Fano resonant metasurfaces at terahertz and infrared regime

Lim, Wen Xiang

2018

Lim, W. X. (2018). Fano resonant metasurfaces at terahertz and infrared regime. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/103723>

<https://doi.org/10.32657/10220/47432>

FANO RESONANT METASURFACES AT TERAHERTZ AND INFRARED REGIME

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NANYANG TECHNOLOGICAL UNIVERSITY**

FANO RESONANT METASURFACES AT TERAHERTZ AND INFRARED REGIME

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A thesis submitted to the Nanyang Technological University in
fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

"If you want to get somewhere you have to know where you want to go and how to get there.

Then never, never, never give up."

Norman Vincent Peale

DECLARATION

This dissertation is the result of my own work and includes nothing, which is the outcome of work done in collaboration except where specifically indicated in the text. It has not been previously submitted, in part or whole, to any university or institution for any degree, diploma, or other qualification.

Signed: LIM WEN XIANG

Date: 22-JUL-2018

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ACKNOWLEDGEMENTS

The time has finally come to complete what seems to be an arduous journey these 4 years in Nanyang Technological University. Pursuing my further studies in physics was not an impetuous decision, as I begin to develop a passion for physics during my high school years. With the continuation of my bachelor's degree in physics, I was even firmed of my decision as I enjoyed learning beyond the textbooks and classes.

The completion of my Ph.D. has been a roller-coaster ride, faced with multiple challenges and obstacles. As I embarked on my next journey, I would like to show my appreciations to my family, peers, colleagues and my supervisors. It would not have been possible without strong support and encourage from them.

First and foremost, I would like to thank my supervisor, Professor Ranjan Singh who has been more than just any supervisor during my Ph.D. studies. Besides his family, he also cares about his students' well-being and engages in candid talks. It was not an easy decision for him as he took me under his helm and I thanked him for his trust and confidence in me. His passion for great science, positive attitude and enthusiasm towards research have motivated me. It is an extremely great honour to be able to work under Prof. Ranjan's supervision, and really no words are enough to express my deep gratitude towards him.

I would also like to my co-supervisor, Professor Kevin F. Macdonald for his great support and supervision from across the globe. I am also sincerely grateful to my colleagues in this fantabulous group: Dr. Sreekanth Kandammathe Valiyaveedu, Dr. Prakash Pitchappa, Dr. Cong Longqing, Han Song, Manukumara Manjappa, Yogesh Kumar Srivastava, Manoj Gupta, Abhishek Kumar and Thomas Tan, who have accepted me into their group and

provided me with constructive and helpful discussions. I wished them great success in their future endeavours.

I would also like to express my greatest thanks to my family for their love and care: my dad, mum, elder brother, elder sister and twin brother. They have been very understanding and supportive of me, despite me missing many family gatherings.

Lastly, to my girlfriend, Miss Wang Huanhuan who have endured countless late nights with me in the campus. I am most grateful to have met her during my Ph.D. journey and it has been a true blessing for me. Her strong support in my decision and encouragement have helped me to persevere and to believe in myself. She has been the strongest pillar of support and strength for me.

If there is something I have learned throughout my journey, I would like to share to anyone that reads my thesis.

Ph.D. has taught me great values in life, which is to have *perseverance* (P), be *hardworking* (H) and have strong *determination* (D).

Wen Xiang, Lim

Aug 2018

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CITATIONS TO PUBLISHED ARTICLES

1. Majority of **chapter 1** is based on a published review article in Advanced Optical Materials.

Wen Xiang Lim, Manu Manjappa, Prakash Pitchappa and Ranjan Singh (2018). *Shaping high-Q planar Fano resonant metamaterials towards futuristic technologies*. Advanced Optical Materials, <https://doi.org/10.1002/adom.201800502>. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

2. **Chapter 3** is based on a published article in Nano Convergence.

Wen Xiang Lim and Ranjan Singh. *Universal behaviour of high-Q Fano resonances in metamaterials: terahertz to near-infrared regime*. Nano Convergence **2018**, 5 (1), 5.

3. **Chapter 4** is based on a published article in Applied Physics Letters. Reproduced from:

Wen Xiang Lim, Song Han, Manoj Gupta, Kevin F. MacDonald and Ranjan Singh (2017). *Near-infrared linewidth narrowing in plasmonic Fano-resonant metamaterials via tuning of multipole contributions*. Applied Physics Letters 111 (6), 061104, with the permission of AIP Publishing.

4. **Chapter 5** is based on a published article in Advanced Materials.

Wen Xiang Lim, Manu Manjappa, Yogesh Kumar Srivastava, Longqing Cong, Abhishek Kumar, Kevin F. MacDonald and Ranjan Singh. *Ultrafast All-Optical Switching of Germanium-Based Flexible Metaphotonic Devices*. Advanced Materials **2018**, 30 (9), 1705331. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

ABSTRACT

Metamaterials has transformed our perception of artificial materials being simply just man-made materials constructed from natural materials. In the context of metamaterials, "artificial" materials can also be referred to as materials that have gone beyond human's imagination and are not existent in nature. They are subwavelength in scale and manifest extraordinary material properties. In this regard, metamaterials can be engineered to manifest Fano resonance through symmetry breaking of the metamaterial system. It is a scattering phenomenon with an asymmetric lineshape and possesses exceptional characteristics such as high-quality (Q) and strong electromagnetic field confinement. Thus, it has great potential for applications in sensing, dynamic switching and enhanced luminescence.

For practical applications of Fano resonance across the electromagnetic spectrum, we investigated the decay trend of high- Q Fano resonance and established the universal behaviour of Fano resonance from terahertz (THz) to near-infrared (NIR) regime. This suggests that the scattering phenomenon of Fano resonance is prominent irrespective of the dimensions of the metasurfaces and hence, appropriate for scalability of devices.

In addition, to improve the performance of the device in terms of Q -factor, we also demonstrated and showed that by inverting the unit cell configuration of complementary asymmetric dipole bars, we are able to achieve an enhancement of the Q -factor in the NIR frequency. Multipole analysis reveals that linewidth narrowing of Fano resonance is due to the contributions from the magnetic quadrupole, but for non-inverted unit cell configuration, the toroidal dipole acts to broaden the linewidth.

