quad (1.12)$$

Here, $|e; 0\rangle$ represents the atom in the excited state, $|g; 1\rangle$ is for the atom at the ground state, θ_n is the mixing angle depends on the detuning, Δ between ω_a and ω_c .

The corresponding energy eigenvalues of UP and LP for the above eigenstates can be given by,

$$E_{UP} = \hbar \left(\omega_B + \sqrt{\frac{\Delta^2 + \kappa^2}{2}} \right) \quad (1.13)$$

$$E_{LP} = \hbar \left(\omega_B - \sqrt{\frac{\Delta^2 + \kappa^2}{2}} \right) \quad (1.14)$$

From these expressions, the Rabi splitting energy can be found as,

$$\hbar\Omega_R = 2\hbar\sqrt{\left(\frac{\Delta}{2}\right)^2 + g^2} \quad (1.15)$$

in the strong coupling regime, the coupling strength between molecular transition and the cavity mode should be higher than the decay rates of individual oscillators, i.e., $g \gg \kappa, \gamma$.

1.2.3 Vibrational Strong Coupling

Apart from the excitonic transitions, the vibrational mode of molecules has also been studied to realize strong coupling phenomena back in 2015 [29][30]. In this case, a molecule that has a strong vibrational mode is placed into an optical microcavity. If the thickness of the cavity is properly adjusted to generate a resonance that spectrally matches with the molecular vibrational peak, Rabi splitting

can be observed in the transmission spectra of the coupled system [21]. For instance, the vibrational mode of the $\nu(\text{C}=\text{O})$ bond has a very sharp resonance at 1730 cm^{-1} . When a material that has a $\nu(\text{C}=\text{O})$ chemical bond is placed inside a microcavity with a thickness of approximately $2\text{ }\mu\text{m}$, vibrational strong coupling (VSC) can be observed.

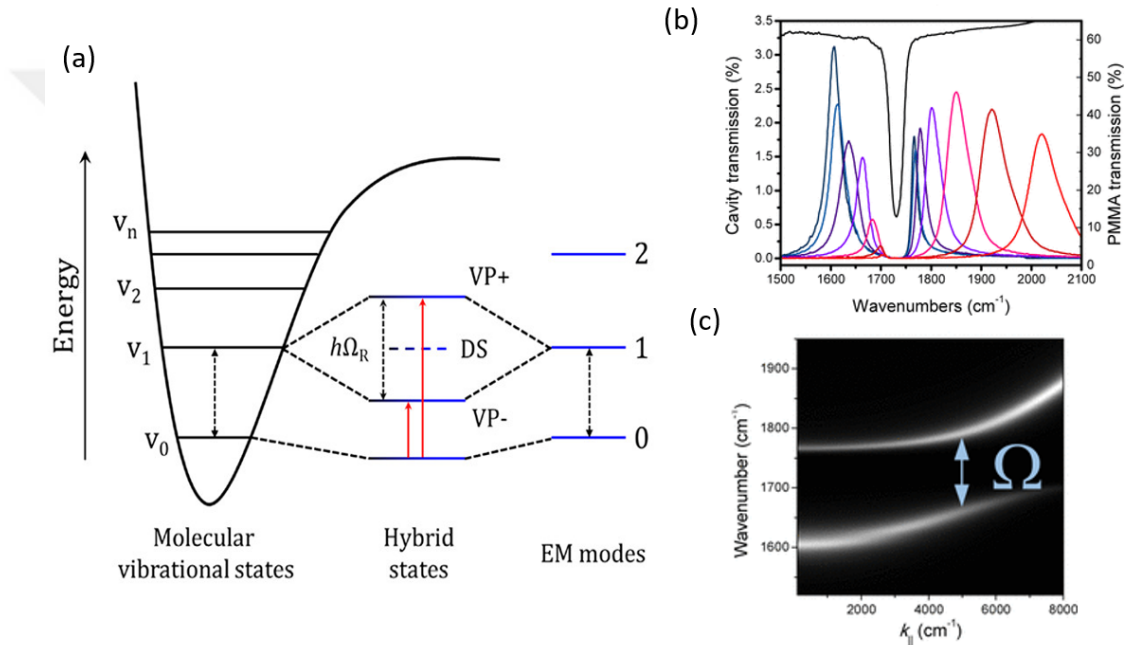


Figure 1.4: (a) Vibrational energy state transition explaining VSC. $VP+$ and $VP-$ are the upper and lower polaritons, respectively. (Reprinted with permission from “J. Am. Chem. Soc. 2021, 143, 41, 16877–16889”. Copyright © 2021 American Chemical Society) (b) Transmission curves obtained at varied incident angles and Rabi splitting along the $\nu(\text{C}=\text{O})$ peak from poly(methyl methacrylate) (PMMA) located inside an FP cavity, (c) An avoided crossing and Rabi splitting from the dispersion curve. (Reprinted with permission from “ACS Photonics 2015, 2, 1, 130–136”. Copyright © 2014 American Chemical Society)

Similar to the excitonic strong coupling, VSC also produces hybrid energy states known as upper ($VP+$) and lower ($VP-$) polaritonic states separated by Rabi energy $\hbar\Omega_R$. The Rabi energy is proportional to the square root of the concentration of the molecule, $\hbar\Omega_R \propto \sqrt{C}$. Unique to its nature, VSC provides a novel avenue for modulating chemical reactivity since molecular vibrational modes entail nuclear motions along the reaction coordinates associated with the bond

formation and dissociation [31][32]. Alongside the impact of VSC on reaction kinetics, it also allows selective modulation of ground-state reactivity [33], energy transfer between molecules [34], and modulation of enzyme activity [35].

1.3 Motivation

So far, the most utilized optical resonator to investigate VSC is the FP cavity. However, there is a nonuniformity of the light momentum inside an optical microcavity [36]. Therefore, the light-matter interaction varies at different special locations inside the cavity, and it is not always possible to achieve strong coupling in a selected location of an optical cavity. Moreover, the FP cavity has some limitations in spatial control as it only allows access to molecules participating in VSC at its narrow edges. These limitations necessitate an open cavity design where the molecules present outside the cavity so that the molecules participating in strong coupling will be accessible. To address the limitations, I have employed an open optical resonator made of deep metal grating. Previously, some plasmonic metal grating has been employed to investigate VSC with shorter depth [37]. However, these gratings are extremely sensitive to the incident angle; even 1° variation of angle can greatly affect the response. In our study, I utilized a deep metal grating with a depth ranging from 0.5 to $1.0\ \mu\text{m}$ that is capable of utilizing the magnetic response generated due to the anti-parallel current loop along the grating trench as well as plasmonic enhancement at the edges of the metal grating. Moreover, it shows significant angle insensitivity until 20° of incident angle.

Modulation of the energy eigenstates generated from strong coupling opens up the possibilities of more controllable integrated photonics and quantum computing when molecular excitation is used. However, the polaritonic energy modulation in the case of VSC is still unexplored. In this study, I have investigated the impact of graphene plasmon (GP), which is active in the mid-IR range, on the modulation of vibrational polaritonic energy states. I have shown that extreme electromagnetic wave confinement happens in the upper and lower polaritonic spectral locations through the utilization of GP. Due to its tunability with the

variation of the chemical potential, these energy states can be altered by tuning the biasing voltage applied to the graphene sheet.

1.4 Simulation Methodology

To investigate optical properties of the deep metal grating structure, I used commercially available Ansys Lumerical v2019. For the periodic structure simulation, I employed the finite difference time domain (FDTD) module of the software. I utilized the 2D environment of the FDTD model that considers the geometry to be infinitely uniform to the Z-direction. In the X-direction, I used periodic boundary condition (BC) for the normal incident angle and Bloch BC for the oblique incident angle. However, for the Y-direction, I used perfectly matched layer (PML) BC. For normal incidence, the number of layers in the PML setting was 20, and for angular incidence, the layer number was 60 for higher accuracy. An auto non-uniform mesh setting with mesh accuracy 4 was used for all the cases. In addition, an extra uniform mesh with 5nm in the X-direction and 10nm in the Y-direction was also inserted throughout the geometry. A plane wave source was used with polarization angle = 0° to ensure transverse magnetic (TM) polarized light. As the simulation environment is 2D, there is no angle between the incident light and the positive Y-axis; hence, $\phi = 0^\circ$. For normal incidence, the plane wave type was considered to be Bloch/ periodic with $\theta = 0^\circ$. However, for oblique incidence, the plane wave type was changed to the broadband fixed angle source technique (BFAST). Two linear X-monitors were used to capture the reflection and transmission light. The source was placed double the magnitude above the top surface of the geometry, and the reflection monitor was placed above the source. To capture the E-field and H-field, a 2D Z-normal frequency domain field profile monitor was used.

In the materials properties, I used Ag refractive indices provided by Yang et al. 2015 [38]. For the PMMA refractive index, I used the data provided by Zhang et al. 2020: Mitsubishi [39]. The Palik models built in the software were used as the optical constants of Cr, Al, and SiO₂. A 2D graphene sheet with scattering

rate, $\Gamma = 7.81 \times 10^{11} \text{ s}^{-1}$ for an energy equivalent, $E = \hbar\Gamma = 0.00051423 \text{ eV}$, and temperature, $T = 300 \text{ K}$ was implemented from the software normal to the Y-axis.

To normalize absorption spectra, the following formula was used,

$$\text{Normalized Absorption} = \frac{A - \min(A)}{\max(A) - \min(A)} \quad (1.16)$$

where A is the absorption value found from the simulation.

For plotting, Matlab 2022b and Origin 2019 were used.

Chapter 2

Fano-Resonance Induced by Graphene Plasmon Interacting with Hybrid Localized Surface Plasmon and Magnetic Polariton Resonances from Deep Metal Grating

2.1 Introduction

The Lorentzian formula has been used for a long period of time to describe physical resonances. In this case, the combination of several independent Lorentzian peaks where no interference is involved was presented to describe the multiple spectral peaks [40]. However, in 1935, Beutler described that there are some atoms that exhibit Rydberg lines that are sharp and asymmetric in nature [16]. Then, it was Ugo Fano who theoretically described and formulated this asymmetric spectral feature. According to him, such an asymmetric spectrum is the result

of the superposition of the energy level of an excited state and the continuum states with the same energy level of an atom [41]. In addition, he described a functional formula to mathematically describe the asymmetric shapes [42].

Following the invention, there are many quantum and classical [43] phenomena entangled in Fano resonance. For instance, a significantly asymmetric spectrum was observed for the photo absorption of helium atoms caused by the excitation of the $2s^2p^1p^0$ state [44]. This phenomenon was also observed in nuclear scattering, which happens between two closely located scattering channels [45]. Apart from that, in the electron transport of semiconductors, quantum dots, and nanowires [46] [47], Fano resonance was demonstrated. Such resonance has also been observed in acoustic systems, e.g., phononic crystals and acoustic metamaterials [48]. However, Fano resonance is very widely studied in the field of optics and photonics. Probably the first demonstration of Fano resonance caused by optical resonances is Wood's anomaly that involves the excitation of leaky mode by external radiation [49]. In the context of a coupled oscillator system, Fano resonance falls into the weak coupling regime where the coupled states' strength is much less compared to individual oscillators. Fano resonance can be distinguished from other weakly coupled oscillator systems, such as the Electromagnetically induced transparency (EIT) or Borrmann effect, by the asymmetric parameter q in the Fano formula [50].

Fano resonance can be induced by the interference of different optical modes from different photonic structures. The interference between guided mode and radiative modes act as discrete and continuum modes interchangeably in different photonic crystals, creating Fano-type resonance [51][52]. Furthermore, many studies have shown Fano resonance from nanostructures [53][54][55] and metamaterials [56][57][58] having plasmonic response. These asymmetric resonances can happen due to the interference of discrete localized surface plasmonic resonance (LSPR) mode generated by metal nanoparticles and the surface plasmon polaritons (SPPs) in the metal-dielectric interface that is considered as bright mode [40]. Fano resonance can also be caused by the interaction between LSPR from metal nanoparticles and the guided mode propagating through the dielectric media [59]. Some other studies showed that the hybridization of different plasmonic

modes leads to the Fano-resonance [60].

The observation of Fano resonance in the mid-IR region is crucial as it has various applications in gas sensing [61], refractive index sensing [62], biosensing [63], or switching [64]. On the other hand, graphene has significant plasmonic properties in the mid-IR region as it has a suitable optical conductivity value with a usual doping or tolerable biasing voltage [65]. Subsequently, there are reports on Fano resonance caused by graphene plasmons (GP) in the mid-IR range for various metamaterial structures [66][67][68].

In this research, I investigated optical properties of the deep metal grating. Upon the excitation of TM polarized light, deep metal grating supports LSPR at the edges of the metal grating opening and MP resonances in the trench gap of the grating, induced by the circulating electric field around the deep grating due to the high imaginary part of the metal's permittivity, especially in the IR range. The angular incidence of TM polarized light separates the two modes, and the LSPR mode creates asymmetric Fano resonance due to the symmetry breaking of the structure. Moreover, I also observed that by implementing a graphene sheet over the deep metal grating, asymmetric Fano resonance line shapes are shown due to the interaction of hybrid LSPR-MP mode from deep metal grating and graphene plasmon propagating in the interface of grating gap and graphene. While inducing Fano resonance, the hybrid mode from metal grating acted as a continuum, and the GP resonance, which can only be excited over the grating, was considered to be the discrete mode. The Fano parameter q showed remarkable tunability with grating height in the absorption response.

2.2 Results and Discussion

2.2.1 Superposition of Magnetic Polariton and Localized Surface Plasmon Resonance

The metal grating employed in this study is shown in Figure 2.1(a). Usually, deep metal grating where the trench width is much less compared to the grating height has been reported to give MP resonance. When such grating, periodic in the x-direction, is subjected to the TM polarized light that has a magnetic field propagating in the y-axis, there is a formation of oscillation of electrons along the grating gap that causes a magnetic field resulting in so-called magnetic polariton [69]. This is the most prevalent resonance when the trench is very narrow and has few nanometers in dimension. In our case, the grating trench is still very small compared to the grating height. However, if we look at the electric field distribution in Figure 2(a), we can see a field enhancement in the edges of the grating corners that looks like the LSPR response that usually happens on the surface of metal or metal nanoparticles [70]. The frequency location of LSPR can be found by the following expression:

$$\omega_{\max} = \frac{\omega_p}{\sqrt{2\epsilon_m + 1}} \quad (2.1)$$

where, $\omega_{\max}$ is the LSPR peak frequency, ω_p is the plasma frequency of metal, and ϵ_m is the dielectric constant in metal. As the dielectric constant of metal increases by decreasing EM wave frequency, the LSPR location of metal also shifts to a lower frequency while IR light is incident on it. As a result, LSPR excitation from our metal grating structure is expected when subjected to mid-IR light in our frequency range. Moreover, the real part of E_y component mapping in Figure 2.2(b) shows a formation of electrical dipole due to LSPR propagation [70]. Therefore, the resonance we have in this case is significantly influenced by this dipole LSPR resonance.

On the contrary, as discussed above, the electric field oscillation shown by

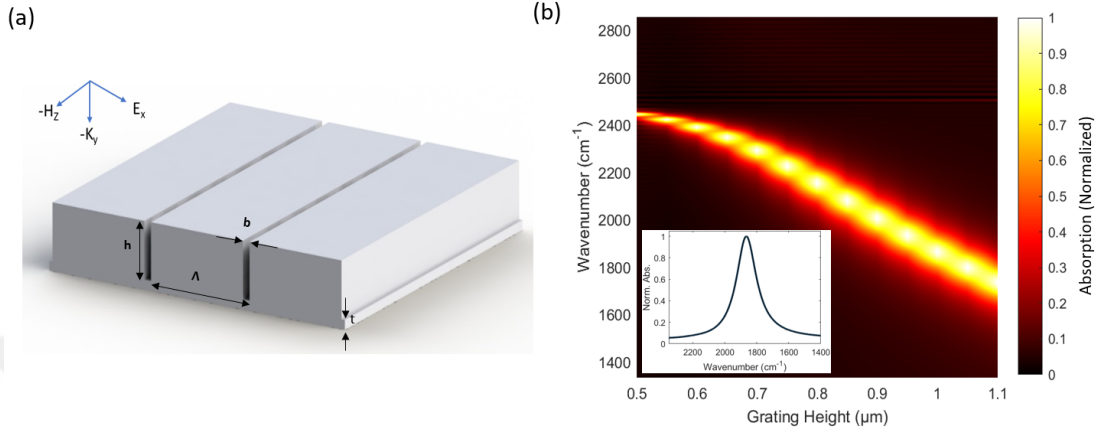


Figure 2.1: (a) Deep metal grating with the geometric parameters indicated as periodicity Λ , grating height h , width of grating trench b , and thickness of grating t . (b) Absorption intensity map of the deep metal grating for varied h values with $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, and $t = 0.05 \mu\text{m}$. A normalized absorption spectrum is shown in the inset figure for $h = 1 \mu\text{m}$.

the vector distribution in Figure 2.2(a) contributes to the MP resonance. Here, the arrow shows the normalized electric field vector components, and the reason to normalize the electric field is in the opening, the field intensity is very high; hence, the field vectors are much higher in that location, which doesn't allow us to see the direction of the electric field in other locations. The vector mapping is presented here for the zero phase angle of the E-field. The bigger arrows show the trend of the electric field. Here, we can see that the E-field vector direction is opposite to each other along the wall of the grating, and the field is directed from right to left along the trench as well as above and below the grating. The E-field intensity reduces almost linearly from the opening to the bottom of the grating. In contrast, the H-field distribution shown in Figure 2.2(c) shows the opposite trend. Most of the H-field is confined to the bottom of the grating. Current density J was calculated as

$$J = -i\omega(\epsilon_{\text{material}} - \epsilon_0)E \quad (2.2)$$

where, $\epsilon_{\text{material}}$ is the effective permittivity of the metastructure. The vector

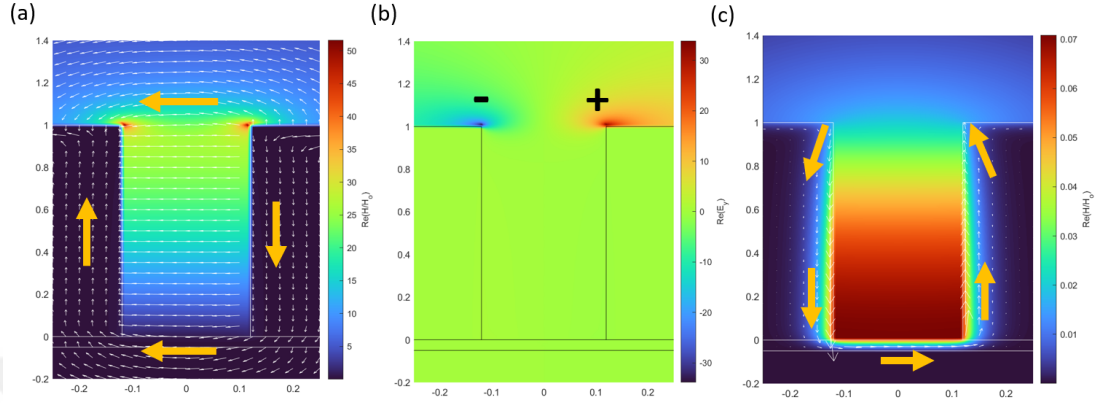


Figure 2.2: (a) For grating parameter $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, and $h = 1 \mu\text{m}$, the peak of the curve shown in the inset of Figure 2.1(b) at 1865cm^{-1} . (a), (b) and (c) is the mapping for normalized electric field real magnitude, the y component of the electric field, and the magnetic field distribution, respectively.

field for the current density is shown in Figure 2.2(c), where the contour represents the H-field distribution. From the current density vectors, we can see that most of the current is induced through the boundary of the grating wall, creating a current loop, and in the bottom, the current density is the highest. That proves the high magnetic field intensity at the bottom of the grating induced by the circulating current along the grating according to Lenz's law [69]. Therefore, at normal incidents, we hybridize both LSPR and MP resonances, which finally gives us one single peak.

2.2.2 Fano resonance for angular incidence in metal grating

From the angle-dependent absorption spectrum represented in Figure 2.3(a), we have a deeper insight into the mode hybridization as well as Fano resonance caused by changing an angle of incident light. For only MP resonance features, the peak location is independent of the incident angle [71]. On the contrary, LSPR has a strong angle dependency. Unlike an MP resonance, by changing the angle, we can see a clear shift of the major peak for our deep metal grating structure. That indicates the presence of LSPR in all the angle-dependent peaks and the

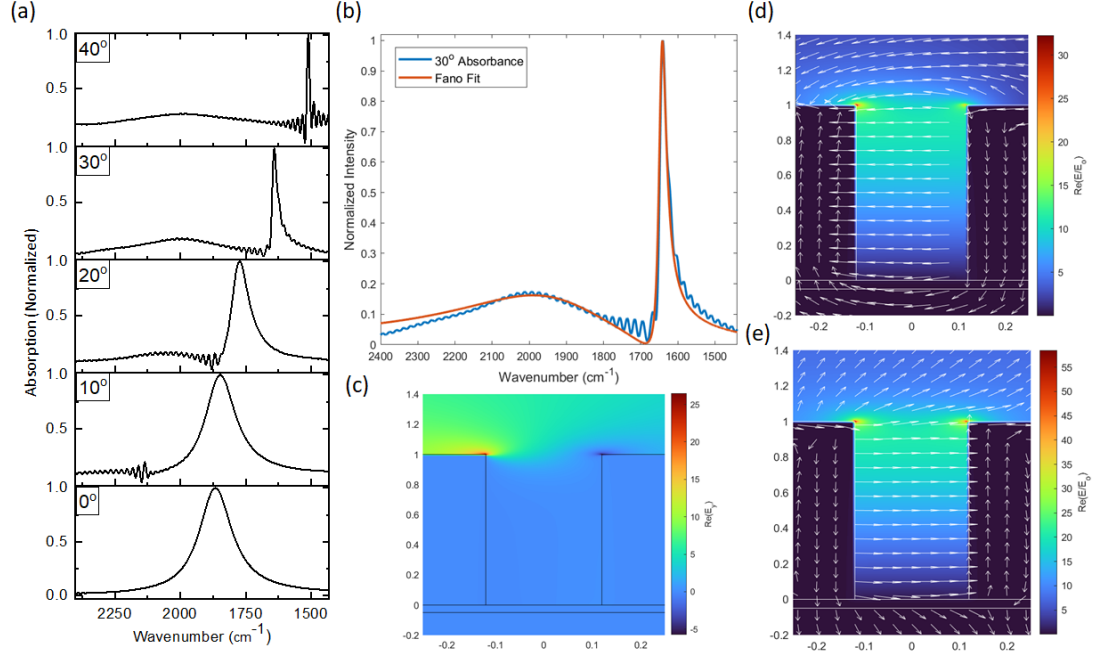


Figure 2.3: (a) The absorption spectra of the grating structure with the same grating parameters as in Figure 2.1 for the incident angles of light ranging from 40° to 0°; (b) The absorption spectrum at an incident angle of 30° showing Fano type asymmetric line shape (blue). The spectrum was fitted to the Fano formula (orange); (c) Asymmetric electric dipole shown for the Real (E_y) component of the electric field at 1640cm⁻¹ for 30° angle of incidence; (d) and (e) are electric field distributions along with vector mapping at 1992cm⁻¹ and 1640cm⁻¹ respectively.

normal incidence resonance as well. It can also be observed that the pronounced peak becomes narrower, and an additional broad peak starts to appear at $\sim 2000\text{ cm}^{-1}$ at a higher incidence angle. The separation of peaks and the presence of broad peak is more evident in the transmission (normalized) spectrum shown in Figure S2.1(a). The broad peak remains at a nearly constant spectral location for different angles, which is the nature of the MP resonance. On the contrary, when LSPR resonance has low radiative loss, the LSPR peak is usually narrower with a high Q-factor. That tells us the peak that is getting narrower has the most contribution from the localized plasmonic response. In addition, the purely plasmonic resonance wavelength (λ_{SPP}) of a periodic structure can be calculated from the following expression [72]

$$\lambda_{\text{SPP}} = \Lambda(\sin \theta + n_s) \quad (2.3)$$

where θ is the angle of incidence and n_s is the uniform refractive index of the surrounding medium, which is air in our case. In our structure with the periodicity $4 \mu\text{m}$, that results in $\lambda_{\text{SPP}} = \Lambda(\sin \theta + n_s) = 4 \mu\text{m}(\sin 30^\circ + 1) = 6 \mu\text{m}$ that is equivalent to 1666 cm^{-1} which is very close to the narrow peak location nearly at $6.1 \mu\text{m}$ or 1639 cm^{-1} .

In addition, the broad peak has the electric field circulation, whereas the narrow peak E-field vectors are scattered. As shown in Figure 2.3(d), at 1992 cm^{-1} for 30° angle of incidence, the electric field vectors are creating regular circulation like at the normal incidence (Figure 2.2a), which is the key reason to have MPs. However, for the narrow peak at 1640 cm^{-1} , the electric field vectors are very scattered to make an electric field loop, which represents a minimal contribution of MP in that location (Figure 2.3e). Moreover, the E-field vector direction flips at 1640 cm^{-1} compared to 1992 cm^{-1} .

The spectral shape of the narrow peak for 30° incidence is significantly asymmetric, that is the signature property of Fano resonance. The broad peak has no asymmetry and thus can be considered as the Lorentzian resonance. To verify the Fano resonance, we consider the spectrum to be a combination of a Lorentzian function $L(\lambda)$ and a Fano function $F(\lambda)$ expressed as a function of wavelength expressed below [73],

$$L(\lambda) = \frac{1}{\pi} \frac{\gamma_1}{(\lambda - \lambda_1)^2 + \gamma_1^2} \quad (2.4)$$

$$F(\lambda) = f + \frac{(q\gamma_2 + \lambda + \lambda_2)^2}{(\lambda - \lambda_2)^2 + \gamma_2^2} \quad (2.5)$$

Here, λ_1 and λ_2 are the spectral wavelength location of the Lorentzian and Fano peaks, respectively, γ_1 and γ_2 are the widths of each peak, and f and q are the constant factors that determine the peak height and background of the

resonance. The parameter that determines the asymmetry of the Fano curve is q . The combined resonance, $R(\lambda)$, has been calculated as

$$R(\lambda) = L(\lambda) \times F(\lambda) \quad (2.6)$$

By fitting the absorption curve of 30° incident angle using $\lambda_1 = 5.109 \mu\text{m}$, $\lambda_2 = 6.081 \mu\text{m}$, $\gamma_1 = 0.726 \mu\text{m}$, $\gamma_2 = 0.0445 \mu\text{m}$, $l = 0.05$, $f = 9 \times 10^{-10}$, we obtained the Fano asymmetric parameter, $q = 3.5095$, which is in the range to show the asymmetry of the resonance as the curve gets Lorentzian for $q = 0, +\infty$ or $-\infty$ [74]. The absorption intensity and the fitted data are normalized, as presented in Figure 2.3(c). The mean standard deviation between the fitted data and the absorption data is as low as 0.015.

The oblique incidence of light on a periodic grating structure gives rise to the symmetry breaking of the phase matching of the propagating plane wave [75]. This symmetry breaking causes the asymmetric dipole shown in Figure 2.3(c) through the mapping of the y component of the electric field distribution. Such asymmetry is the base reason for the formation of Fano resonance that ultimately yields the asymmetric LSPR peak.

2.2.3 Fano Resonance Due To Integration of Graphene on Metal Grating

In the interaction between graphene and grating, the governing property of graphene is its optical conductivity. As monolayer graphene is infinitesimally thin, considering the optical conductivity between two materials would be enough to deduce its optical response. Kubo formula is employed to calculate the graphene optical conductivity σ that is a function of frequency ω , chemical potential μ_c , scattering rate Γ that is independent of the energy ξ , and temperature T . The conductivity σ has a contribution from intraband and interband electronic transition; hence, the total optical conductivity can be found as [76]

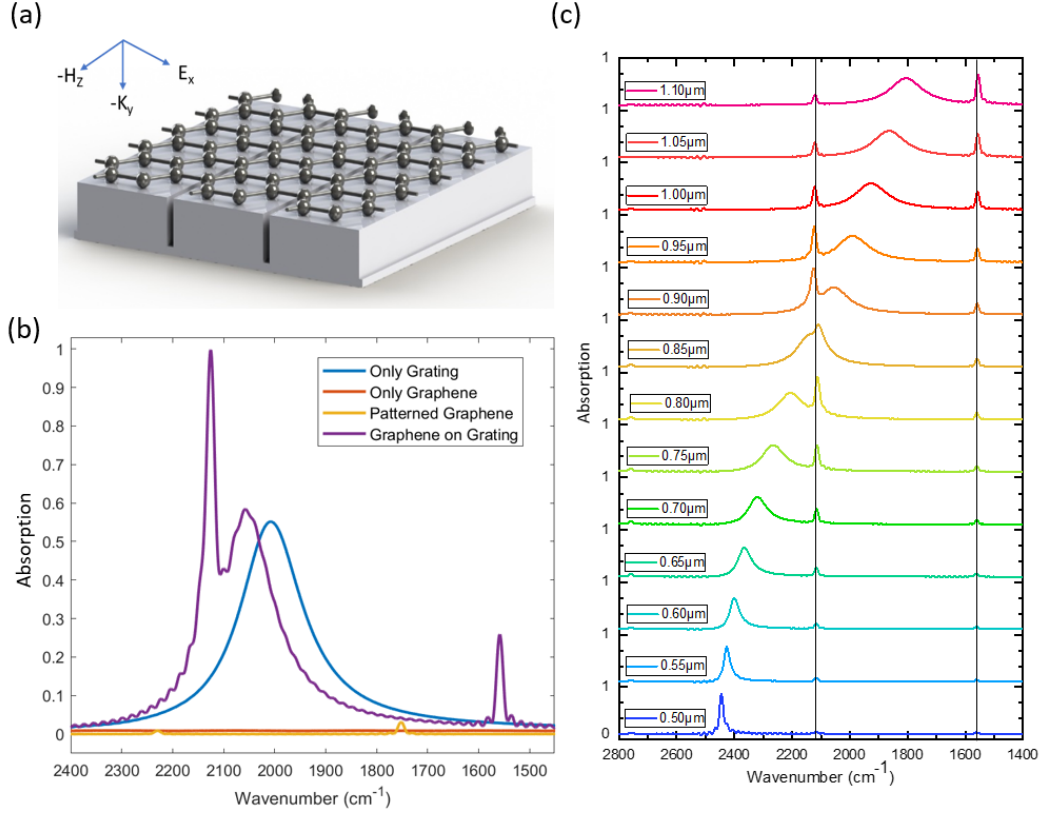


Figure 2.4: (a) Graphene-integrated metal grating, (b) Fano resonance by the interference of the continuum mode from metal grating and the dark mode from graphene, (c) Absorption spectrum for the increasing grating height with grating parameters of $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, and graphene chemical potential $\mu_c = 0.5 \text{ eV}$. The black lines show the graphene plasmonic response at 1560 cm^{-1} and 2120 cm^{-1} spectral locations that do not change by changing the grating height.

$$\sigma(\omega, \mu_c, \Gamma, T) = \sigma_{\text{intra}}(\omega, \mu_c, \Gamma, T) + \sigma_{\text{inter}}(\omega, \mu_c, \Gamma, T) \quad (2.7)$$

$$\sigma_{\text{intra}}(\omega, \mu_c, \Gamma, T) = \frac{-ie^2}{\pi\hbar^2(\omega + i2\Gamma)} \int_0^\infty \xi \left(\frac{\partial f_d(\xi)}{\partial \xi} - \frac{\partial f_d(-\xi)}{\partial \xi} \right) d\xi \quad (2.8)$$

$$\sigma_{\text{inter}}(\omega, \mu_c, \Gamma, T) = \frac{ie^2(\omega + i2\Gamma)}{\pi\hbar^2} \int_0^\infty \frac{f_d(-\xi) - f_d(\xi)}{(\omega + i2\Gamma)^2 - 4(\xi/\hbar)^2} d\xi \quad (2.9)$$

Here, e is the magnitude of charge of an electron, reduced Planck constant $\hbar = \frac{h}{2\pi}$, and $f_d(\xi)$ is the Fermi-Dirac distribution function that can be expressed as [76]

$$f_d(\xi) = \frac{1}{e^{\frac{\xi - \mu_c}{k_B T}} + 1} \quad (2.10)$$

where k_B is the Boltzmann constant. According to the thickness of the graphene layer, this conductivity value will be scaled down to $\sigma_t = \frac{\sigma}{t_g}$ when t_g is the thickness of graphene.

If the graphene sheet alone is subjected to the EM wave illumination, it doesn't show significant light absorption, as shown in Figure 2.4(b). A monolayer graphene sheet with $\mu_c = 0.5$ eV shows nearly zero absorption in the mid-IR range (red solid line). If the graphene array is patterned according to the grating dimensions, i.e., a patterned array of graphene with $0.24 \mu\text{m}$ width and 0.5 eV chemical potential, it shows very small resonances (orange). Between 1450 cm^{-1} and 2400 cm^{-1} , the patterned graphene showed two sub-radiant resonance peaks at 2230 cm^{-1} and 2750 cm^{-1} . The electric field of these two frequency points is presented in Figure S2.2, which shows the enhanced light absorption on the surface of patterned graphene at both frequencies. The nature of the resonance is similar to the Dirac plasmonic response that can be excited for longer wavelengths like our spectral region. The reason behind having the Dirac plasmonic response for patterned graphene but not for a plane graphene sheet is that the patterning of graphene facilitates the momentum matching between the Dirac plasmon and the incident light [77]. Due to the weak resonance nature of patterned graphene, it can be considered as the sub-radiant or dark mode in the induction of Fano resonance. Such dark plasmonic modes are excited by bright hybrid dipolar LSPR and MP emissive mode from the metal grating [78].

When graphene is integrated with the metal grating, as shown in Figure 2.4(a), it starts to show enhanced plasmonic peaks at different frequencies (Figure 2.4b: purple). The purely plasmonic response doesn't change its spectral location by changing the grating height, as described by Wang, L. P. et al. [70]. For the

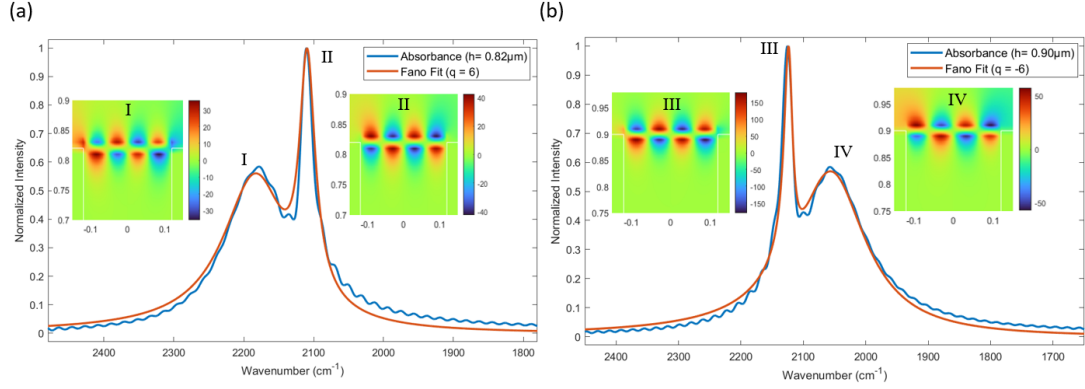


Figure 2.5: The absorption spectra (blue) and fitted Fano curves (orange) for the grating with the grating heights of (a) $h = 0.82 \mu\text{m}$ and (b) $h = 0.90 \mu\text{m}$. The rest of the grating and graphene parameters are the same as those used in Figure 2.4(c). The insets represent the real component of E_y at each peak location of (I) 2185cm^{-1} , (II) 2110cm^{-1} , (III) 2125cm^{-1} , and (IV) 2055cm^{-1} .

grating parameter $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$ and graphene chemical potential $\mu_c = 0.5 \text{ eV}$, two graphene plasmonic resonances at nearly the same wavelength location of 1560cm^{-1} and 2120cm^{-1} are observed in the spectral range for different grating height (Figure 2.4c). For the graphene on the grating case shown in Figure 2.4b (purple), we can see the hybrid grating resonance mode is blue-shifted relative to the metal grating-only case (orange). On the contrary, both of the plasmonic resonances from patterned graphene have red-shifted while interacting with the grating resonance that facilitates the coupling between hybridized and GP modes.