As proof of concept of the capability of Fano resonance, we demonstrated an ultrafast all-optical switching of Fano resonance using THz asymmetric split ring resonators (ASRR). The incorporation of germanium, or semiconductor as an optically active medium serves as an avenue to achieve switchable and dynamic tuning of Fano resonance. When free carriers are photoexcited above the conduction band, germanium transits from a semi-metallic to metallic state and shunts the capacitive split gap of THz ASRR. The transmission of Fano resonance is modulated and recovers within 17 ps, hence achieving the effect of photoswitching. The photoswitching of Fano resonance in THz band is beneficial in telecommunications when a signal transmission has to be routed around a fault in the line or employed in logic gates operation. Photoswitch can also be utilized in electric field sensing or security purpose where a modulation of transmission signal can trigger the alarm.

The multipurpose of Fano resonance is associated to its non-radiative nature, high- Q and strong confinement of electric field. Therefore, it is with great ambitious that we hope our findings will promote further research in Fano resonant metasurface, so as to fully exploit the potential of Fano resonance. We envision that Fano resonance could be the ideal solution of modern technologies.

1 INTRODUCTION

1.1 Metamaterials

The earth as we know, is filled with abundance of natural resources which humankind have rigorously utilized to shape the current developments in science and technology. However, there remains much to be discovered which prompted scientists and researchers to begin searching for materials beyond the categories of natural materials. This have led them to uncover a contemporary system of material which is known as metamaterials.¹ Metamaterials are artificial materials that are composed of a lattice of sub-wavelength "meta-atoms" engineered to exhibit electromagnetic properties that cannot be derived from natural materials. Meta-atoms are the basis of the lattice where they are positioned into every lattice position in metamaterials. Hence, the optical and physical properties of the metamaterial are controlled by changing the shape, orientation, size or geometry of meta-atoms.

Unlike naturally occurring (conventional) materials, metamaterials are created to possess negative refractive index (n) due to their negative permeability (μ) and negative permittivity (ϵ). The electromagnetic properties of any material are determined by its μ and ϵ , which is a consequence of its interaction with the electric or magnetic field of the propagating wave. As shown in Figure 1.1, materials are conveniently categorised into four quadrants which forms a combination of both μ and ϵ .

In the first quadrant, conventional materials are classified with positive μ and ϵ , so the refractive index of the material is also positive. These materials are isotropic dielectrics which are transparent and energy loss is low. Wave travelling through conventional materials is deflected away from the surface normal (indicated by the grey dash lines). In the second quadrant, it contains plasmas and wire structures where their ϵ is smaller than zero. The wave

is reflected off the surface due to non-transmissive nature of the medium at optical frequencies. The third quadrant is where metamaterials lie, with negative μ and negative ϵ . The wave is refracted away from the surface normal, opposite in direction to the deflection of wave that passes through conventional material. The last, and the fourth quadrant is made up of gyrotropic magnetic materials which are hard to demagnetize. They confine wave evanescently to the surface and reflect wave similar to materials in the second quadrant.

Figure 1.1. Classification of materials based on their permeability and permittivity, and the type of refraction that will occur.

1.1.1 Validation of negative index of refraction

In 1968, Victor Veselago predicted that material with negative refractive index requires that the group velocity points opposite in direction with the phase velocity.² In the case of conventional materials, the group and phase velocity point parallel to each other. The predicted behaviour was conclusively proven when Smith *et al.* demonstrated negative μ and negative ϵ based on a composite medium that comprises of a periodic array of circular split ring resonators (SRR) in the microwave region.³

In the subsequent year, negative index of refraction was experimentally verified using similar metamaterial structures (but with square SRR as shown in Figure 1.2) in the microwave region.⁴ The experiment was conducted based on Snell's Law of refraction, which states that the ratio of the sines of the angle of incidence, θ_i and the angle of refraction, θ_r is equivalent to the ratio of the refractive indices of both media (in the region of refraction, n_r or incidence, n_i),

$$\frac{\sin \theta_i}{\sin \theta_r} = \frac{n_r}{n_i} \quad (1)$$

Since n_i is air, the index of incidence is 1 which simplify the formula to,

$$\frac{\sin \theta_i}{\sin \theta_r} = n_r \quad (2)$$

The refracted power of microwave beam was recorded around the circumference of the possible regions of refraction (brown area in Figure 1.1). The results clearly show a peak power where the beam is refracted away from the surface normal in the second medium, along the same side as the incident beam for a negative index material, and when a positive index material is used, there is a peak power on the deflected side, away from the surface normal in the second medium. These results have shown to be consistent with Snell's Law.

Figure 1.2. A left-handed metamaterial sample demonstrates negative index of refraction that comprises of square copper split ring resonators and continuous wires fabricated on a circuit board.⁴

Since then, the successful prediction and experimental verification of negative index metamaterials have sparked off intense research in metamaterials with a new focus and direction driven towards sub-wavelength devices and technologies. The popularity of metamaterials stems from its ability to mimic the optical properties of conventional material or to create an entirely new paradigm of materials not available in nature (e.g. THz metamaterial). In addition, by elegantly designing the artificial meta-atoms, we can "reconfigure" the optical and physical properties of metamaterials which allow them to control, modulate or guide electromagnetic wave in ways that cannot be achieved with conventional materials.

1.1.2 The charm of metamaterials

Today, metamaterials involve not only negative-index materials, but also other artificial materials made from multiple elements of composite materials such as semiconductors,^{5, 6} superconductors⁷⁻⁹ or perovskites.¹⁰ Metamaterials have pioneered major scientific breakthroughs, namely invisibility cloaking and superlenses, and have also initiated new possibilities in diverse optics and photonics platforms where their potentials have been extensively taken advantage of.

What may seem like a fantasy or science fiction has become a reality when invisibility cloaking was accomplished using metamaterials which cloak an object based on transformation optics.¹¹⁻¹³ With transformation optics, the coordinates of the electromagnetic fields of the propagating wave is redirected and controlled to bend around an object when it travels through the metamaterial which acts as an optically transmissible medium, hence

forming the illusion of optical cloaking. In addition, the "cloaking" metamaterial can be designed to interact with certain parts of the electromagnetic spectrum which is not possible with natural materials. Invisibility cloaking has since transcended from being realizable only in two-dimensional¹⁴ to three-dimensional.^{15, 16}

Diffraction limit in optics has been a stumbling block to ultrahigh-resolution imaging. This is because conventional lenses only captures far-field information while near-field information remains localized within the given object. As a result, features smaller than half the wavelength of light are lost inevitably. Ultimately, an optical microscope is unable to differentiate between two objects that are placed apart with less than a distance, $d = \frac{\lambda}{2NA}$ where λ is the wavelength of light and NA is the numerical aperture of the optical lens.¹⁷ With the discovery of metamaterials, metamaterial lenses also known as superlenses are developed to overcome diffraction limit based on the recovery of exponentially decaying evanescent fields.¹⁸⁻²⁰ Superlens enhances the fields of the evanescent waves at the near-field surface of the object and converts them into propagating waves, hence retrieving the subwavelength features which can be viewed in the far-field.^{21, 22}