As the graphene plasmonic mode was invisible without the presence of grating and started to emerge for the patterned case, the plasmonic response excited in the combined case is primarily due to the graphene on top of the grating gap. This interaction of graphene and air in each of its surfaces is more evident from the E_y field distributions shown in the inset figures of Figure 2.5. In all the cases, a strong enhancement of electric fields is observed on the graphene surface. Another observation from these field maps is the formation of four dipoles in each of the wavelengths. These dipoles indicate the formation of surface plasmon polaritons (SPP) through the oscillation of the electron in the interface of graphene and air. In both of the cases in Figure 2.5 (a) and (b), we can see the positive and

negative poles are flipped from broad peak to narrow peak.

The enhanced absorption was observed at the narrow GP peaks represented as (II) and (III) for both of the grating heights. Moreover, for peaks (I) and (IV), there is an outward enhancement at the edges of the grating that is a signature of LSPR contribution. Due to the presence of localized plasmons and the broad nature of the peaks, these two peaks can be considered as the continuum hybrid LSPR and MP mode in the coupling condition. However, as the overall field density is higher compared to the bare grating case, GP is significantly influencing the field enhancement in these two peaks as well.

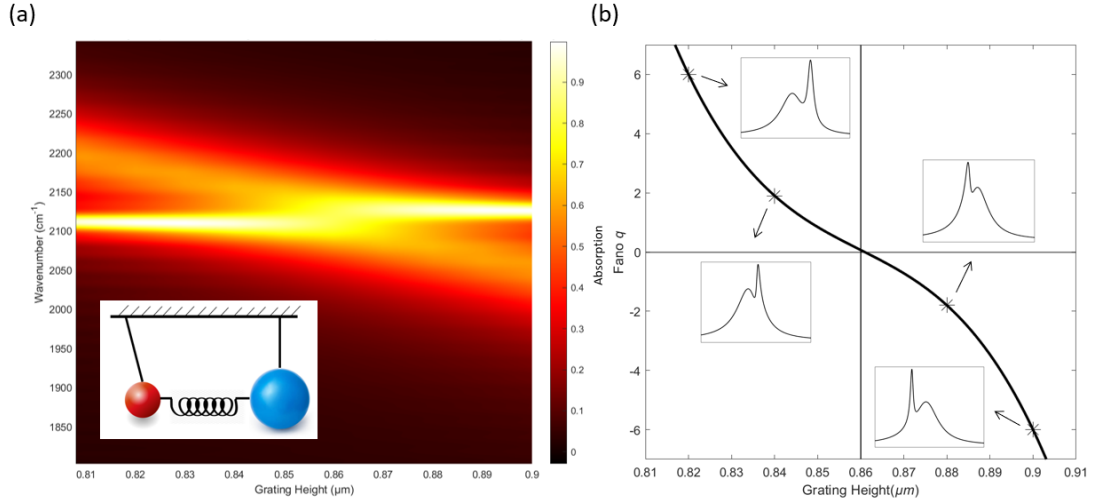


Figure 2.6: (a) Intensity plot of absorption as a function of the grating height for the coupling between the hybrid LSPR and MP resonance from the metal grating with GP resonance. The plot represents the coupled oscillation of two dissimilar oscillators shown in the inset figure where the red ball represents the GP, and the blue ball resembles the grating resonance. (b) Tunability of Fano parameter q over the grating height.

From Figure 2.6(a), we can see the intensity plot of absorption of two coupled oscillators is shown from the absorption data from grating height 0.81 μm to 0.90 μm for the same grating and graphene parameters described previously in Figure 2.4. As Fano resonance happens due to the interaction of two disproportionate oscillators shown in the inset of Figure 2.6(a), GP mode is more pronounced than the grating resonance mode in the absorption intensity plot. Such interaction of dissimilar oscillators yields weak light-matter coupling.

The Fano parameter q presented in equation 5 is a measure of asymmetry, hence the Fano resonance strength. If the q value moves from 0 to $+\infty$ or $-\infty$, the resonance becomes more and more symmetric. For our structure, we can have a tuneability of Fano asymmetry as it has a varying q value for the grating height range where we observe the absorption intensity plot. In the fitting of the absorption spectrum in this case, the narrow GP peak is considered to be the Fano peak, and the broad hybrid peak is calculated as the Lorentzian peak. Hereby, calculated q values are positive when the Lorentzian peak location is in a lower wavelength position than the Fano peak location and vice versa. These calculated parameters are presented in Table 1.

Table 2.1: Fano fitting parameters for different grating heights

$h(\mu m)$	q	$\lambda_1(\mu m)$	$\lambda_2(\mu m)$	$\gamma_1(\mu m)$	$\gamma_2(\mu m)$	f	l
0.82	6	4.58	4.74	0.116	0.030	8.6	1
0.84	1.9	4.652	4.731	0.135	0.020	3.64	1
0.88	-1.8	4.71	4.79	0.028	0.15	3.78	1
0.90	-6	4.71	4.86	0.0178	0.162	15.9	1

For all the fitted curves, the *mean standard deviation* is less than 0.02. From Figure 2.5(b), it can be observed that when two peaks are approaching closer, i.e., when the distance between λ_1 and λ_2 is less, the asymmetry of the Fano curve is higher. Therefore, q values closer to zero mean higher coupling strength. At $h = 0.86 \mu m$, the absorption spectra shown in Figure S2.3(b) represent that both the hybrid grating peak and the GP peak overlap together and merge into one Lorentzian peak. This is the reason why we have $q = 0$ in this case, which implies no asymmetry.

2.3 Summary

In this chapter, the origin of metal grating resonance in mid-IR is explained as the hybridization of LSPR and MP resonance. The two modes can be separated by the incident angle of light that induces angle-dependent Fano resonance from the deep metal grating. Then, a planar graphene sheet was introduced over the metal grating. GPs are excited over the grating trench, which confines and enhances the electric field at the interface of graphene and air. The GPs interact with the hybrid LSPR and MP modes, resulting in the formation of Fano resonance, where GPs act as a sub-radiant mode and the hybrid modes the super-radiant mode. The Fano resonance showed significant tunability over a range of grating heights, which also gives a similar curve nature of a coupled oscillator relation between two dissimilar oscillators.

Chapter 3

Deep Metal Grating: A New Optical Resonator to Realize Weak to Strong Vibrational Coupling

3.1 Introduction

Modulation of atomic energy states through the interaction of light and matter is of great interest due to its implications in various fields. Depending on the strength of the light-matter interaction, it can be classified as weak coupling or strong coupling. To realize such coupling, different excitonic materials are introduced inside a Fabry-Pérot (FP) cavity illustrated by two parallel reflecting mirrors. The excitonic molecules exchange energy with the photons in such cavity setups. If the decay rate of the coupled state is lower than the individual decay rates of the cavity and molecular transition, the coupling is weak coupling, which is explained by the Purcell effect. However, the coupling is in strong coupling regime if the coupled state's energy decay is slower than the individual state's energy decay rate [21]. The formation of polaritonic states is evidenced by peak

splitting in the cavity transmission and anti-crossing in the energy dispersion, resulting in so-called Rabi splitting, Ω_R .

The most widely known example is the strong coupling of light with excitonic materials such as j-aggregates [[79], quantum dots [80][81], and organic dye molecules [82]. Excitonic-polaritonic states have been shown to modulate the course of nonlinear optical phenomena such as Bose-Einstein condensation [83], low-threshold lasing [84] and superfluidity [85]. However, strong coupling of light is not limited to excitonic materials and has also been shown to occur in materials with strong vibrational transitions [30][29]. The rates [31][86] and products [33] of a chemical reaction are influenced by vibrational strong coupling (VSC), which has a significant potential impact on the reaction chemistry [87][88][89].

The FP cavity is the most commonly used optical resonator in this case because of its significant electromagnetic field enhancement capability that allows higher photon interaction [90]. The resonant wavelength of the cavity mode is easily tuned by changing the cavity thickness from the visible to the mid-infrared spectral ranges. The optical modes generated by the FP cavity show strong angular dependence, making it convenient to tune the resonance frequency by changing the angle of the incident light. However, FP cavities have limited spatial control over the coupling, although spatially varying optical modes of the FP cavity result in the coupling strength Ω_R varied inside the cavity [36]. Unable to achieve strong coupling at the selected location within the cavity, the strong coupling by FP cavities represents ensemble-averaged interaction between broad cavity modes and material transitions. Moreover, an FP cavity, which is usually in a closed platform, makes it difficult to access molecules experiencing strong coupling. Open cavity designs with molecules located outside the cavity would be extremely useful as they allow access to external chemistry and measurements using near-field probes.

To address some of the issues associated with the FP cavity, I use a deep metal grating structure as a mid-infrared optical resonator to induce VSC. Previous studies reported plasmonic metal grating structures for VSC with the grating depth (h) ranging from 30 to 100 nm [91][37][92]. However, our metal grating

structures have a lot deeper h ranging from 0.5 to 1.0 μm . In such a deep metal grating, magnetic resonances are supported by the formation of antiparallel current loops induced by the magnetic field of the incident wave, producing magnetic polaritons (MPs) [71][71]. As I have shown in Chapter 2 for our structure, this MP resonance hybridizes with the localized surface plasmonic resonance (LSPR) mode, yielding a high-Q resonance mode. The resonance mode is tunable by varying geometrical parameters such as height h and width b of the grating, as well as the types of materials used to make the grating. A deep metal grating structure was used to improve the thermophotovoltaic power efficiency [93], mid-infrared (IR) transmission [94], and enhanced absorption of graphene [95]. Nevertheless, it has not been used to demonstrate the VSC between MPs and molecular vibrations despite its ability to generate spectrally and spatially tunable strong mid-infrared resonances with advantages over conventional FP cavities. As a result, this deep metal grating that allows one to place molecular absorbers in the maximum optical field is investigated to realize weak to strong coupling between molecular vibrational mode and hybrid LSPR-MP mode. From the results will be shown in this chapter, we can say that when the molecular layer, poly-methyl methacrylate (PMMA), in this case, is placed on the top surface of the grating, it only interacts with the LSPR in the grating edges and forms a weak vibrational coupling. However, when PMMA is added to trench gaps of the metal grating, the coupling strength is increased, and VSC is achieved.

3.2 Results and Discussion

3.2.1 Molecular Layer on Top of Metal Grating

As described in Chapter 2, deep metal gratings generate a single peak resonance through the hybridization of LSPR and MP resonances. To investigate the interaction between molecular vibration and this hybrid resonance, I first embedded a molecular layer of PMMA on top of an Ag metal grating. The reason for selecting PMMA is its strong vibrational resonance at 1730 cm^{-1} due to the presence of

the $\nu(\text{C}=\text{O})$ group in its molecular structure. For the excitation of the grating response, TM polarized light was implemented in which the electric field propagates perpendicular to the direction of the periodicity of the grating, and the magnetic field propagates parallel to the grating line.

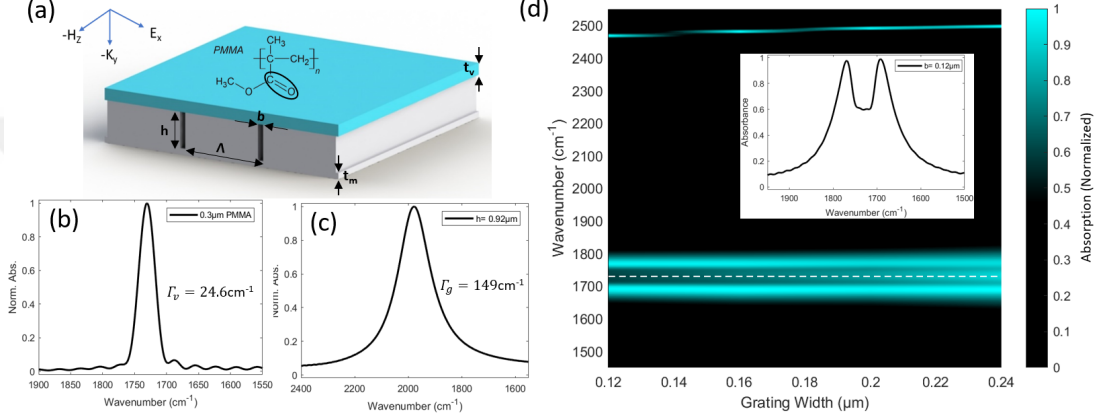


Figure 3.1: (a) Schematic illustration of the deep metal grating with a PMMA layer on its top under TM polarized light illumination. The molecular structure of PMMA is shown where $\text{C}=\text{O}$ is indicated by a black circle; (b) and (c) are the absorption spectra of a 300nm-thick bare PMMA layer and a bare metal grating without PMMA, respectively. The grating parameters include $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $h = 0.92 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$. Γ_v and Γ_g represent the full-width half maxima (FWHM) of the $\nu(\text{C}=\text{O})$ and grating resonance peaks, respectively. (d) An absorption intensity map of the metal grating with a PMMA layer on top ($t_v = 0.3 \mu\text{m}$) when b is varied. Other grating parameters remained constant. A frequency of $\nu(\text{C}=\text{O})$ is indicated at 1730 cm^{-1} (white dashed line). An absorption spectrum for $b = 0.12 \mu\text{m}$ is presented in the inset.

When both $\nu(\text{C}=\text{O})$ and grating resonance peaks are spectrally matched, we can see a symmetric splitting of the peak across the molecular vibrational location, which is called the Rabi splitting. Rabi splitting (Ω_R) is determined by the energy difference between the two peaks. In the case of $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $h = 0.92 \mu\text{m}$, $t_v = 0.3 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$, the location of these two peaks are at 1770 cm^{-1} and 1689 cm^{-1} , hence $\Omega_R = 81 \text{ cm}^{-1}$. On the other hand, the linewidth of the two peaks, Γ_v and Γ_g , are the indicators of the energy dissipation rate of the individual oscillators. The coupling can be considered as strong coupling if the following condition satisfies [25]

$$\Omega_R > \frac{(\Gamma_v + \Gamma_g)}{2} \quad (3.1)$$

At the coupling condition for the molecular layer on top of the grating case, we have $\frac{(\Gamma_v + \Gamma_g)}{2} = 87.05 \text{ cm}^{-1}$, which is greater than Ω_R . Therefore, in this configuration of the metal grating with PMMA on its top, a strong coupling between optical resonator (i.e., metal grating) and molecular absorber (i.e., PMMA). Rather, we have a weak coupling between them.

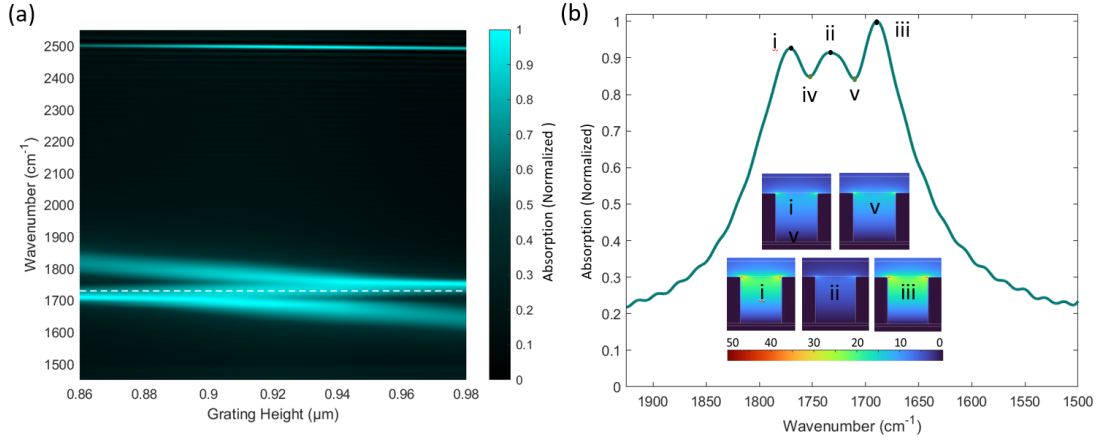


Figure 3.2: (a) Absorption mapping for varying height when $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $h = 0.92 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$. The dotted line is at 1730 cm^{-1} , which is the location of $\nu(\text{C=O})$. (b) The absorption spectrum for $h = 0.92 \mu\text{m}$, which is symmetry between two coupled states, is observed. The real component of electric field distribution at the pointed peaks and deeps are presented in the inset.

However, instead of keeping the air in the grating gap, if I fill the gap with a dielectric material such as SiO_2 , we can push the weak coupling limit to strong coupling. Filling the gap by SiO_2 reduces Γ_g from 149 to 108 cm^{-1} for the same grating parameters mentioned above. Such reduction yields the reduction in $(\Gamma_v + \Gamma_g)/2$ to 66.3 cm^{-1} , which is less than $\Omega_R = 68 \text{ cm}^{-1}$ in this case. The higher refractive index of SiO_2 induces a higher dipole electric field at the edges of the metal grating, as illustrated in Figure S3.2. It causes a sharper resonance peak than the air grating.

For considering air grating, we can observe an anti-crossing behavior of the

two coupled states in the absorption intensity map shown in Figure 3.2(a) for different grating heights around the height where the symmetry of two coupled peaks happens. A similar anti-crossing trend is shown for the grating gap filled by the SiO_2 case in Figure S3.1(c). Moreover, from the inset of Figure 3.2(b), we can see that the maximum electric field intensity is at the coupled state's peak locations at (i) and (iii). However, for all the locations, most electric field enhancement occurs at the edges of the grating. That implies that the coupling of two resonances happens mostly due to the interaction between the grating LSPR and the molecular layer on top of it.

Primarily, the molecules near the hotspots are participating in the coupling phenomena. From Figure 3.1 (d), we can observe that a peak along the molecular vibration location, at 1730 cm^{-1} , starts to appear by increasing the grating width. This peak is a representation of the uncoupled molecules in the system that are also known as the dark states [96]. When the grating width is less, that leads to a reduced interacting area for the molecular layer on top of the grating gap. Consequently, the number of molecules in the vicinity of the LSPR hotspots is fewer. However, a higher width increases the number of interacting molecules on top of the grating gap, which is more than sufficient for the coupling to happen. That results in an extra molecular vibration peak of the uncoupled molecules in between the two coupled state peaks.