Although metamaterials have opened the gate to a wide range of functionalities in science and technology, large losses in metamaterials hamper further development of feasible metamaterial-based devices. This is mainly due to dissipative losses in metals that have been the conventional material employed in metamaterials.²³ Resistive heating and radiative scattering are the leading processes of energy loss in metamaterials. This is even more apparent as the dimensions of metamaterial scale down, especially in the optical spectral region. It has been shown that geometric tailoring of metamaterials reduce ohmic losses by redistributing the surface currents.²⁴ Bearing strong resemblance to this approach, reducing

radiative losses in metamaterials can be achieved in subwavelength metamaterial structures by exciting Fano resonance in symmetry broken metamaterial systems.²⁵

1.2 High-quality (Q) Fano resonance

In most metamaterial systems, the lineshape of fundamental resonance mode resembles a Lorentzian function. Lorentzian function is commonly used to describe the nature of resonance in mechanical, acoustic or electromagnetic systems in which the lineshape is entirely symmetrical with a wider tail as compared to Gaussian function. It became evident that resonance lineshape need not be symmetric in 1935, when Ugo Fano experimentally observed an asymmetric lineshape in the scattering spectrum related to the absorption spectra of noble gases. Fano postulated that the sharp asymmetric profile is the consequence of the superposition between the distinctive spectral line of Rydberg atom with a continuous spectrum.²⁶ In 1961, Fano revisited his previous study and established a formula to quantitatively describe the sharp asymmetric profile observed in the scattering spectrum which later became known as the Fano resonance.²⁷ The Fano formula which describes the optical spectra, R (such as absorption, transmission or scattering) as a function of frequency, ω is written as below,

$$R(\omega) = A_0 + F_0 \frac{\left[q + \frac{2(\omega - \omega_0)}{\Gamma} \right]^2}{1 + \left[\frac{2(\omega - \omega_0)}{\Gamma} \right]^2} \quad (3)$$

whereby A_0 and F_0 are constant factors, q is the asymmetry parameter of the system defined as the ratio between resonant and non-resonant state, ω_0 is the resonance frequency and Γ is the full-width at half maximum of the resonance frequency.

Fano resonance in metamaterials was first reported in optical resonators that are composed of planar asymmetric split ring resonators and named as "trapped-mode" resonance²⁸ The

origin of Fano resonance in metamaterial arises from symmetry-breaking of the physical geometry of the metamaterial structure. The narrow and sharp Fano resonance is unable to couple directly with propagating electromagnetic wave in free space, so breaking the symmetry of the metamaterial system provides an avenue for the radiative mode to excite Fano resonance through near-field interaction. As a consequence, Fano resonance suffers from minimal radiative losses and optical energy is well-retained in the metamaterial system.

The performance of an optical resonator is determined by its ability to trap the optical energy within the cavity and is usually characterized by quality (Q) factor. Q -factor is a dimensionless parameter that quantifies the amount of energy stored as a ratio to the amount of energy lost per cycle through dissipation in a resonator system. In other words, a resonator with low- Q loses energy more quickly over time due to stronger damping, while resonator with high- Q would retain the energy in the system for much longer time.

In photonics, the quality factor of a resonator system is defined as the ratio of the resonant frequency, f_0 to the full-width at half maximum at the resonant position, δf and is written as,

$$Q = \frac{f_0}{\delta f} \quad (4)$$

or from the Fano formula,

$$Q = \frac{\omega_0}{\Gamma} \quad (5)$$

The full-width at half maximum (or resonance linewidth) also corresponds to the bandwidth which dictates the broadness of the resonance. For a less damping system, the bandwidth is narrower with a higher- Q as compared to a system with higher damping. Hence, in high- Q system more energy can be stored. However, in all optical systems, energy losses are unavoidable, and they are associated with the radiative and non-radiative scattering of charge

carriers. The situation worsens and becomes more apparent as the overall size of the system reduces from micro- to nanoscale dimensions.

In this respect, high- Q Fano resonance weakly couples with free-space and provides a solution to suppress radiative losses. Moreover, Fano resonance boasts an intense confinement of electromagnetic field in an extremely narrow region which enhances the interaction time of particles or molecules by trapping photons in the cavity. The superiority of high- Q Fano resonance in metamaterials has attracted large growing interests that sought to exploit the nature of its sharp asymmetric lineshape and explore the future of its applications.

1.2.1 Characterization of Fano resonance

1.2.1.1 Hybridization model

In recent years, E. Prodan *et al.*²⁹ has proposed a hybridization model, an electromagnetic analogy to the orbital hybridization theory, which can be used to visualize the plasmonic interactions between two or more metallic bodies. From this model, nanostructure with complex geometry is decomposed into several components that make up the design. Interpretations based on the spectral distributions of the individual bodies in the coupled and uncoupled states can be utilized to further modify the state of the plasmonic system. As an example, when an electromagnetic wave is incident onto the metal nanoshell, surface charges are induced along the inner radius (a) and outer radius (b) of the metal shell, whereby the modes of the sphere and the cavity interact with each other and hybridize. Using spherical harmonics, the plasmon frequencies of these modes are represented as:³⁰

$$\omega_{l\pm}^2 = \frac{\omega_B^2}{2} \left[1 \pm \frac{1}{2l+1} \sqrt{1 + 4l(l+1) \left(\frac{a}{b}\right)^{2l+1}} \right] \quad (6)$$

where $\omega_B = \sqrt{\frac{2\pi e^2 n_0}{m}}$ is the surface plasmon frequency (n_0 is the electron density, e is the electronic charge and m is the effective mass of electron) and $l > 1$ is the degree of the associated plasmon mode.