Furthermore, we can observe an additional pronounced peak at around 2500 cm^{-1} or $4\text{ }\mu\text{m}$ in all the absorption mapping. This peak can be explained in terms of SPP propagation in a grating structure. The expression for the spectral location of SPP in a periodic structure is as follows [72]

$$\lambda_{\text{SPP}} = \Lambda(\sin \theta + n_s) \quad (3.2)$$

where θ is the incident angle, and n_s is the surrounding refractive index. At the normal angle of incidence, λ_{SPP} will be equal to Λn_s with $n_s = 1$ for air. In the above case, Λ is $4\text{ }\mu\text{m}$, and the peak appears at $4\text{ }\mu\text{m}$ regardless of the width or height of the grating, confirming that the peak at 2500 cm^{-1} is due to

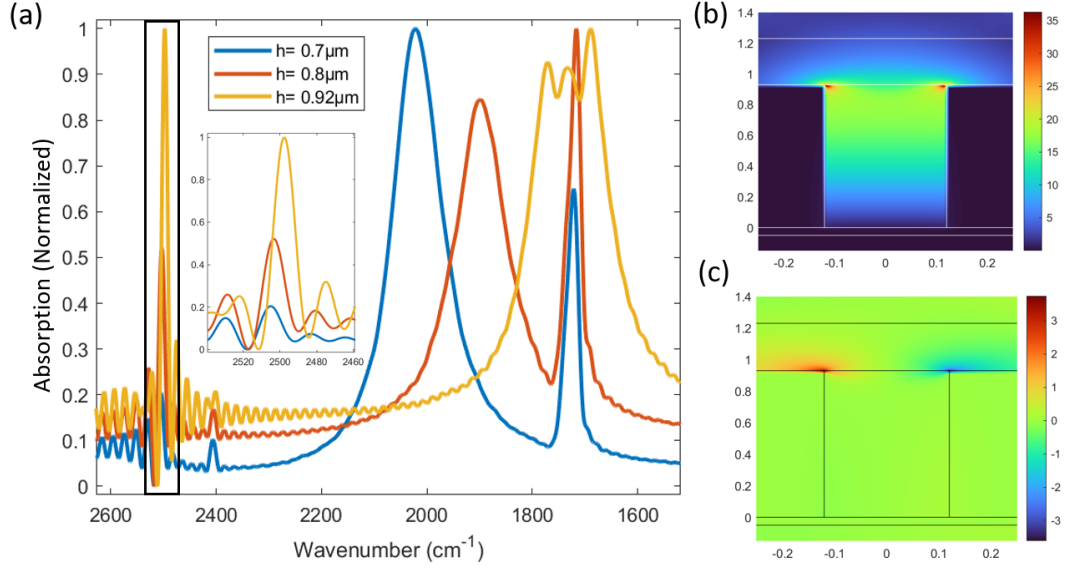


Figure 3.3: (a) Absorption spectra for three different grating heights. The inset represents the zoomed area for the peak around $4\ \mu\text{m}$. (b) and (c) are $Re(E/E_o)$ field and $Re(E_y)$ field distributions respectively.

SPPs. From the observation of Figure 3.3(b) and (c), we can say this plasmonic propagation is mostly in the edges of the grating, which is due to the creation of a dipolar electric field. However, from Figure 3.3(a), we can see that the intensity of the SPP peak increases with the increase in grating height. At the same time, for higher grating height, the hybrid LSPR and MP resonance peak red-shifts, i.e., moving away from the SPP peak. That represents the hybrid resonance, which affects the SPP resonance when they get closer, and the SPP starts contributing to the mode hybridization between LSPR and MP resonances. On the other hand, the $\nu(\text{C}=\text{O})$ peak gets more pronounced by the increase in grating height until it couples with the hybrid resonance.

3.2.2 PMMA in the grating gap

When PMMA is embedded on top of the grating as a molecular layer, the molecular vibration couples with the plasmonic response at the edges of the grating. However, as the grating resonance is also contributed by the magnetic polaritonic

resonance that is mostly confined at the bottom of the grating explained in Chapter 2, we need to ensure the molecular vibrational resonance interacts with the MP response to have a greater coupling. As a result, to introduce the interaction between $\nu(\text{C}=\text{O})$ and MP, I filled the grating gap by PMMA.

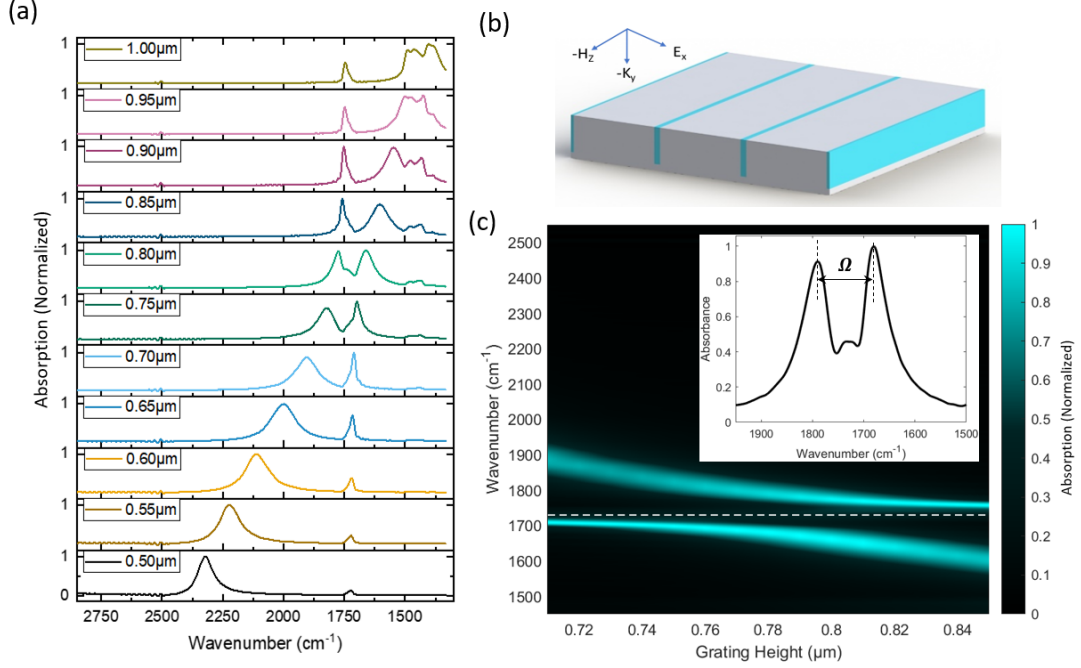


Figure 3.4: (a) The absorption sweeping over a varying height for the grating parameters $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$ when PMMA is in the grating gap. (b) Schematic illustration of the metal grating with the gap filled by PMMA. (c) Absorption intensity map to illustrate the anti-crossing behavior of vibrational strong coupling for the variation of grating height. The dotted line is at the location of $\nu(\text{C}=\text{O})$, and the inset is the absorption spectra at $h = 0.78 \mu\text{m}$ where symmetric polaritonic states formed that are separated by Rabi frequency Ω_R .

When the grating gap is filled by PMMA, we can observe a significant red-shift of the grating response compared to the air in the gap case. For instance, if we compare the grating resonance location for $h = 0.7 \mu\text{m}$ in the case of PMMA on top of grating and PMMA in the grating gap, the peak shifts from 2001 cm^{-1} to 1905 cm^{-1} illustrated in Figure 3.3(a) and Figure 3.4(a), respectively. As the grating resonance peak has a contribution from LSPR, the resonance frequency of LSPR, ω_{LSPR} is a function of the permittivity surrounding medium, ϵ_{STT} along with the metal's permittivity, ϵ_{m} expressed by the following

correlation [97]

$$\omega_{\text{LSPR}} \approx \frac{\omega_p}{\sqrt{1 + 2\epsilon_{\text{sr}}}}, \text{ and } \omega_p = \sqrt{\frac{n_e e^2}{\epsilon_0 m_e}} \quad (3.3)$$

Here, n_e is the electron charge density in the metal, ϵ_0 is the vacuum permittivity, e is the electron charge, m_e is the effective mass of an electron, and ω_p is the metal's plasma frequency. From this equation, we can see that ω_{LSPR} is inversely proportional to the surrounding refractive index, ϵ_{srr} . When PMMA is used in the grating gap, the effective refractive index of the surrounding medium increases, which leads to the redshift of the grating peak. This peak shifting causes the coupling to happen at a lower grating height where the linewidth of the resonance is less.

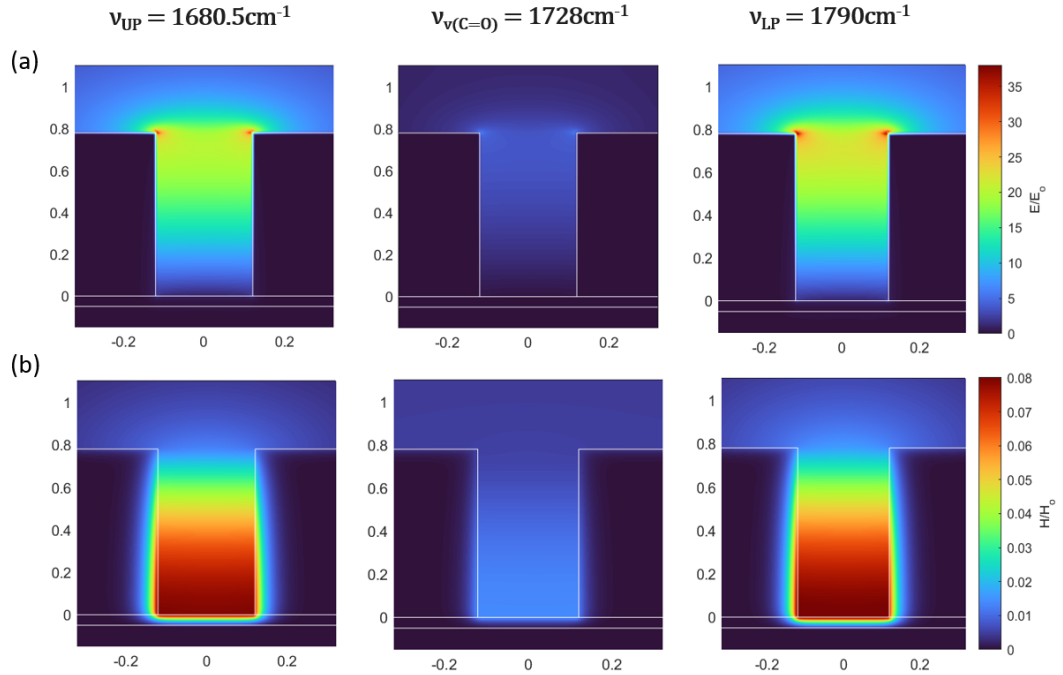


Figure 3.5: (a) and (b) are the electric and magnetic field distributions at the upper polariton (UP), $\nu(\text{C=O})$, and lower polaritonic (LP) spectral locations for $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$, $h = 0.78 \mu\text{m}$ when PMMA in the grating gap. The x-axis of the color map is the x-coordinate of the geometry, and the y-axis is the y-coordinate of the 2D grating.

To verify the vibrational strong coupling, if we calculate the average peak

width of the $\nu(\text{C=O})$ and grating resonance, we find $\frac{\Gamma_v + \Gamma_g}{2} = 73.8 \text{ cm}^{-1}$ and the difference between two polaritonic states where the symmetrical peaks are found shown in the inset of Figure 3.4, $\Omega_R = 109.5 \text{ cm}^{-1}$. As Ω_R is significantly higher than the average linewidth of the individual resonances, this vibrational coupling surely falls in strong coupling regime. The reason for having greater Ω_R compared to the previous cases is that in this configuration, both of the resonance modes, LSPR and MP, participate in coupling with the molecular vibration. Moreover, as the molecules in the gap interact with MP, more molecules are taking part, resulting in greater VSC ($\Omega_R = 109.5 \text{ cm}^{-1}$) compared to PMMA only on the top case ($\Omega_R = 87.05 \text{ cm}^{-1}$).

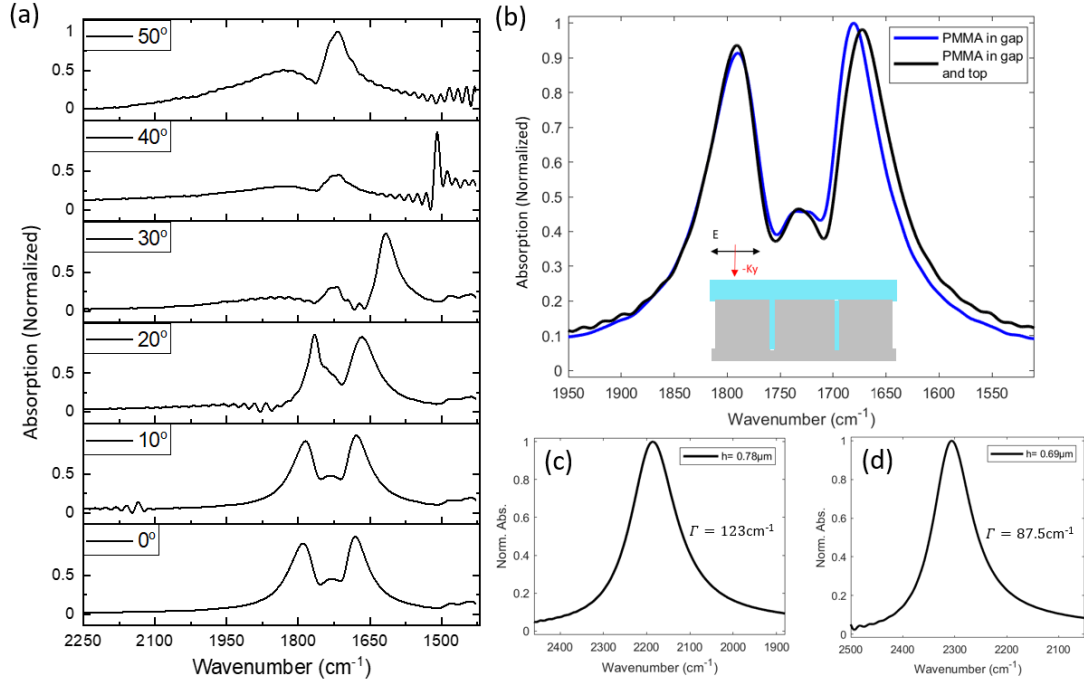


Figure 3.6: (a) Angle-dependent spectrum for PMMA in the grating gap case for $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$, and $h = 0.78 \mu\text{m}$ when PMMA is in the grating gap. (b) The absorption plots for PMMA in the grating gap when $h = 0.78 \mu\text{m}$ and PMMA in the gap and on top of the grating when $h = 0.69 \mu\text{m}$. The inset illustrates the 2D view of PMMA in the gap and on top of the metal grating under the illumination of TM polarized light. (c) and (d) is the absorption curve for only grating with $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, $t_g = 0.5 \mu\text{m}$, where $h = 0.78 \mu\text{m}$ and $h = 0.69 \mu\text{m}$, respectively.

Due to strong coupling, hybrid polaritonic states, namely upper polariton (UP)

and lower polariton (LP), form. The electric and magnetic field distributions for both UP and LP are pretty much similar. In both of these cases, we have enhanced electric and magnetic field confinement. However, in the molecular vibrational location, both of the fields are suppressed. This phenomenon describes the formation of hybrid polaritonic states that are distinctive from each individual mode responsible for VSC.

If I add an additional molecular layer of 300nm of PMMA on top of the grating while its gap is filled by PMMA, only a little difference was observed in absorption spectra, as shown in Figure 3.6(b). However, the average linewidth reduces to $\frac{24.6 \text{ cm}^{-1} + 87.5 \text{ cm}^{-1}}{2} = 56.05 \text{ cm}^{-1}$ as the symmetry of coupling happens at lower grating height, $h = 0.69 \mu\text{m}$. That also causes a slight increase in Rabi splitting to 118.5 cm^{-1} . Nevertheless, the presence of the dark states at the location of molecular vibration gets more pronounced in this case, which shows most of the molecules from the extra PMMA top layer remain uncoupled.

For the angular incidence on the coupled PMMA in the grating gap scenario, until the 20° incident angle, the polaritonic states prevail unchanged in their spectral location, as shown in Figure 3.6(a). Moreover, for higher incidence angles, as the LSPR and MP grating modes start to separate, the overall coupling breaks. In this instance, the LSPR peak location significantly shifts, although MP and $\nu(\text{C=O})$ remain nearly at the same location.

3.3 Summary

While investigating the metal gratings as a new optical resonator to demonstrate VSC, I have found that embedding a molecular layer over the grating results in weak coupling. However, it creates an SPP resonance peak due to the presence of metal and dielectric interfaces. Moreover, filling the grating gap by SiO_2 can reduce grating linewidth, resulting in satisfying the VSC condition. PMMA in the grating gap leads to a significant increase in Rabi splitting, resulting in hybrid polaritonic states that have both the properties of molecular vibration and metal

grating resonance. The small peak along the $\nu(\text{C}=\text{O})$ spectral location for the coupled cases represents the uncoupled molecules in the system or so-called dark states.



Chapter 4

Modulation of Polaritonic Energy States Generated from Vibrational Strong Coupling by Utilizing Graphene Plasmons

4.1 Introduction

In the context of light-matter interaction, when the strong coupling between an optical mode and an excitonic transition of a molecule happens, it forms hybrid energy states that are known as excitonic-polaritonic states. Likewise, when a vibrational mode of molecules interacts with an optical mode, mostly an optical cavity mode, in the strong coupling regime, it creates two half-matter half-light vibrational-polaritonic states resulting in the upper (UP) and lower polaritonic (LP) states. When vibrational strong coupling (VSC) happens, due to reversible energy exchange between spectrally matched molecular vibration $\hbar\omega_v$ and optical cavity mode $\hbar\omega_c$, forms two energy eigenstates separated by Rabi energy ($\hbar\Omega_R$) [21]. These polaritonic states can be identified from the transmission spectrum through a splitting of peaks and by the anti-crossing behavior of the angular

dispersion.

Whether it is excitonic or vibrational strong coupling, the modulation of polaritonic energy levels plays a vital role in manipulating the statics of the quantum field that can be applicable to the field of integrated photonics or quantum computing [98][99]. Different methods have been applied to facilitate polaritonic modulation. For instance, in the context of excitonic strong coupling, it has been shown that effective tuning of the polaritonic energy states is possible by the polariton-polariton interaction [100], electrochemical modulation of the redox cycle of dye molecules [82], and variation of the light polarization for the MoS₂ excitation [101]. It has also been shown that the vibrational polaritonic states are modulated by femtosecond ultraviolet laser pulses [98]. While graphene has shown a significant impact in modulating the plasmonic resonance [102][103][104] and magnetic polaritonic resonance [105][106], its capability in controlling VSC has not been studied yet.

In this chapter, we demonstrate the impact of graphene plasmons (GP) in modulating the polaritonic energy states formed via VSC. In Chapter 2, we demonstrated that the deep metal grating creates hybridization of localized surface plasmon resonance (LSPR) and magnetic polariton (MP) that yields a resonance peak in the mid-IR range. We also showed interactions between GPs and hybrid grating resonances. In Chapter 3, we showed that the metal grating structure serves as an infrared resonator to induce VSC.

Unique to our design approach, we integrate single-layer graphene into a deep Ag grating. There are several reasons for using graphene in the VSC study. First, strong electric fields localized at the trench opening of a deep metal grating excite GPs, and consequently, the highly confined GPs further increase the coupling strength between hybrid LSPR-MP resonance of the grating and molecular vibrations. Second, the mode volume decreases dramatically with graphene, approximately four orders of magnitudes, when a single layer of graphene with a thickness of 0.35 nm is added to the conventional Fabry-Pérot (FP) cavity [107]. This allows the formation of vibrational-polaritonic states with a significantly reduced number of molecules and may offer the potential for single-molecule VSC.

Third, single-layer graphene with a thickness of only 0.35 nm can be located at the maximum optical fields of the deep metal grating, providing a spatial control of the molecular absorber relative to the spatially varying optical fields. Lastly, with external gate intensity altered, resonant peaks of the GPs can be tuned, further enhancing the coupling strength between grating LSPR resonance and molecular vibrations.

This work aims to modulate the optical modes of an infrared resonator with graphene to facilitate and tailor the strong coupling of light with molecular vibrations. To achieve this aim, a graphene-integrated deep metal grating is used to control the vertical and horizontal position of the maximum electric fields relative to the embedded molecular absorber and thus ensure that VSC takes place at pre-defined locations and frequencies. Through a combination of electromagnetic simulations, we characterize VSC between the hybrid resonance mode of the deep Ag grating and the carbonyl (C=O) stretch mode of poly(methyl methacrylate) (PMMA), which is modulated by GPs. Our design approach for the graphene-integrated deep metal grating provides new opportunities for electric field enhancement and optical spectrum shaping for impactful VSC studies.

4.2 Results and Discussion

As described in Chapter 2, a planar graphene layer on top of a deep metal grating creates plasmonic resonances at different locations of frequency due to the momentum matching between the Dirac plasmon and incident EM wave.

From the normalized absorption spectrum for different grating heights shown in Figure 4.1, the formation of four graphene plasmon resonance peaks can be observed. In the same spectral range of 1400 cm^{-1} to 2800 cm^{-1} , the number of GP resonance peaks was doubled when a layer of PMMA is placed on top of the grating (Figure 4.1a) compared to the graphene-integrated metal grating without a PMMA layer (Figure 2.3c). These results show a higher frequency interaction mode of GP induced due to the refractive index mismatch between the metal

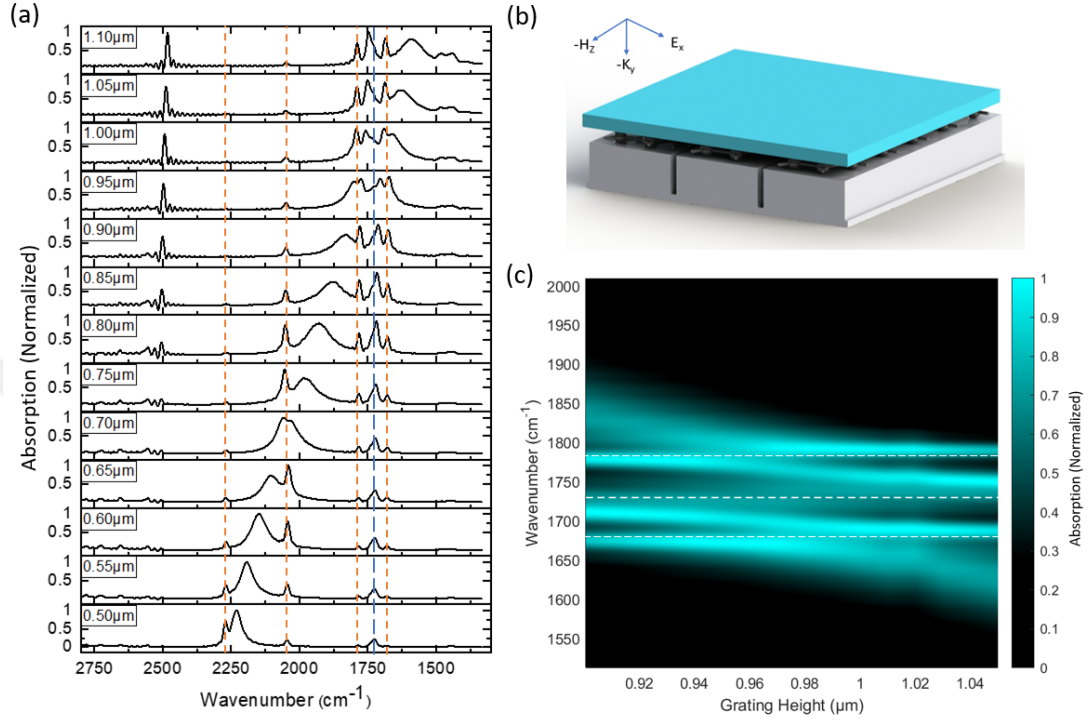


Figure 4.1: (a) Normalized absorption spectra for graphene integrated metal grating with a PMMA layer on top for grating parameter $\Lambda = 4 \mu m$, $b = 0.24 \mu m$, PMMA = $0.3 \mu m$ and chemical potential applied to graphene, $\mu_c = 0.5 eV$. Red dotted lines indicate the locations of GPs, and blue lines indicate the location of the carbonyl stretching band of PMMA. (b) A schematic diagram for the graphene-integrated metal grating that has a PMMA molecular layer on top. (c) Anti-crossing behavior for varying grating height through 1730 cm^{-1} .

and PMMA. For grating heights ranging from $0.65 \mu m$ to $0.75 \mu m$, we observe Fano resonance lineshapes at around 2042 cm^{-1} due to the interaction between a narrow GP mode and a broad grating resonance. At a lower wavenumber range between 1625 cm^{-1} and 1875 cm^{-1} , we observed multiple coupling events between the GPs, grating resonances, and molecular vibrations.

In Chapter 3.2.1, we discussed the coupling between hybrid LSPR-MP grating resonance and molecular vibration when a molecular layer is put on top of a grating (i.e., no graphene was added). The results showed that the coupling is mostly due to the LSPR at the metal grating edges falling into the weak coupling regime: $\Omega_R < \frac{(\Gamma_v + \Gamma_g)}{2}$. However, when single-layer graphene is added to the top of the grating with a chemical potential, $\mu_c = 0.5 eV$ (Figure 4.1), two GP modes at

1679 cm^{-1} and 1783 cm^{-1} interact with the LP and UP states, respectively. These additional couplings between GPs and UP/LP modes cause two extra minor anti-crossing across 1680 cm^{-1} and 1780 cm^{-1} apart from the major anti-crossing along 1730 cm^{-1} . For the grating width of 0.24 μm , we have the symmetry of the polaritonic states. In this unique coupling phenomenon, the wavenumber difference between two extreme maxima or the Rabi splitting ($\Omega_R = 123 \text{ cm}^{-1}$) is higher than the average linewidth (83.3 cm^{-1}) of the grating resonance (152 cm^{-1}) and molecular vibration (24.6 cm^{-1}) and is the highest value in comparison with the strong coupling cases described in Chapter 3. Such avoided crossing can be achieved by using different kinds of metals, for example, gold as shown in Figure S4.1.

The presence of graphene allows us to achieve electric-field confinement at the interface between the grating opening and the PMMA layer (Figure 4.2). The highest electric field confinement is achieved at the two extreme maxima points of 1669 cm^{-1} and 1792 cm^{-1} , and the lowest confinement at the location of $\nu(\text{C}=\text{O})$. In addition, the field confinement intensity at 1767 cm^{-1} and 1697 cm^{-1} are very close to each other. That shows the mirror images of the peaks along the wavelength value of 1730 cm^{-1} have similar characteristics.

Moreover, for all the $\text{Re}(E/E_o)$ field mapping, we can observe the formation of nodes with high E-field intensity and anti-nodes with low E-field intensity that resembles a standing wave. From the E-field vector distribution, we can observe that despite having different intensity nodes and antinodes in different wavenumber locations, the vector fields maintain a periodic distribution similar to a standing wave along the graphene surface. If the vectors generate from one anti-node, it collapses in another anti-node circulating around a node, and an adjacent pair of node anti-node creates the opposite electric vector field distribution, ensuring the collapse of two opposite direction fields in one anti-node.

Unlike the molecular layer interacting with metal grating, when graphene is introduced in between grating and PMMA, it facilitates the confinement of both x and y components of the electric field to have greater interaction with the

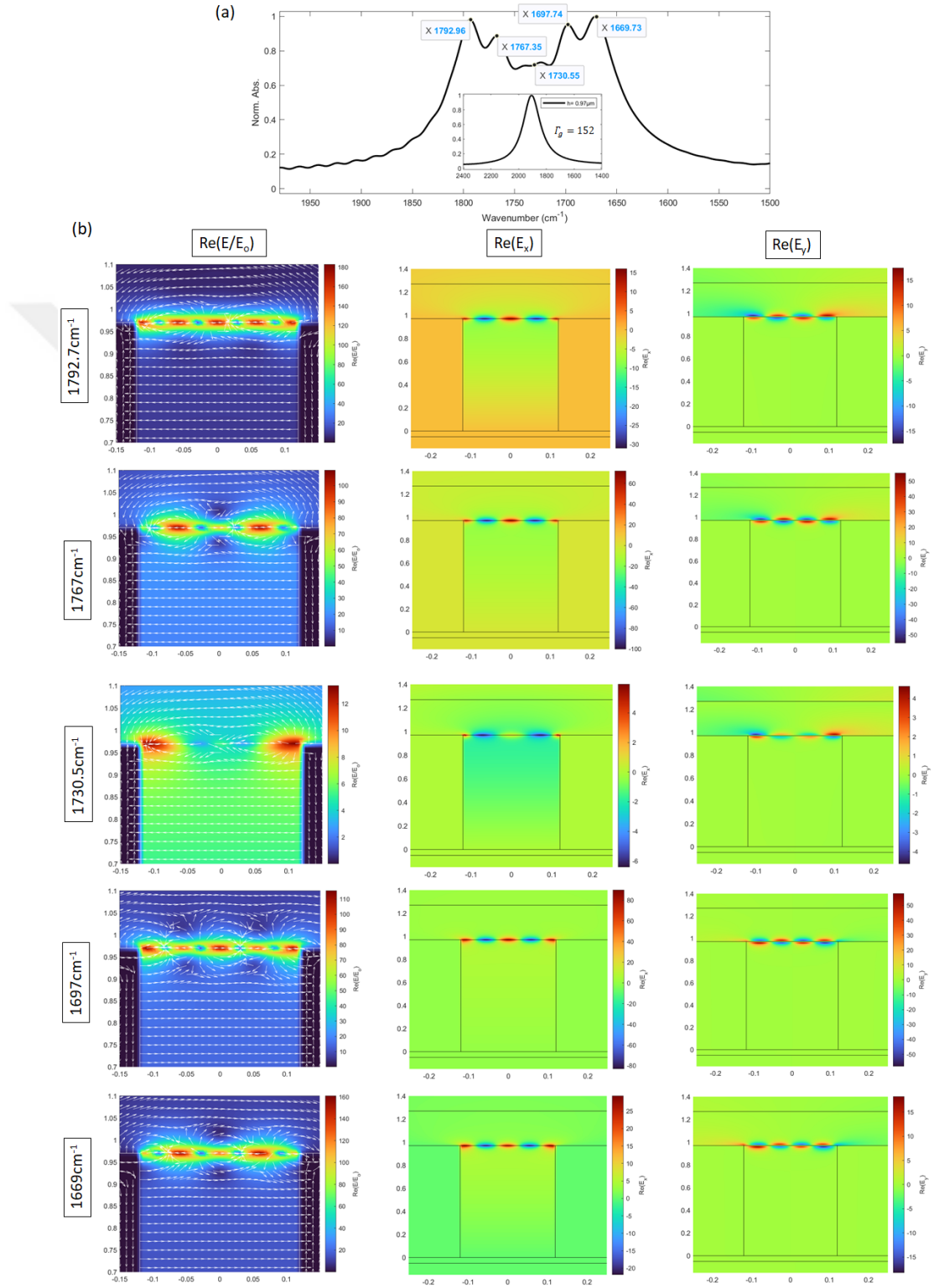


Figure 4.2: (a) The normalized absorption spectra for $\Lambda = 4\mu m$, $b = 0.24\mu m$, $h = 0.97\mu m$, PMMA = $0.3\mu m$ and chemical potential applied to graphene, $\mu_c = 0.5\text{eV}$. The x-values indicated are the wavenumber values of the four peaks and $\nu(\text{C=O})$ dip. The inset is the only grating response for the grating parameter mentioned in Figure 4(a). (b) Real components of the electric field (E/E_0), x component (E_x), and y component (E_y) are shown for four peaks and a dip indicated in Figure 4.2(a). The x and y axis are the x and y coordinates of the geometry of the periodic structure.

molecules. In all the wavenumber points, E_y field creates multiple dipoles, in this case, four dipoles, in the contact area of air, graphene, and PMMA. However, due to the LSPR from the edges of the metal grating, the field is extended beyond the edges. In addition, for the case of the molecular layer in the grating, the E_x field is not significantly enhanced. However, when graphene has an impact on the VSC, the electric field confinement in the x-direction is also quite significant, illustrated in the $Re(E_x)$ field mapping in Figure 4.2(b). For all the wavelength locations, there are pairs of positive nodes and negative anti-node charges. Therefore, the E_x distribution is mostly responsible for the formation of nodes and anti-nodes in the E-field magnitude distributions.

From the electric field distributions and the vector field distributions, it is clear that when graphene is introduced to a metal grating, it ensures a higher interaction between the light and the molecules compared to the case without graphene. When a molecular layer is placed on top of metal grating without graphene, the field confinement is only at the edges (Figure 3.2b). Hence, the interacting molecules are primarily those in contact with the edges of the grating. On the contrary, graphene allows plasmonic propagation throughout the grating trench and molecular layer above. Therefore, it results in a greater interaction volume compared to without graphene case.

The GPs show tunability in spectral frequency and intensity with the variation of chemical potential, μ_c . As discussed in Chapter 2, the optical conductivity of graphene is a function of μ_c , and in turn, the spectral location and intensity of the GPs are determined by μ_c . However, the change of GP as a function of μ_c is not linear. From Figure 4.3(a), we can see that there is a GP peak

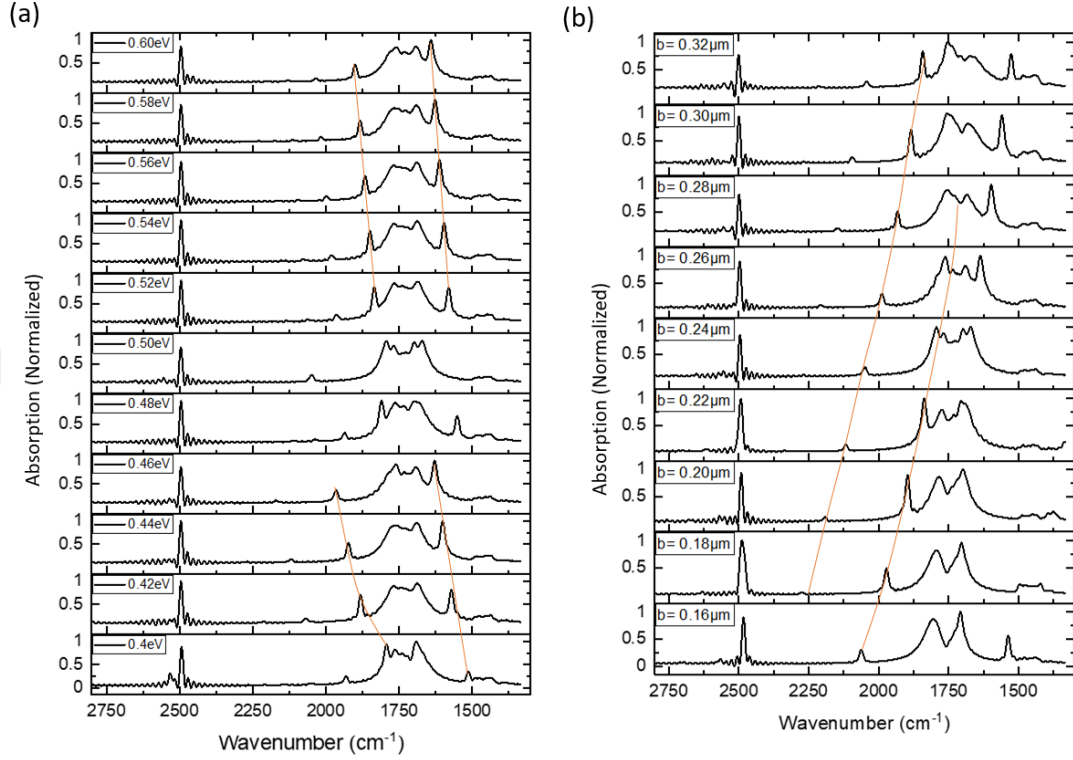


Figure 4.3: Graphene-integrated metal grating with a PMMA layer on top with grating parameters of $\Lambda = 4 \mu\text{m}$, $h = 0.97 \mu\text{m}$, and PMMA = $0.3 \mu\text{m}$ (a) Absorption spectra with the chemical potential varied from 0.4 to 0.6 eV and the grating trench width, b , fixed to $0.24 \mu\text{m}$. (b) Absorption spectra with the b varied from 0.16 to $0.32 \mu\text{m}$ and the chemical potential, μ_c fixed to 0.5 eV. The red curves were added to guide eyes to GPs with the variation of the chemical potential (a) and the grating trench width (b).

around 1500 cm^{-1} when μ_c is 0.4 eV. This peak blue-shifts with the increased μ_c until it interacts and hybridizes with the molecular vibrations at 1730 cm^{-1} at $\mu_c = 0.48 \text{ eV}$ and 0.50 eV . With the further increased μ_c , the peak continues to blue-shift. It is also noticeable that, by increasing μ_c , new GP peaks emerge in our focus spectral range. For instance, when $\mu_c = 0.48 \text{ eV}$, a new GP peak appears around 1600 cm^{-1} . This peak participates in the coupling phenomena at $\mu_c = 0.5 \text{ eV}$ and follows a linear blue shifting by increasing the μ_c similar to the previous peak. Although there is not any linearity in the GP peak shifting by changing μ_c , being blue-shifted for higher μ_c is true for all the four red lines indicated in Figure 4.3(a).