For a dipolar mode ($l = 1$), and in the limit of the inner radius approaching zero, the plasmon frequencies of the cavity ω_c and sphere ω_{sp} modes are correspondingly represented as,

$$\lim_{a \rightarrow 0} \omega_+ = \omega_c = \sqrt{\frac{2}{3}} \omega_B, \quad (7)$$

$$\lim_{a \rightarrow 0} \omega_- = \omega_{sp} = \sqrt{\frac{1}{3}} \omega_B, \quad (8)$$

The hybridization of the sphere and cavity modes generate two nanoshell resonances, which in the energy-level diagram is categorized as longitudinal coupling, whereby the higher energy plasmon mode $|\omega_+\rangle$ is anti-symmetric or antibonding and the lower energy plasmon mode $|\omega_-\rangle$ is symmetric or bonding (Figure 1.3). The other form of hybridization is a transverse coupling, in which the higher energy plasmon mode is symmetric and the lower energy plasmon mode is anti-symmetric.³¹ The energy of the plasmon modes depends on the aspect ratio of the inner radii to the outer radii of the nanoshell and is independent of the overall size of the nanoshell. For the smallest nanoshell, the optical response is due to strong single-particle excitation, which eventually weakens in larger nanoshells and gets dominated by collective excitations of the plasmon modes. In the more complicated case of a "nano-matryushka" structure, there are four linearly independent plasmon modes, which split into other four hybridized plasmon resonances. The Coulombic interactions between the four linearly independent plasmon modes are dependent on the thickness of the dielectric spacer layer which separates the inner and outer metal shells. Therefore, as the thickness of the

dielectric spacer layer increases, the coupling strength shifts from strong to weak, and finally to an uncoupled case. Ever since the establishment of this model, it has been applied as a simple and intuitive tool to understand the plasmonic resonances, which include Fano resonance of complex nanostructures in several demonstrations.³²⁻³⁹

Figure 1.3. The energy-level diagram of the hybridization between the sphere and cavity modes.²⁹

1.2.1.2 Coupled oscillator model

The origin of Fano resonances in the classical systems is theoretically modeled using the coupled oscillators,⁴⁰⁻⁴⁷ where one of the oscillator is strongly driven by the external field that is termed as the 'bright mode' while the other oscillator termed as 'dark mode' is not coupled to the free space field. Equations of motion determining the coupling between the bright and the dark modes are described by the following set of coupled equations,

$$\ddot{x}_b(t) + \gamma_b \dot{x}_b(t) + \omega_b^2 x_b(t) + \Omega^2 x_d(t) = f_b E \quad (9)$$

$$\ddot{x}_d(t) + \gamma_d \dot{x}_d(t) + \omega_d^2 x_d(t) + \Omega^2 x_b(t) = 0 \quad (10)$$

where, (x_b, x_d) , (ω_b, ω_d) and (γ_b, γ_d) are the scattering amplitudes, angular resonance frequencies and the linewidths of the bright and dark modes, respectively. Ω defines the coupling strength between the bright and dark modes. $f_b = q_b/m_b$ quantify the free space coupling strength of bright mode with the incident light, where q_b and m_b are the effective charge and mass of the oscillator, respectively. The dark mode oscillator is completely decoupled from the incident driving field. The coupled equations provide insight into the interactions that leads to the Fano type of destructive interference in the amplitudes x_b and x_d for contrasting linewidths γ_b and γ_d of bright and the dark modes. After solving for the scattering amplitudes x_b and x_d in the coupled equations 9 and 10, one can arrive at the susceptibility expression for light-matter interactions given by,

$$\chi = K \left(\frac{(\omega^2 - \omega_d^2) + i\omega\gamma_d}{\Omega^4 - (\omega^2 - \omega_d^2 + i\omega\gamma_d)(\omega^2 - \omega_b^2 + i\omega\gamma_b)} \right) \quad (11)$$

The real part ($\text{Re}[\chi]$) of the susceptibility expression in equation 11 represents the dispersion and the imaginary part ($\text{Im}[\chi]$) gives the absorption losses in the system, where K is the normalizing constant. $1 - \text{Im}[\chi]$ represents the transmission response of the system for the appropriate fitting parameters of ω_b , ω_d , γ_b , γ_d and Ω . The strength of the Fano resonance depends on the coupling strength Ω which in turn relates to the asymmetry parameter α in the metamaterial structures.

1.2.2 Babinet's Principle for Electromagnetic Fields

Fano resonance has also been studied in complementary counterparts, which are the inverse design of positive metamaterial structures. As dictated by the Babinet's principle, the transmission spectra of the positive structures and complementary structures should sum up to the initial intensity of the electromagnetic wave that passes through, as if nothing existed.⁴⁸

In complementary structures, contrary to positive structures, the electric field component

should be interchanged with the magnetic field component of the same electromagnetic wave. Hence, the transmission spectrum of the complementary structure corresponds to a mirror-image of the transmission spectrum of the positive structure in a way that the peaks and dips are interchanged.^{49, 50} Complementary split ring resonators (CSRR) and positive split ring resonators (SRR) were first reported for this phenomenon in metamaterials as shown in Figure 1.4(a).⁵¹ Near-field microscopy was performed by A. Bitzer et. al and agreement between the theoretical, simulation and experimental results fully validate the Babinet's principle.⁵² The concentration of the electric field in positive asymmetric split ring (ASR) relates to the accumulation of surface current in complementary asymmetric split ring (CASR), and the surface current accumulates at a region in positive ASR which relates to the concentration of the electric field in CASR as shown in Figure 1.4(b).⁵³ Subsequently, complementary structures of various designs could be promising as polarization-sensitive modulator,⁵⁴ high- Q chiral metasurface for circular polarizers,⁵⁵ and directional filters.⁵⁶ In a recent work, by strategically positioning the dust particle along the nanoslit, the phononic mode of the particle is detected along the Fano lineshape, with maximum signal as the dust particle move towards the middle of the nanoslit. The presence of the dust particle breaks the symmetry of the nanoslit, hence inducing a Fano feature on the plasmonic background. Narrower nanoslits are beneficial for the detection of ultra-fine dust particle via surface-enhanced infrared absorption.⁵⁷ Thus, in many possible ways, Fano resonance is manifested in a variety of systems composed of positive or complementary geometries.

Figure 1.4. Illustration of Babinet's principle. (a) Measured transmission coefficient of a unit cell of SRR and CSRR, spectra showing mirror-image of each other.⁵¹ (b) Simulated surface current and electric field distributions of the ASR and CASR.⁵³

1.2.3 Classification of planar Fano metasurfaces

Planar metasurfaces are by far the easiest electromagnetic metamaterials to study light-matter interactions in Fano resonant plasmonic systems, due to the simplicity of the fabrication process as compared to 3D metamaterials. In addition, owing to the ease of modifying the spectral response of the plasmon resonance, a plethora of unit cell designs based on symmetry-broken configurations have been conceptualized to observe the Fano resonant scattering phenomenon across a broad frequency (optical to microwave) spectrum. These planar Fano metamaterials can be broadly categorized into single-particle, dual-particle or multi-particle systems based on the number of physical resonators present in a single unit cell. In all of these systems, the contrast in the electromagnetic field distribution among the sub-unit cells leads to the resonant coupling of the bright and dark hybridized plasmon modes, which give rise to Fano resonance.⁵⁸ Bright mode is often associated with the finite dipole mode of the metamaterial structure which is radiative in nature and can

interact with the far-field of the propagating electromagnetic wave in free space. The spectrum of a bright mode is broadened due to radiative damping. Intuitively, dark mode is non-radiative and prohibited in perfectly symmetric system. It is represented by higher order mode that exhibit weak dipole moment and can only be excited through near-field coupling with the radiative mode, hence making it accessible in the spectroscopy (transmission, reflection or absorption) spectrum. Thus, Fano resonance is also termed as "trapped-mode" resonance when first discovered in planar metamaterials.²⁸ It is evident that symmetry breaking of the geometry of a unit cell, permits the excitation of high- Q Fano resonance.

1.2.3.1 Single-particle

Nanodisk on its own, is one of the simplest geometrical structure that requires only one particle in the unit cell to generate Fano resonance. The shape of the nanodisk is circular and it possesses a perfect rotational symmetry. Therefore, to break the symmetry of the nanodisk, a defect is introduced into the structure as a wedge, which is angle controllable (Figure 1.5(a)).³⁵ According to the hybridized model, the nanodisk contributes to the broad dipole plasmon mode whereas the cut-out wedge contributes to the narrow quadrupole plasmon mode. As a result, the spectral overlap of the two plasmon modes lead to the effective generation of high- Q Fano resonance. Upon symmetry breaking (by increasing the angle of the wedge), the intensity of the Fano resonance increases with a distinct appearance of an asymmetric lineshape. However, further increase in the angle of the wedge (beyond the range of 90° to 105°) weakens the resonance due to a reduction in the edge charge density at the wedge. In addition, the radial size of the symmetry broken nanodisks ranges from 140 to 200 nm where Fano resonance in the visible spectrum can be easily achieved. Closely related is a distorted nanodisk, shaped in the form of an ellipse. The elliptical disk fabricated on top of the Mylar film (membrane substrate) is etched with double gaps along the long axis of the ellipse and separated by a rectangular bar, whose position along the long axis determines the

asymmetry of the system.⁵⁹ The presence of the Fano resonance is illustrated clearly from the antiparallel surface currents flowing on each side of the long axis. Further studies conducted on the properties of membrane substrate reveal that membranes with small dielectric loss tangent and thicknesses in the range of 10 to 50 μm are essential for achieving high- Q Fano resonance at terahertz (THz) frequencies. This is attributed to a reduction in the amount of energy dissipated through a less lossy substrate membrane, and so it interacts effectively with the electromagnetic field, hence improving the sensitivity of THz membrane devices.

1.2.3.2 Dual-particle

Fano resonance in metamaterials was first reported in asymmetric split ring resonators (ASRRs) in the microwave region that are composed of two arms with different lengths.²⁸ Metallic resonators in the microwave region behave as almost perfect electrical conductors in which the main dissipative losses is attributed to absorption in substrates. Despite of that, metallic resonators still losses energy radiatively. In ASRRs, the unit cell is designed such that antisymmetric surface currents are excited on each arm with unequal amplitude. The induced surface currents at the arms of each neighbouring unit cell cancel with each other leaving only the peripheral surface currents at the edge of the array, and the overall dipole moment is reduced greatly.⁶⁰ Furthermore, the magnetic dipole of the excited Fano resonance does not interact with the propagating fields of the electromagnetic wave and radiative losses to free space are significantly suppressed. An experimentally measured high- Q of ~ 200 for Fano resonance has been obtained.⁶¹ This effect is more strongly observed in coherent arrays comprising of larger number of unit cells, and the Q -factor of the Fano resonance can be significantly improved.⁶⁰

Other dual-particle unit cell systems that have been successful in their demonstrations of high- Q Fano resonance include nanocross-bar,³⁶ asymmetric double bars,⁶²⁻⁶⁸ ring-disk^{34, 37}

and concentric rings.⁶⁹ By employing the plasmon hybridization model, the evolution of Fano resonance in nanocross-bar configuration was elegantly pictured with the help of charge density distributions as depicted in Figure 1.5(b). For this instance, the excitation of the Fano resonance is only achievable for light incident at grazing angle. This is because it introduces a field gradient along the surface of the nanocross and results in a quadrupole mode (grey dot - forbidden for normal incidence) appearing at the broad resonance of the dipole nanocross (blue dot). As a result, the quadrupole of the nanocross couples strongly with the dipole of the bar (black dot) to form a hybridized mode, whose resonance mode spectrally overlaps with the broad dipole resonance of the nanocross-bar. The destructive interference of both modes suppresses the radiative dipole mode, hence creating a high- Q Fano resonance (green dot) at the optical region.³⁶

Thus far, the simplest asymmetric geometry model used for excitation of Fano resonance at optical frequency is the asymmetric double bars.⁶² Fano resonance originates from the destructive interference between the bright mode of the double bars and the dark mode of the asymmetric double bars which is indirectly excited through near-field coupling. Electric field distributions attribute the bright mode to two in-phase dipoles (parallel currents) that interfere constructively, while the dark mode is due to destructive interference of out-of-phase dipole oscillation (antiparallel currents).^{63, 66} It was further reported that at a certain length displacement for one of the double bar, the plasmonic system is optimized and a high- Q Fano resonance can be obtained in the infrared region.⁶³