The GP spectral location also varies depending on the grating trench width, b . In Figure 4.3(b), when $\mu_c = 0.5eV$, we identified two GP peaks red-shift by increasing b . New GP peaks are formed for a greater b as well. When the trench width is greater, the area of interaction increases. This increased area supports more GP modes than a narrower trench, and hence, we can introduce greater GP modes by increasing the grating width.

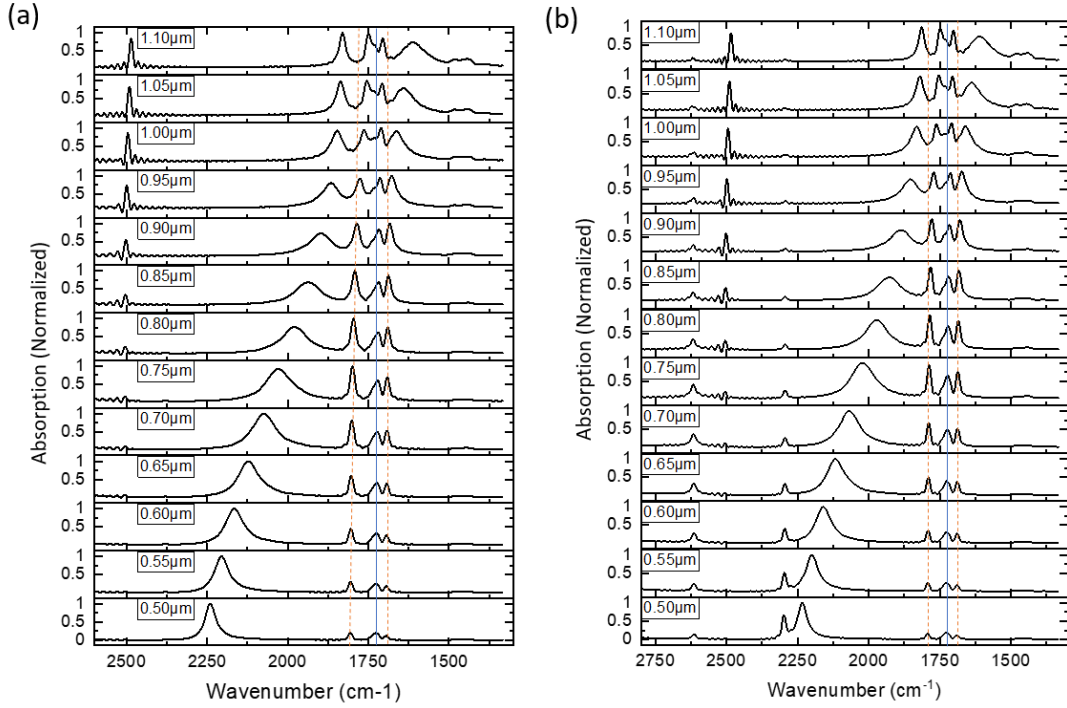


Figure 4.4: For a Ag grating with grating parameters of $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, and PMMA $= 0.3 \mu\text{m}$. Absorption spectra for different grating heights, h , when (a) double-layer graphene is used with $\mu_c = 0.5eV$, and (b) triple-layer graphene is used with $\mu_c = 0.35eV$. Blue dotted lines represent molecular vibration, $\nu(\text{C=O})$, and location. Red dotted lines show GP locations.

The GPs can be excited from graphene with more than a monoatomic layer. However, the optical conductivity of graphene will be scaled down to $\sigma_t = \frac{\sigma_{\text{mono}}}{t_{\text{grp}}}$, where σ_t is the multi-layer graphene's optical conductivity, σ_{mono} is monolayer layer graphene's optical conductivity, and t_{grp} is the thickness of graphene [108]. Figure 4.4(a) indicates that the double-layer graphene with $\mu_c = 0.5eV$ still excites two GP peaks on both sides of $\nu(\text{C=O})$. However, the double-layer GP peaks shift to 1693 cm^{-1} from 1680 cm^{-1} and from 1783 cm^{-1} to 1804 cm^{-1} compared to

the single-layer graphene. Nevertheless, the double-layer GPs still have an influence on VSC for grating heights $0.95\ \mu\text{m}$ to $1.00\ \mu\text{m}$. For triple-layer graphene, the GP resonance peaks change significantly if we maintain the chemical potential $\mu_c = 0.5\text{eV}$ (data not shown). However, as shown in Figure 4.4(b), for $\mu_c = 0.35\text{eV}$, we observe the GP resonance peaks near the molecular vibrational peak location that influences the polaritonic states, specially the upper polariton, in between $0.95\ \mu\text{m}$ to $1.05\ \mu\text{m}$ grating height.

4.3 Summary

In this chapter, we showed how the graphene plasmon impacts the polaritonic states created by VSC. Under the influence of the GP, the graphene-integrated metal grating has very high electric field confinement in both the x and y direction for TM polarized light that facilitates higher EM wave interaction with the molecular layer on top of the graphene. Due to the plasmonic propagation of graphene in the total area on top of the grating, the interaction volume significantly increases compared to the case without graphene that only has LSPR propagation at the edges. Graphene also offers great tunability in altering polaritonic energy levels as its plasmon energy changes by changing the chemical potential. We also showed that a double or triple layer of graphene is also capable of generating GPs, which can influence the VSC.

Chapter 5

Experimental Development

5.1 Introduction

In chapters 2,3 and 4, the main optical resonator is the deep metal grating to observe Fano resonance, vibrational strong coupling (VSC), and the impact of graphene plasmon (GP) to modulate polaritonic energy. In addition, we also implemented graphene, single and multilayers, to show the GP effects when it interacts with the deep metal grating resonance. To experimentally validate the results described in the previous three chapters, we fabricated the deep metal grating and generated large-area graphene ($2 \times 2 \text{ cm}^2$). In this chapter, we will describe the fabrication process of metal grating and graphene.

5.2 Fabrication Process

The fabrication of deep metal grating structures involves lithography and multiple metal or dielectric layer depositions. As described in Figure 5.1, at first, we took an undoped silicon (Si) wafer as it is fully transparent in the mid-IR region. The undoped Si wafer was cut into a $1 \times 1 \text{ cm}^2$ chip by using a dicing saw and washed in

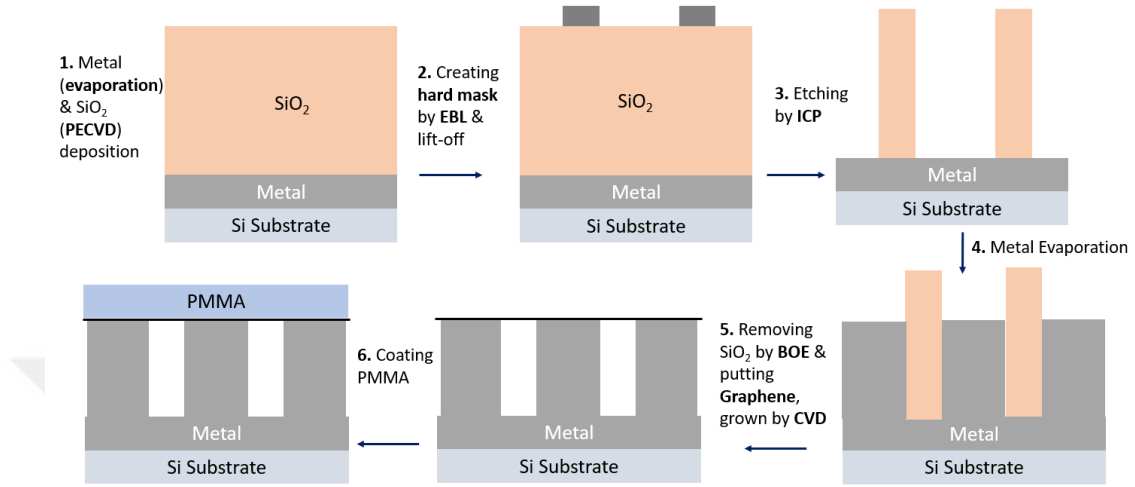


Figure 5.1: A flow diagram of the fabrication steps for the graphene-integrated metal grating structure with a PMMA layer. See the main text for details.

a piranha solution. First, we deposited a bottom metal layer (either Ag or Al with a thickness of 50nm) using an e-beam evaporator on the Si substrate to support the MPs as described in Chapter 2. A sacrificial layer of SiO₂ was also coated on the metal layer by plasma-enhanced chemical vapor deposition (PECVD). We need this sacrificial layer to make the grating pattern using e-beam lithography (EBL) and inductively coupled plasma (ICP) etching. In Step 2, a 320nm-thick layer of poly methyl methacrylate (PMMA) was coated by spin-coating on the SiO₂ layer for EBL. After the development of the EBL patterned sample, we coated a metal film (Cr with a thickness of 100nm) that resulted in a patterned hard mask after lifting-off PMMA. The patterned hard mask with SiO₂ sample was then subjected to ICP etching from which we obtained arrays of SiO₂ pillars with a height of $1.5\ \mu\text{m}$ (Step 3). A 700nm-thick metal layer (Ag) was deposited using e-beam evaporator (Step 4). Finally, arrays of SiO₂ wires were removed by buffered oxide etching (BOE), resulting in a deep metal grating structure (Step 5).

To investigate the effect of GP, we generated bilayer large area graphene ($2 \times 2\ \text{cm}^2$) by chemical vapor deposition (CVD). We characterized the graphene and determined the number of layers by the Raman spectroscopy. This graphene with a PMMA layer on top can be embedded on the metal grating to measure

the absorption spectra (Step 5 and 6).

5.3 Metal and Dielectric Layer Deposition

5.3.1 Metal Deposition

In this part we will discuss the deposition of various types of metals and their parametric optimization in e-beam evaporator. We used a Vaksis PVD Vapor 4S e-beam evaporator in this process. We deposited three metals in the fabrication steps, Al (Step 1), Ag (Step 2) and Cr (Step 4).

Al was deposited as a bottom layer of the structure. The reason for selecting Al instead of Ag is its good adhesion capability to the SiO₂ layer. In Figure S5.1, we can see that SiO₂ peels off from the Ag layer. To deposit Al, we used a Fabmate crucible and applied a voltage of 7 kV with currents of 40 – 45 mA by which we maintained a deposition rate of 0.3 Å/s. Initially, we deposited a 30nm-thick Al film, considered a tooling factor of 100, and measured the thickness of the film at different locations using a Dektak profilometer. We found an average thickness of 32.5nm ±3nm. Then, the tooling factor expression can be given by

$$\text{Tooling factor} = \text{Initial tooling factor} \times \left(\frac{\text{Real thickness}}{\text{Deposition thickness}} \right) \quad (5.1)$$

$$\text{Tooling factor} = 100 \times \left(\frac{32.5}{30} \right) = 108$$

Considering the tooling factor of 108, we deposited a 50nm-thick Al layer on an undoped Si wafer. The reason for choosing an undoped wafer is its complete transparency in the mid-IR range.

As described in the fabrication steps, we deposited Cr as a hard mask after performing EBL. To calculate the tooling factor of Cr, we applied a voltage of

7 kV with a current of ~ 15 mA to deposit a 100 nm-thick Cr layer. An average thickness was measured as $135 \text{ nm} \pm 6 \text{ nm}$ by the Dektak profilometer. The tooling factor was obtained as $100 \times \left(\frac{135}{100}\right) = 135$. For all Cr deposition, we used 135 as a tooling factor.

We used e-beam evaporator to deposit Ag. We maintained a voltage of 7 kV with a current of 25 – 30 mA to deposit Ag with a deposition rate of $0.2 - 0.3 \text{ \AA/s}$. After depositing a Ag film with a thickness of 50 nm using a tooling factor of 100, we found the thickness of the Ag film is 50 nm by using a profilometer. Therefore, the calculated tooling factor of 100 was used for Ag.

5.3.2 SiO₂ Deposition

In the fabrication step 1, we used SiO₂ as a sacrificial layer. To make a deep metal grating structure, we needed to deposit a thick layer of SiO₂ (thickness reaching up to 1500 nm). In such a case, PECVD is a reasonably fast process.

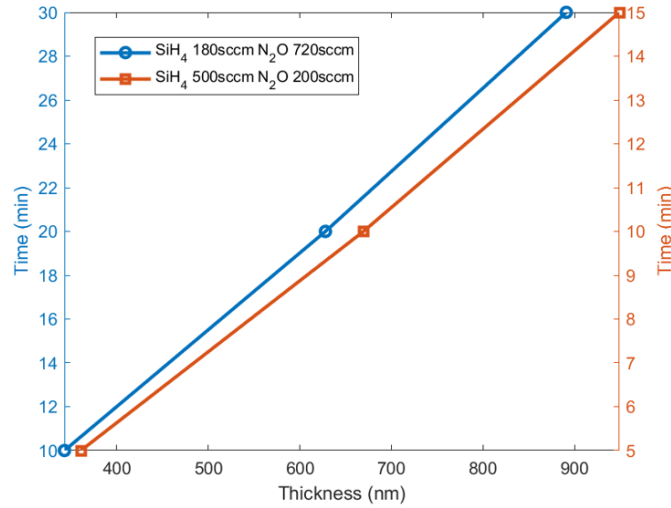
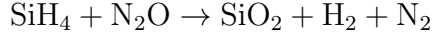


Figure 5.2: A Calibration curves of SiO₂ for the recipe 180sccm of 2% SiH₄ (N₂) and 720sccm of N₂O (blue line); 500sccm of 2% SiH₄ (N₂) and 200sccm of N₂O (orange line).

To deposit a thick dielectric film. The chemical reaction to have SiO₂ layer in

a PECVD chamber is:



The SiH_4 supplied in the chamber is dissolved in N_2 at a 2% concentration. The deposition rate depends mostly on the SiH_4 to N_2O flow rate ratio.

Figure 5.2 shows the effect of relative flow rate between SiH_4 to N_2O . We measured the thickness of the SiO_2 deposited on a Si substrate by a V-Vase ellipsometer where the Cauchy model was used for the curve fitting. The deposition rates were almost doubled for 2% SiH_4 (N_2) : N_2O = 5 : 2 compared to 1:4 when the other parameters are same. The rate of deposition did not change much by changing the temperature and RF power. However, higher temperature and RF power may facilitate the reaction between the metal and the supplied gases under plasma condition. Considering every factor, we maintained 600sccm of 2% SiH_4 , 300sccm N_2O , 600mTorr chamber pressure, 100°C chamber temperature, and 100W RF power that has a deposition rate of 61.65nm/min. For our structure, we continued this recipe for 23min to deposit an approximately 1450-1500nm thick SiO_2 layer.

5.3.3 PMMA Spin-Coating

In our study, a PMMA film served as an e-beam resist for fabrication and a molecular absorber bearing a strong molecular vibration due to a carbonyl stretching mode at 1730cm^{-1} . We made the PMMA layers by spin-coating on a Si substrate with different spin speed (rpm). We used PMMA with a molecular weight of 950K dissolved in anisole at 3% (A3) or 8% (A8) (Micro Resist Technology).

The spinning speed was maintained at 3000rpm for 1min with an acceleration of 250 rpm/sec for all the coating. After coating PMMA, the samples were baked for 10 min on a hot plate at 170°C. For this recipe, we have a thickness between 240nm- 125nm for A3 and 1700nm-800 nm for A8. However, we need the e-beam resist thickness to be around 300nm for a proper liftoff, and the molecular layer thickness is considered to be 300nm as well. As both of the PMMA, A3 and

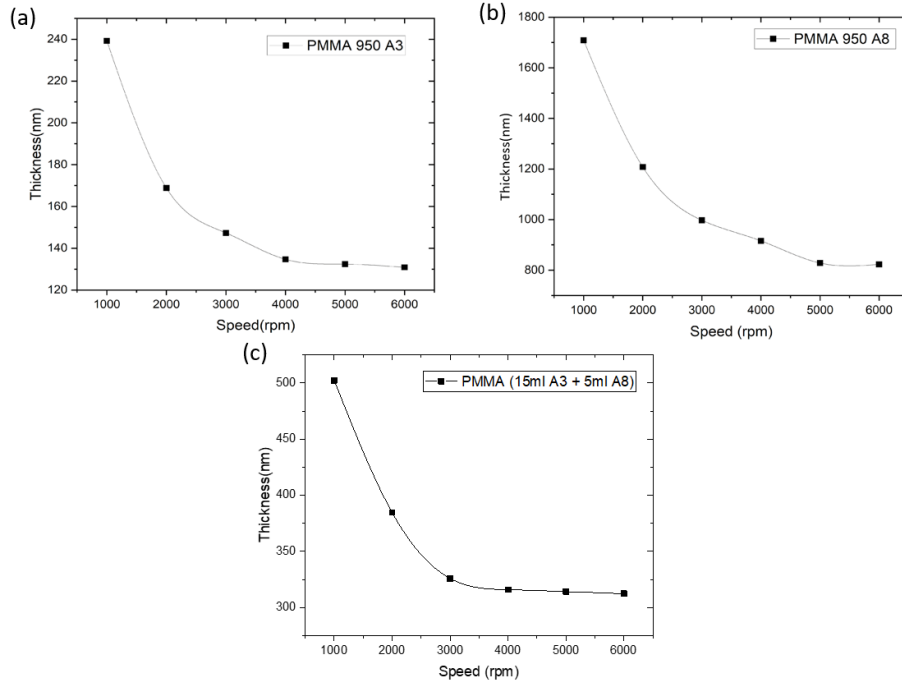


Figure 5.3: Calibration curves for spin-coating (a) PMMA 950K A3, (b) PMMA 950K A8, and (c) a mixture of PMMA 950K A3 (15ml) and A8 (5ml).