The geometrical structures reviewed so far are composed of elements whose strong field enhancements are located near the sharp edges. Besides, circular or round geometrical structures such as a ring-disk^{32, 34, 37} or concentric rings have also been fabricated. For a non-concentric ring-disk configuration, the inner dipole disk is either displaced from the central

position in the quadrupolar/higher order ring or placed alongside the ring. In a similar way to other configurations, the plasmon hybridization model provides a visual interpretation to describe the nature of the plasmon modes. Here, Fano resonance arises from the destructive interference between the dark quadrupolar ring plasmon mode and bright dipole disk plasmon mode. Angle dependence of the incident light was also performed on non-concentric ring-disk configuration, which reveals the spectral shaping of Fano resonance between asymmetric and symmetric shape, at which higher order modes start appearing. Therefore, these higher order dark modes hybridize with the broad continuum to form higher order Fano resonance modes. A relatively high- Q factor of 5.2 is obtained in the optical region.^{32, 37} Concentric rings configuration has been demonstrated across a wide electromagnetic spectrum which includes infrared,⁶⁹ terahertz^{70, 71} and microwave.⁷² The benefit of concentric rings is that it is independent of polarization, and so symmetry breaking is achieved without breaking the geometry of the structure, but instead achieved through variation in the electromagnetic field of the two rings. The difference in the circumference of the inner and outer rings leads to induced currents which flow opposite to one another in both rings. Such current configurations cancel each other, leaving an overall weak magnetic dipole moment which does not scatter to the free space.⁷² Every unit cell in the metamaterial array does not interact with the surrounding unit cells, hence concentric ring configuration is an incoherent metamaterial array.⁶⁰ Further enhancement (more than 4 times) to the Q -factor of concentric ring resonators is achieved by adding interdigitated finger pairs between the inner and the outer rings, illustrated in Figure 1.5(c). Such concept improves the coupling between both rings so that the induced currents are able to cancel out more effectively, leading to higher Q -factor.⁷⁰ An interception cut created at the minimum electric field positions of the concentric rings allows the Fano resonance to be switched on and off, by changing the polarization of light.⁶⁹

1.2.3.3 Multi-particle

In multi-particle plasmonic system, more than two sub-unit cells such as dolmen or heptamers are used to excite Fano resonance. Although not as deeply explored as single or dual-particle system, multi-particle system provides more degree of freedom to break the symmetry of a unit cell, since it is composed of several sub-unit cells. Dolmen structures^{34, 73} are composed of three rectangular slabs whose arrangement is depicted in Figure 1.5(d). Two rectangular slabs are placed parallel to each other to form a dimer and the third slab is placed perpendicular to them along the shorter edge of the slabs. For polarization parallel to the symmetry axis of the dolmen, a broad dipole moment is excited (orange dot), while a perpendicular polarization induces an overall quadrupole charge distribution in the dimer (blue dot). The spectral overlap between the quadrupole and dipole modes results in the appearance of a sharp asymmetric Fano lineshape in the optical regime. The evolution of the Fano resonance is also shown clearly in Figure 1.5(d) by rotating from perpendicular to parallel polarization. Multiple Fano resonances can be induced for dolmen structures with a larger dimension. On the other hand, heptamer is a unit cell composed of seven sub-unit cells arranged in a hexagonal shape with the seventh sub-unit cell positioned at the centre (6-sided polygon). In this arrangement, heptamer has six lines of reflection, and so it possesses a 6-fold rotational symmetry. The bonding bright mode is due to all seven particles oscillating in-phase, while the antibonding dark mode is due to the out-of-phase oscillation of the six outer particles with the central particle.⁷⁴ Therefore, destructive interference between the bright and dark modes, create the Fano resonance which is otherwise forbidden in the quasi-static nonretarded limit. Such system can be expanded to polygon with n -sides, but dipole moments that are equal and opposite must cancel to result in a net zero dipole moment to satisfy the criteria for strong Fano resonance.⁷⁵

Figure 1.5. Single, dual and multi-particle planar Fano metasurfaces.(a) Calculated and simulated extinction cross-section spectra of the symmetry-broken nanodisk with increasing angle of wedge. Middle portion shows the SEM images of fabricated nanodisk with varying wedge size.³⁵ (b) Experimental extinction spectra of the nanocross, nanocross-bar and bar structures with their simulated charge density distributions in the inset.³⁶ (c) Simulated and measured transmission spectra of the interdigitated concentric ring resonators that are independent of *p*- and *s*- polarization.⁷⁰ (d) Experimental and simulated extinction spectra of the single dolmen structure. Top right shows the measured extinction spectra by rotating

from perpendicular to parallel polarization. Bottom shows the surface charge distributions at different position of the spectra in top left.³⁴

1.3 Prospective applications of Fano resonance

Fano resonance as a type of resonant scattering phenomenon is ideal for preserving energy in the plasmonic system, since self-cancellation of dipole moments caused by antiparallel induced currents dramatically reduce the radiative losses. Consequently, several of the proposed unit cell designs have been adopted as part of the strategies for the realization of a wide variety of applications that can provide solutions to overcome challenges and limitations in the current technologies. They have been developed in passive or active control applications such as sensors, surface-enhanced infrared absorption, lasing spaser and optical switch, which will be reviewed accordingly.

1.3.1 Fano sensors

In plasmonic sensors, detection of weak signals coming from the analyte is strongly elevated due to the presence of electromagnetic field enhancement which is supported by surface plasmon resonance located at the interface of metal and dielectric.^{76, 77} However, another class of sensors based on Fano resonances in plasmonics has also seen an impressive rise in the sensing community. At Fano resonance frequency, high resonant field can be confined at regions of gaps or along the edges of the planar structures. Any perturbations that are introduced into their local environment disturbs the sensitive nature of the resonant field. This enable the slightest detection or sensing of the variations near the vicinity of the field. As such, Fano sensors utilize the unique scattering phenomenon of Fano resonance which possesses not only intense confinement of electromagnetic field, but also the sharp asymmetric high- Q lineshape that are pivotal to making sensors with better sensitivity and selectivity.

As one of the prominent structure that was conceived in the early stage of metamaterials,¹ SRRs have played significant role in THz sensing. For an asymmetric THz SRRs that is equipped with a relatively high- Q of 65 for quadrupole and 28 for Fano resonances, a superior analyte sensitivity of 5.7×10^4 nm/refractive index unit (RIU) was achieved for Fano resonance compared to the quadrupole resonance with sensitivity of 7.75×10^3 nm/RIU.⁷⁸ Hypothetically, the higher the Q factor of the metamaterial, the longer the photon lifetime and light-matter interactions should be greatly enhanced. Simulated electric field distributions of the quadrupole, dipoles and Fano resonances reveal that the tightly confined fields at the Fano resonance frequency is much stronger than the quadrupole and dipole resonances whose electric field enhancements are spread across four nodes at the arms and two nodes in each arm of the SRRs respectively, as shown in Figure 1.6(a-d). Therefore, given the high field confinement in the small spatial volume of the capacitive split gaps, Fano resonance has the upper hand and a significantly higher analyte thickness sensitivity as compared to the quadrupole resonance is obtained. In addition, when the refractive index of the analyte is varied from $n = 1$ to $n = 1.6$, the Fano resonance shows a sensitivity of 4.23×10^4 nm/RIU, while the quadrupole resonance had a sensitivity of 5.62×10^3 nm/RIU. The results affirm Fano resonance as a good candidate for achieving highly sensitive refractive index sensing capabilities, even at other regimes of the electromagnetic spectrum.^{36, 37, 66} It was further reported that a thinner substrate would promote a greater sensitivity using such high- Q resonances as it allows for a stronger interaction between the intense field and the analyte.^{59, 78, 79} With another two split gaps imposed onto the adjacent arms of the already asymmetric SRRs, Fano resonance and quadrupole resonance can be excited simultaneously which could be utilised for thickness sensing and to also serve as a double referencing for increasing the accuracy of the sensitivity results.⁷⁹ Recently, Y. K. Srivastava et. al have demonstrated dual-surface sensing based on a flexible platform suggesting the possibilities

of incorporating sensor devices onto non-uniform surfaces.⁸⁰ The results presented is consistent with the use of an ultrathin substrate for improved sensing capabilities⁵⁹ and to increase the amount of fringing electromagnetic fields accessible on either side of the substrate. Compared to previous works,⁷⁸ the use of the underside of the substrate for sensing contributes to an additional red shift of the Fano resonance frequency by 6 GHz, which amounts to a total red shift of Fano resonance frequency by 89 GHz for a 100 nm thick germanium deposited onto a low refractive index substrate of 25 μm thickness. These results clearly demonstrate the advantages of using dual surfaces of the substrate as the overall sensitivity of the analyte can be increased even if the sensitivity of an analyte reaches saturation on the top side of the substrate. In addition, the use of a thin substrate with low refractive index could possibly show enhancement in thin-film sensitivity when it comes to detecting small volume of biomolecules.

So far, Fano sensors have been explored for its improved sensitivity towards different refractive indices of analytes. In a more advanced scenario, these sensors can be used to differentiate between a target molecule and its group of molecules.^{81, 82} Such Fano sensors have been achieved in the mid-infrared regime, whereby a modified dolmen structure comprised of the monomer adjoined to one slab of the dimer is used as illustrated in Figure 1.6(e).⁷³ In this system, Fano resonance is excited for electric field polarized parallel to the dimers. When the Fano resonance is far from the vibrational modes of the amide, it yields information about the thickness of the protein molecules with an accuracy difference of 0.1 nm between theoretical and experimental results. If the Fano resonance matches with the vibrational modes of the proteins, strong interaction between the proteins and the asymmetric dolmen structure enhances the amplitude of the vibrational modes which provides indications of the protein's secondary structure and orientation. This is important because

ascertaining the orientation or conformational state of the protein molecules helps to find suitable biotarget for functional availability.

Complementary Fano resonant structures of coupled annular and rectangular aperture have shown tremendous high- Q Fano resonance of 79 (simulated) and 38 (experimental), which were excited based on whispering gallery approach in the near-infrared frequencies.⁸³ The high- Q Fano resonators exhibit spectrally tunable single and multiple Fano resonances by changing the polarization of the incident light. The realization of such high- Q Fano resonance is a feat, and as a proof-of-concept, the Fano resonators (with a modified geometrical structure – inclusion of multiple concentric ring apertures) as shown in Figure 1.6(f) have demonstrated ultrasensitive detection of molecular vibrational modes of poly(methyl methacrylate) (PMMA) using surface-enhanced infrared absorption spectroscopy (SEIRA).⁸⁴ When the position of the Fano resonance spectrally aligns with the vibrational modes of C-O-C and C-H; -CH₂ and -CH₃; and C=O; spectral fingerprints that were absent in the reference spectra are precisely identified from the amplified spectra. By using the whispering-gallery-mode-based Fano resonators, weak signals of ultrathin PMMA (50 nm thickness) are enhanced, overcoming the limitation imposed by the exponentially decreasing absorption as thickness decreases.

Figure 1.6. Fano sensing. Simulated electric field distribution of (a) quadrupole and (b, c) two different dipoles under horizontal polarization, (d) Fano resonance under vertical polarization, without and with an analyte above the asymmetric THz SRRs.⁷⁸ Schematic diagrams of the (e) modified dolmen structure used in the identification of vibrational modes of protein molecules⁷³ and (f) coupled annular and rectangular apertures used in the SEIRA of PMMA (inset shows the different metasurfaces used to excite multiple Fano resonances).⁸⁴

1.3.2 Lasing spaser

Light amplification by stimulated emission of radiation (LASER), has been widely used in optical systems for broad applications in telecommunications, health technology, military defence, research industry and other commercial purposes. With miniaturization of devices being a trend in the modern world, it is a challenge to fit a laser into nanoscale devices. Bergman and Stockman first proposed the concept of surface plasmon amplification by stimulated emission of radiation (SPASER) in 2003, which suggests that surface plasmons can be used to confine and concentrate optical energy into dimensions smaller than a

wavelength, beating the diffraction limit of light.⁸⁵ A spaser works on the principle similar to a laser, but with a resonant cavity made up of its nanoparticle and emits surface plasmons. By introducing a gain medium into the spaser, self-sustaining stimulated amplification occurs within, whereby energy is transferred between the luminescence resonance of the gain medium and the surface plasmon modes, thus stimulating more identical surface plasmons as illustrated in Figure 1.7(a).⁸⁶ A high- Q resonance is preferred for its ability to sustain both phase and energy when subjected to external electromagnetic field, in which an ideal choice would be Fano resonance. N. Zheludev and his group proposed the combination of strong coherent planar metastructures with a gain material to generate spatially and temporally confined coherent electromagnetic radiation (Figure 1.7(b)).⁸⁷ It was theoretically demonstrated using asymmetric SRRs which exhibits reduction of radiation losses in an infinite periodic array.⁶⁰ Therefore, if a high- Q Fano resonance is employed with a gain material, losses can be sufficiently overcome to the extent that the minimum condition set by the lasing threshold of the plasmonic system can be met for lasing action to occur, hence successfully realising a lasing spaser at nanoscale dimensions. As a first step, lead sulphide (PbS) semiconductor quantum dots were spin coated onto asymmetric SRR array. The Fano resonance was designed such that it matches exactly with the luminescence resonance of the quantum dots and strong coupling between the excitons and plasmon modes leads to multifold enhancement of the quantum dot luminescence and spectral narrowing of the linewidth as shown in Figure 1.7(c-d).^{68, 88} There exists a trade-off between intensity enhancement and FWHM as the luminescence resonance are tuned from the Fano resonance frequency and is optimized for wavelength mismatched by 125nm, as depicted in Figure 1.7(e). Till date, there is no demonstration of a planar lasing spaser based on Fano resonance due to the requirement of high pumping power, which adversely affects the system due to excessive heat losses in plasmonic metamaterials.