A8, are dissolved in anisole, they are miscible. Therefore, we mixed 15ml of A3 with 5ml of A8 to have the PMMA thickness in between. From the calibration curve shown in Figure 5.3, we selected 3000 rpm to coat 320nm thick PMMA for e-beam lithography.

5.4 E-Beam Lithography

As described in the fabrication steps, a metal hard mask is created by EBL. For this purpose, we coated the PMMA A3 and A8 mixture with 3000 rpm on top of the SiO₂ coated substrate. The PMMA film was baked for 10min at 170°C temperature on a hot plate.

For the pattern shown in Figure 5.4, we applied a voltage of 30kV and a current of 0.017nA. The area step size was $0.0063\mu m$ and the base area dose was $150\mu C/cm^2$ with a dose factor of 3. After EBL, the sample was developed

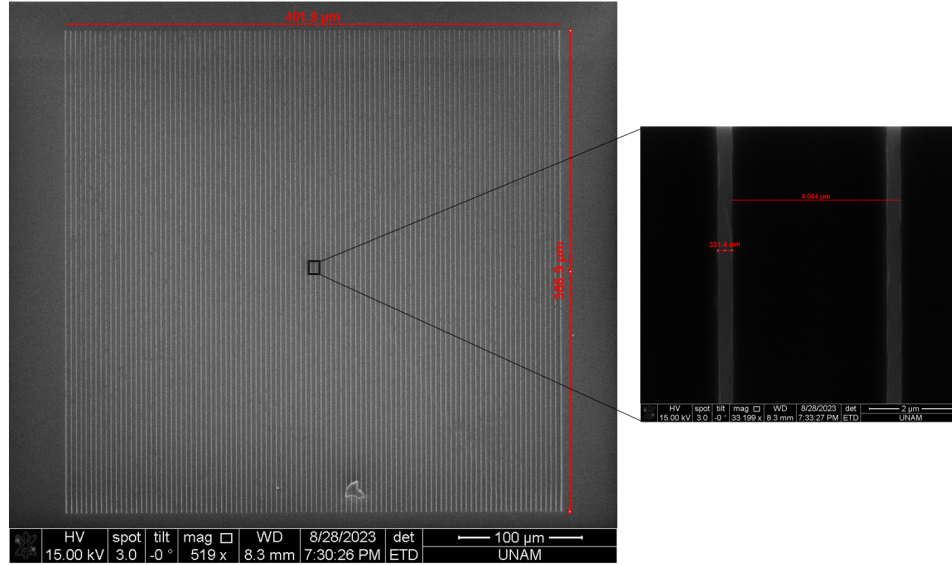


Figure 5.4: SEM images of the Cr hard mask in a grating pattern fabricated by EBL. The total array size is $400 \times 390 \mu\text{m}^2$ with periodicity $4 \mu\text{m}$ and width is approximately 330nm .

in methyl isobutyl ketone (MIBK) for 50sec and then isopropanol alcohol (IPA) for 20sec, followed by washing in de-ionized (DI) water. The patterned PMMA was then transferred to the e-beam evaporator chamber, and a 100nm -thick Cr layer was deposited. After the Cr deposition, PMMA in the unpatterned area was removed by an acetone bath that ultimately yielded the Cr pattern shown in Figure 5.4. A FEI Nova NanoSEM 600 scanning electron microscope (SEM) was used for imaging. The targeted geometry was 50nm width of the grating. However, due to proximity error caused by the EBL, it gave us 330nm of the line width in the end.

To be comparable to the beam size of the Fourier transform IR spectroscopy (FTIR), we needed to make a large area grating up to 1.5mm^2 – 2mm^2 . To achieve such a large area grating with a narrow grating width, we repeated the $385 \mu\text{m}$ by $395 \mu\text{m}$ pattern for 25 times with a satisfactory alignment and achieved a $2\text{mm} \times 2\text{mm}$ total area pattern shown in Figure 5.5. In this case, the declared grating width was 40nm , and the dose factor was 1.5 for a base dose of $150 \mu\text{C}/\text{cm}^2$. Voltage, current, area step size, development process, and lift-off process are the same used for making the pattern in Figure 5.4. In this case, we achieved a

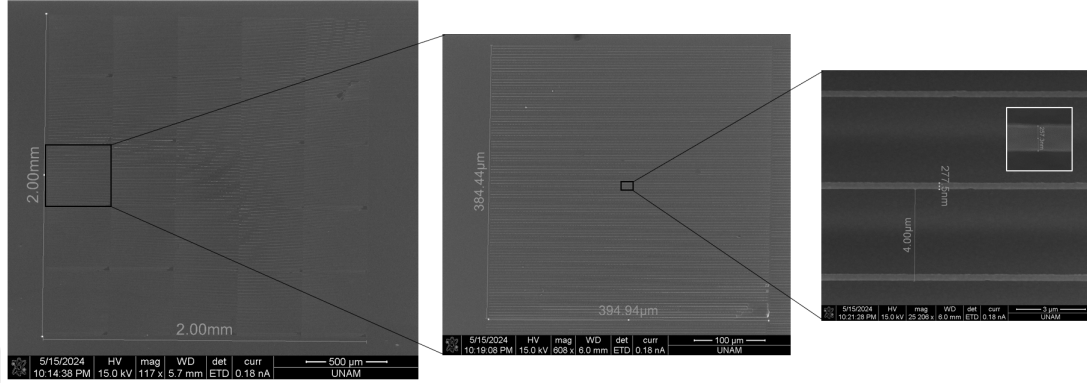


Figure 5.5: SEM images of a large area pattern by making 5×5 arrays of $385 \times 395 \mu\text{m}^2$ Cr hard mask pattern. The periodicity of the grating is $4 \mu\text{m}$, and the width is approximately 275nm .

grating width of around 260- 275nm.

5.5 Inductively Coupled Plasma (ICP) Etching

After making the hard mask by EBL, we etched a SiO_2 layer by ICP. For the ICP etching, first, we cleaned the chamber by running O_2 gas for 10 min. We maintained 100sccm O_2 flow rate with 600W of 13.56 MHz coil power. Then, we pre-conditioned the chamber by using a recipe for etching a SiO_2 layer for 5min without adding the sample. The recipe comprised of 20sccm O_2 and 100sccm of CHF_3 with 250W coil power.

After cleaning and pre-conditioning the chamber, we placed our sample patterned with 1400-1500nm thick SiO_2 pillars on a 4" quartz wafer in the chamber. We used the SiO_2 etching recipe for 60min. We measured the surface profile of the etched sample using a VKX 100 microscope (Figure 5.6). The patterns were shown in the three-dimensional image, and the depth of the SiO_2 patterns was measured as approximately 1500nm with the etching rate of 25nm/min.

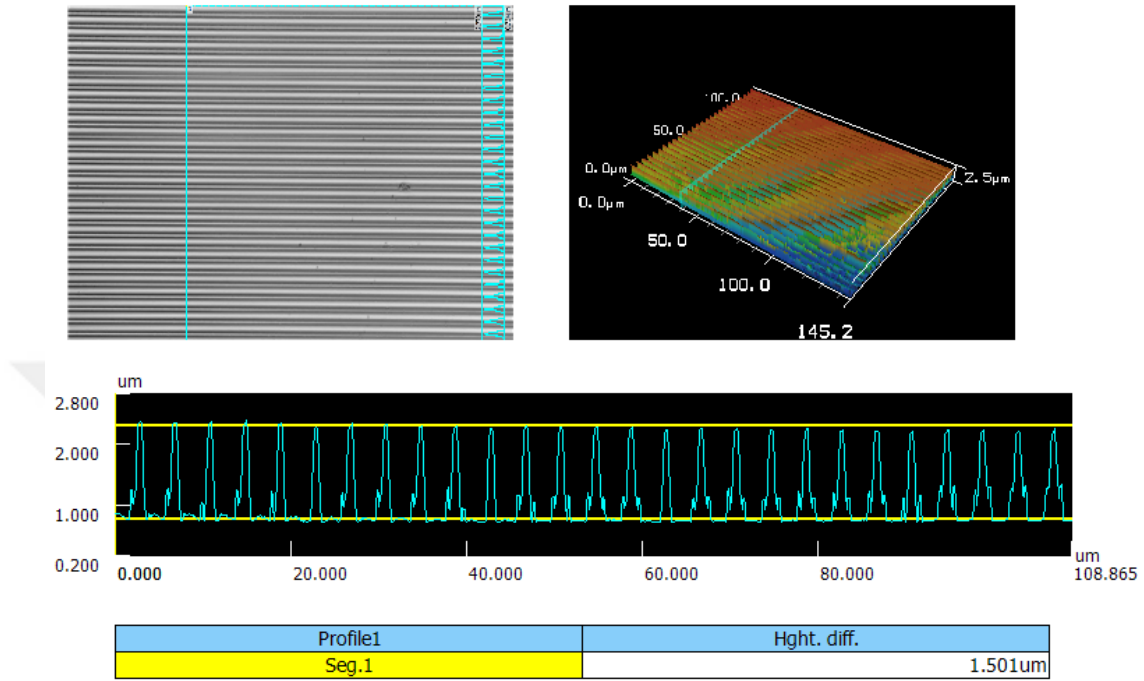


Figure 5.6: 3-dimensional microscopy and profile measurement for the ICP etched SiO_2 using VKX 100 microscope.

5.6 Metal Deposition, BOE Etching, and SiO_2 Lift-off

The ICP etched sample has narrow and deep SiO_2 grating. Now we deposited a metal, Al for the case in Figure 5.6, to fill the gap in between the SiO_2 gratings.

The deposited Al thickness is 700nm this time. After the metal deposition, we immersed the sample in a BOE solution for 2min to remove SiO_2 . The BOE etched sample resulted in a deep metal grating shown in Figure 5.7. This sample is same as the one shown in Figure 5.5, which has a Cr hard mask width of 330nm. However, the final grating has 415nm width due to anisotropic limitation of ICP etching.

The SEM image of the BOE etched sample in Figure 5.7 shows some roughness on the Al surface. The roughness is partially caused by the ICP etching that roughens the bottom layer of the metal. When further Al deposition was done

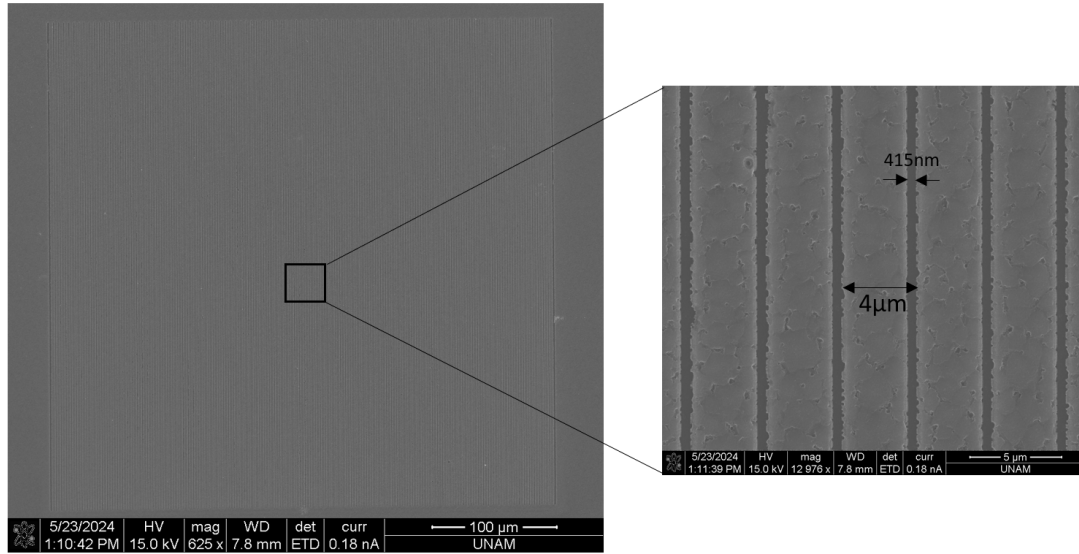


Figure 5.7: SEM images of a Deep metal grating of Al after BOE etching.

on it, the deposited metal followed the surface profile of base Al. Moreover, Al is slightly etched by BOE with a very slow rate [109]. That is why, when the BOE was etching SiO_2 , it affected the Al surface, which created the roughness on it.

5.7 Graphene Synthesis

One very important part of this study is to investigate the GP effect on the metal grating. For that, we need to add a graphene sheet on top of the grating. We used a chemical vapor deposition (CVD) device to grow graphene on a copper foil.

First, a commercially available copper foil with a dimension of 0.05mm thickness, 30mm width, and 30mm length was cleaned by immersing in nitric acid (HNO_3) and sonicated in acetone and isopropanol [110]. Then the cleaned copper foil was placed on a thick quartz plate. The quartz plate was placed inside the CVD chamber that is connected to a vacuum pump. After running the pump for 30min, the chamber pressure reached to 1.4mbar. Then 50sccm H_2 was supplied to the chamber and the temperature of the chamber was ramped up to 1000 °C

in 30min.

Table 5.1: Graphene growth process

T (from)	T (to)	Time	Flowrate
25 °C	1000 °C	30 min	50 sccm H ₂
1000 °C	1000 °C	30 min	50 sccm H ₂
1000 °C	1000 °C	15 min	(10:1) 50 sccm H ₂ : 5 sccm CH ₄
Cooling down the chamber in around 1 hour 30 min (from 1000 °C to 65 °C)			

After that, the Cu foil was annealed for another 30min with the presence of 50sccm H₂. This annealing process in H₂ environment removes the oxides from the copper surface that enhances the carbon atom mobility on its surface [111]. Then 5sccm of CH₄ was introduced while 50sccm of H₂ with 1000 °C chamber temperature was continued and this process prolonged for another 15min. Here H₂:CH₄ = 10:1 ratio was maintained as it has been reported that higher ration increases the possibility of having thicker graphene layer [112]. During this growth process, CH₄ decomposes to C and H₂. The produced carbon atoms form a thin layer of graphene on top of the Cu foil through diffusion and due its low carbon absorptivity it produces single or few layers of graphene. After this growth process, the H₂ and CH₄ flow was stopped and the chamber cooled down to normal temperature within 1.5 hours.

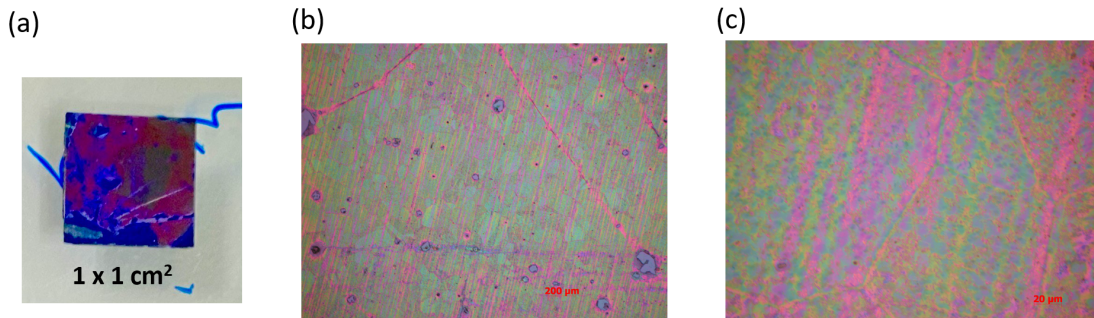


Figure 5.8: A photograph (a) and an optical microscope image (b) & (c) of a 1 x 1 cm² graphene sheet after transferring it to a SiO₂/Si substrate.

To transfer the graphene from the copper foil to the desired substrate, the copper foil with graphene was coated by PMMA (950K A3) at a spin speed of 3000rpm. The PMMA layer was baked for 10min at 170 °C. The Cu was then chemically etched in a 0.5M solution of iron(III) chloride (FeCl_3) for 2.5 hours. When the Cr was completely removed, graphene was wrenched by water and transferred to a SiO_2/Si substrate, as shown in Figure 5.8(a). The residual PMMA was removed by dropping acetone on top of the substrate. The optical microscopic image of the transferred graphene shown in Figure 5.8(b) & (c) indicates the formation of large area grains with clear grain boundaries. These are the copper grains formed due to the annealing and graphene grew following these grains throughout its surface.

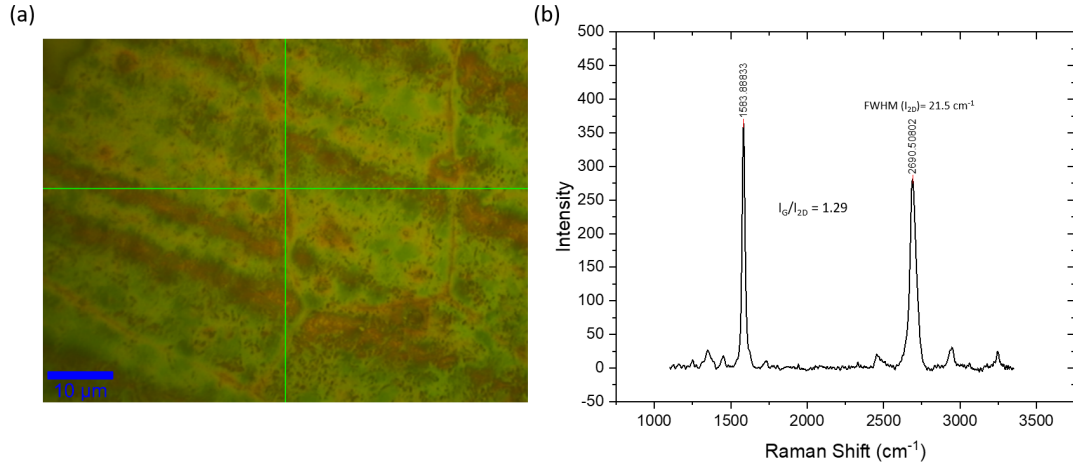


Figure 5.9: (a) A microscope image taken by the optical microscope integrated with a Raman spectrometer. The cross-section of the two green lines shows the laser focusing area during the Raman measurement; (b) Raman spectrum of the graphene sheet synthesized by CVD.

To characterize the properties of the graphene, we took the Raman spectrum of the transferred graphene sheet using Raman Witech Alpha 300S. The Raman spectrum was baseline corrected by commercial software OriginPro 2021. The graphene can be identified by having a G peak at 1580 cm^{-1} and a 2D peak at 2700 cm^{-1} . One indicator of whether the graphene is single-layer or multi-layer is the intensity ratio of G (I_G) to 2D peaks (I_{2D}). For monolayer graphene, I_G/I_{2D} is usually 0.25-0.5 [113]. However, according to the article by Ferrari, Andrea C.,

et al. [113], the driving indicator of single-layer or multi-layer graphene is the width of the 2D peak. The width of the 2D peak is approximately 50cm^{-1} for bulk graphite and any graphene with more than 5 layers, while it is as small as 20cm^{-1} for single-layer graphene. The reason of higher FWHM for more than one layer is the formation of multiple bands in the K space. For the double-layer graphene, there will be a formation of 4 bands, and each of them corresponds to an individual component in the Raman spectrum due to different electron-phonon couplings.

In our case, we observe that the FWHM of the 2D peak is 21.5cm^{-1} in Figure 5.9(b). Therefore, we can argue that even if the graphene we synthesized is not monolayer as I_G/I_{2D} is greater than 1, as the FWHM is very close to that of monolayer graphene. Hence, the graphene we synthesized is close to the bilayer.

5.8 Summary

In this chapter, we describe how we fabricated a deep metal grating made of Al. The process involves metal deposition by an e-beam evaporator, a sacrificial SiO_2 layer deposition by PECVD, and PMMA spin coating for EBL. A Cr hard mask was fabricated by EBL, followed by the development and lift-off of the PMMA layer. The SiO_2 layer was etched by ICP, followed by the deposition of a thick Al layer. The SiO_2 layer was removed by BOE, completing the fabrication of the deep Al grating structure.

We also synthesized graphene by CVD on a Cu precursor. We transferred the synthesized graphene to the SiO_2/Si substrate and used Raman spectroscopy to characterize the thickness of the graphene. Based on the results from the Raman spectroscopy, we concluded that the synthesized graphene is a bilayer graphene.

Chapter 6

Conclusion and Future Prospects

6.1 Conclusion

In this thesis, we have introduced a deep metal grating structure as an optical resonator and explained that the origin of the resonance is the hybridization of localized surface plasmon resonance (LSPR) and magnetic polariton (MP). The hybridized modes start to be separated from each other at the oblique incidence of TM polarized light, which eventually facilitates the formation of Fano resonance due to the symmetry-breaking of the plane wave. Moreover, by implementing a graphene sheet on top of the grating, we observed a formation of Fano resonance caused by the graphene plasmon (GP) with varying interaction strength evident from the asymmetric parameter q over a certain range of the grating height.

Furthermore, deep metal grating is introduced to realize vibrational strong coupling (VSC). We showed that the grating resonance interacts with a vibrational mode of the molecule and achieves the interaction in the strong coupling regime that has insensitivity towards the angular incidence until 20° impact angle. Moreover, by implementing a graphene sheet between the metal grating and the molecular layer on top of the grating, we have shown the modulation of polaritonic energy states formed by VSC between the metal grating resonance and

molecular vibration. Due to the propagation of GP, the E-field confinement is extremely high in the upper and lower polaritonic energy states. As graphene allows surface plasmon polaritonic propagation in the total area between the grating gap and molecular layer, the interaction area is much higher for graphene-integrated metal grating compared to cases without graphene. In addition, GP provides tunability in the modulation of energy eigenstates by altering graphene’s chemical potential, i.e., by changing the biasing voltage.

We also successfully fabricated the deep metal grating structure. We made grating patterns using E-beam lithography and inductively-coupled plasma etching of the sacrificial SiO₂ layer. Finally, the deep metal grating structure was generated by metal deposition and buffered oxide etching. We synthesized a large area (2cm x 2cm) of graphene using the chemical vapor deposition method, transferred and characterized it by Raman spectroscopy.

6.2 Future Work

First of all, the experimental validation of all the results shown numerically will confirm our ideas, and we are working on it. In addition, based on the correlation between the molecular concentration in a microcavity and Rabi energy, we are trying to evaluate the number of molecules necessary to result in VSC by manipulating the thickness of the molecular layer interacting with the metal grating. Furthermore, as we achieved very high E-field confinement due to the interaction of GP with lower polariton and upper polariton, it can be utilized in enhancing the sensitivity of the IR sensor, boosting nonlinear effects of IR light, and better controlling the quantum states. On the other hand, there are other optical modes, for example, waveguide modes, that may give better insight into the mechanism of VSC and open up new ways of VSC utilization. In our study, we could not excite the graphene plasmon inside a Fabry-Pérot microcavity. Despite its limitations, as an optical cavity has many advantages, new ways can be explored to investigate GP-mediated cavity polaritonic states.

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Appendix A

Supporting Information (Chapter 2)

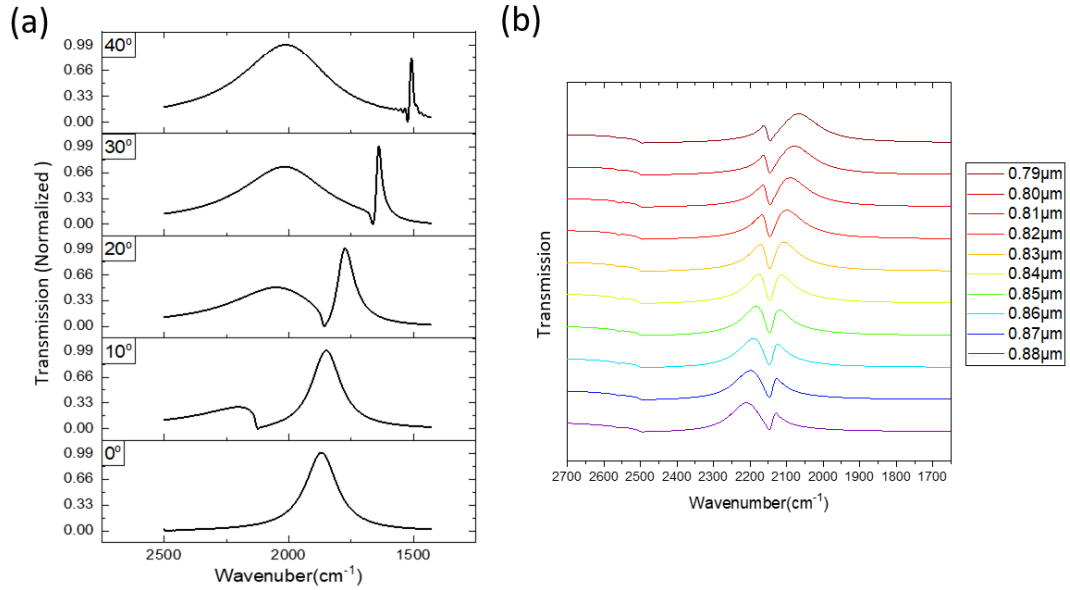


Figure S2.1: (a) Normalized transmission for angular incidence of TM polarized light on the metal grating with dimensions mentioned in Figure 2.1; (b) Transmission spectra for different grating heights with the grating and graphene parameters mentioned in Figure 2.3

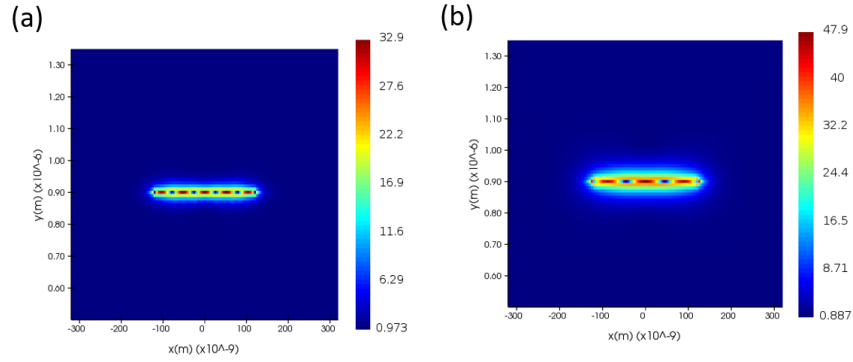


Figure S2.2: (a) and (b) are the electric field distributions for 2230 cm^{-1} and 1750 cm^{-1} wavenumbers for patterned graphene array with a width of $0.24\text{ }\mu\text{m}$ and chemical potential 0.5 eV .

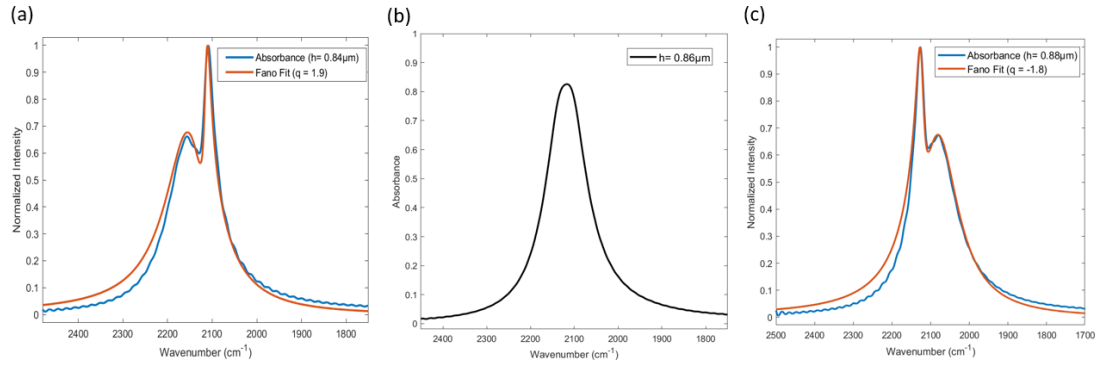


Figure S2.3: (a) and (c) are the absorption data with Fano fitting for $0.84\text{ }\mu\text{m}$ and $0.88\text{ }\mu\text{m}$, respectively. (b) is the absorption spectrum for $h = 0.84\text{ }\mu\text{m}$ where both of the resonance peaks overlap together, yielding one single Lorentzian peak.

Appendix B

Supporting Information (Chapter 3)

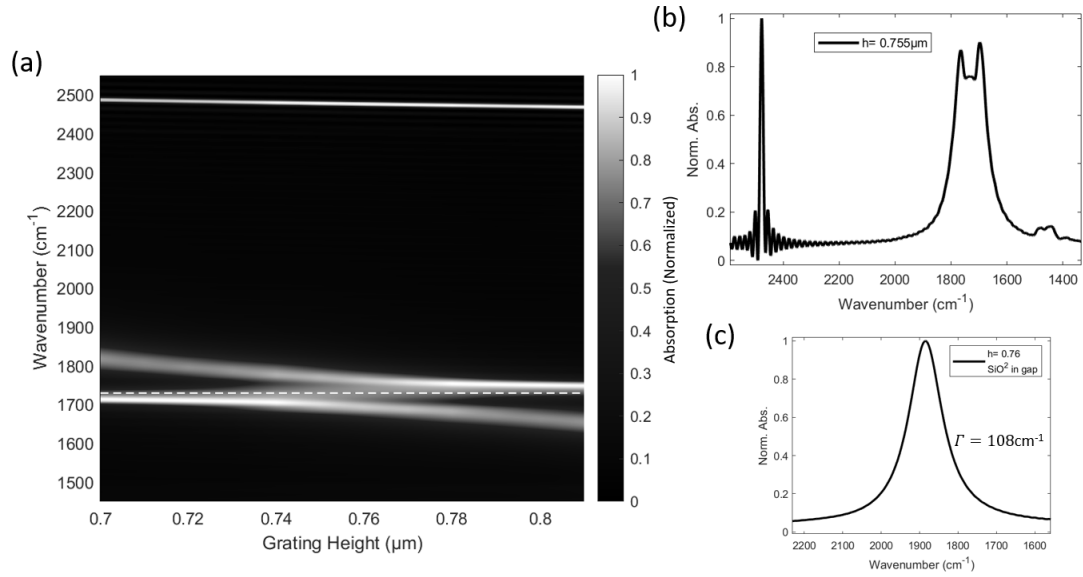


Figure S3.1: (a) Absorption mapping for the coupling between grating resonance and molecular vibration. (b) Absorption spectrum for $h = 0.755 \mu\text{m}$ where symmetrical polaritonic states formed. (c) Grating response when gap is filled by SiO_2

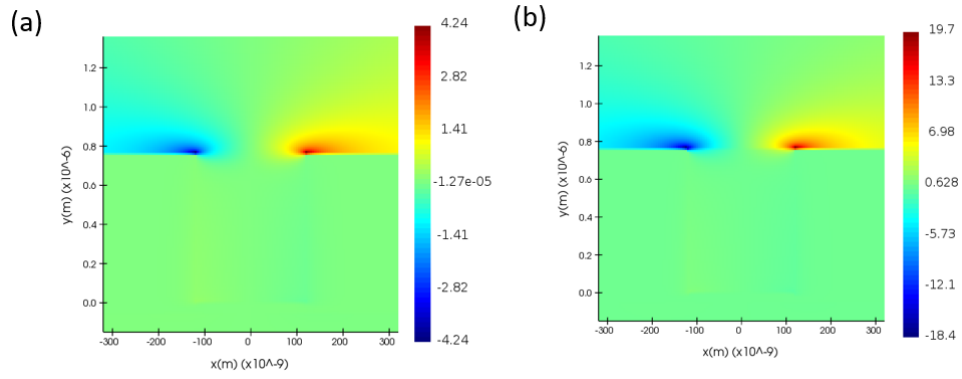


Figure S3.2: (a) and (b) are the E_y field distribution at the resonance frequency for grating with air in the gap and grating with SiO_2 in the gap for $h = 0.76 \mu\text{m}$.

Appendix C

Supporting Information (Chapter 4)

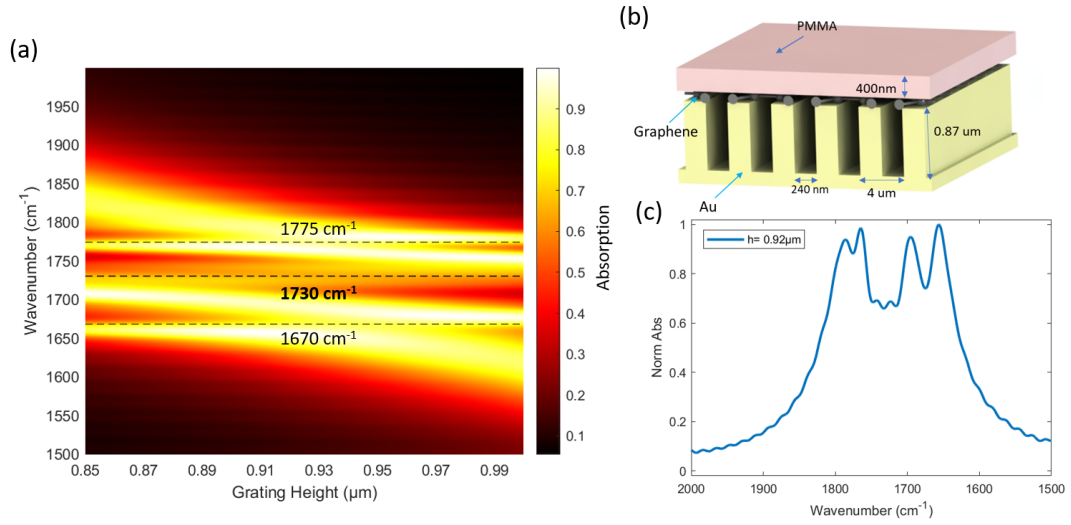


Figure S4.1: (a) Absorption mapping for Au grating when $\Lambda = 4 \mu\text{m}$, $b = 0.24 \mu\text{m}$, PMMA = $0.4 \mu\text{m}$, and $\mu_c = 0.5 \text{ eV}$; (b) Schematics for Au grating; (c) absorption spectrum when $h = 0.92 \mu\text{m}$ where polaritonic symmetry happens.

Appendix D

Supporting Information (Chapter 5)

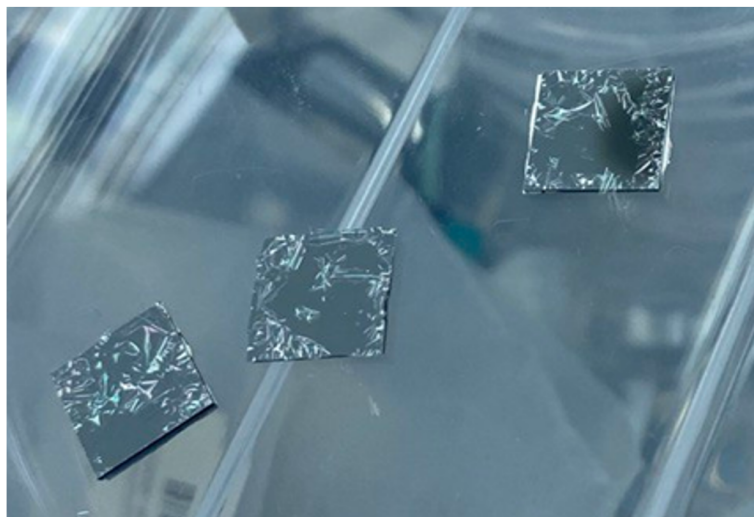


Figure S5.1: A photograph of a 50nm-thick Ag film deposited on an undoped Si substrate using the e-beam evaporator. A 1500nm-thick SiO₂ layer was deposited on the Ag film. The SiO₂ layer was peeled off within several hours at ambient conditions.