Figure 1.7. Principle of SPASER and demonstrations of enhanced fluorescence. (a) Schematic of energy transfer between excitons of nanocrystal quantum dots (gain medium) and surface plasmon modes of metallic nanoshell.⁸⁶ (b) Lasing spaser with planar metastructures on a gain medium slab (green).⁸⁷ Enhanced fluorescence intensity spectra of PbS quantum dots on (c) asymmetric double bars⁶⁷ and (d) complementary asymmetric SRRs⁸⁸ when the luminescence resonances are matched to the Fano resonance frequencies. (e) Intensity enhancement and FWHM of the photoluminescence for asymmetric SRR array coated with quantum dots.⁸⁸

1.3.3 Optical Switch

One of the key strengths of Fano resonance is the sensitive nature of the intense electromagnetic field present in the planar structures. As a result, it could be used for purposes where external influences can be introduced to realise more functionalities of the Fano devices. Active photoswitching of Fano resonance has been demonstrated by R. Singh

and his group using optically active medium such as solution-processed perovskites,^{89, 90} silicon,⁹¹ and MoS₂⁹² in asymmetric SRRs. An ultralow fluence of $<7 \mu\text{J cm}^{-2}$ of the optical pump beam is required for resonant switching behaviour in organic-inorganic lead halide perovskites as shown in Figure 1.8(a). Upon increasing optical excitation fluence, the metadvice manifests phonon-Fano coupling which shows the sensitive nature of Fano resonance to detection of the phonon modes.⁹⁰ Another approach to active switching is via applying a voltage onto a liquid crystal to change the phase of the medium, which alters the polarization of the incident light propagating through and excites the symmetry-broken octamer structure to reveal the Fano resonance. Hence, the switching on and off of the voltage indirectly excites the octamer structure with different polarization of incident light, realizing an electrically switchable Fano switch in the visible spectrum as shown in Figure 1.8(b).⁹³ In addition, phase-transition metal oxide such as VO₂ undergoes an insulator-to-metal transition (IMT) at 68°C and have shown active switching of broadband transmission in the THz band,⁹⁴ which also can be implemented into Fano resonance system. Numerically simulated results show that hybrid VO₂/Au asymmetric double bars induces a relatively high- Q Fano resonance when the dipole resonance arising from VO₂ bar in its metallic state interferes with the dipole resonance of Au bar. In its insulator phase, Fano resonance disappears and a dipole resonance solely contributed by the Au bar appears around 0.95 THz.⁹⁵

Figure 1.8. Photoswitching of resonances. (a) Low power dependence THz transmission spectrum of organic-inorganic lead halide perovskites integrated THz Fano metamaterial for resonant switching behaviour.⁹⁰ (b) A plasmonic Fano switch whose Fano resonance is actively modulated via voltage control under different polarization.⁹³

1.4 Prelude to motivation

As technology progresses, scaling down of devices becomes even more attractive with customizable novel optical properties, hence pushing us to venture into new fields of research. Metamaterials is one such field that has gained huge research interest over the past two decades, owing to the extreme spectral scalability, flexible optical properties and ease of realization and integration. Metamaterial can be easily engineered by design (size, shape, geometry and arrangement of meta-atoms) to exhibit versatile material properties, including those which are not available in nature. Furthermore, the meta-atoms are so small that miniaturization of future devices looks promising. By going smaller, we increase the portability of the device as more components can be packed together, and in doing so, the operational efficiency will also be higher.⁹⁶⁻⁹⁹

However, advancements in technology are not always smooth-sailing and are usually met with several setbacks and challenges. Energy losses remain one of the critical issues for implementing feasible metamaterial-based devices, as it affects the speed, efficiency and reliability of devices. The two dominant energy loss mechanisms in metamaterial are radiative and non-radiative losses. Radiative loss is inherent in metamaterials owing to the subwavelength nature of the resonators, and is the dominant loss mechanism at lower frequencies, while energy loss at higher frequencies is largely dominated by the non-radiative process (ohmic loss). Nevertheless, radiative loss remains present in metamaterials across the electromagnetic spectrum. As an approach, without significantly redesigning the

architecture of the device, radiative loss can be reduced by breaking the symmetry of the metamaterial which in turn induces a trapped-mode resonance termed as Fano resonance.

1.4.1 Motivation of thesis

As discussed earlier, Fano resonance is an efficient approach to suppress radiative losses as it does not interact with far-field propagating wave. In addition, Fano resonance as a high- Q resonance mode possesses strong confinement of electromagnetic field, which is imperative for useful applications in a wide range of frequencies in optics and photonics. *Therefore, an understanding on the behaviour of Q -factor is important for realizing scalable and functional metamaterial devices across the electromagnetic spectrum.*

Although Fano resonance provides an avenue to reduce radiative losses in plasmonic metamaterial system, it does not completely eliminate the presence of radiative losses. A higher Q -factor is evidently more desirable in most metamaterial devices. It is possible to achieve an even higher Q -factor by further exploiting the arrangement of sub unit-cells in Fano metamaterial structures which controls the linewidth narrowing of Fano resonance. *However, there has been little focus to interpret the enhancement of Q -factor in such approach, and it will be essential to quantitatively and qualitatively study the role of multipoles to linewidth narrowing in complementary Fano metastructures.*

The merits of high- Q Fano resonance have empowered the advancements of functional metamaterial-based devices. With technologies progressing, flexibility and speed are the core to modernisation of small-scale optoelectronic devices. *Until now, Fano optical switch has either been fabricated on rigid substrates or displayed no ultrafast capability.* It will be significant to realise an ultrafast and flexible Fano optical switch and one aspect is to exploit *amorphous germanium* as an optically active medium which we have thermally evaporated onto our Fano metadvice made based on *flexible Kapton substrate*.

1.4.2 Choice of THz and infrared regime

THz radiation spans the region in the electromagnetic spectrum that possesses unique properties shared between infrared radiation and microwave radiation. It is non-ionizing with low photon energies, hence very suitable for medical imaging purposes.¹⁰⁰ Besides, THz radiation is transparent to a wide range of non-conducting materials, which allows for the detection of drugs and defects in commercial products.¹⁰¹ Therefore, THz metamaterials are especially enticing because of their ability to effectively manipulate THz waves at the microscale level and also enhance the THz signal, which provides useful information such as THz spectral fingerprint of explosive materials.¹⁰² On top of that, the longer wavelength of THz benefits optical communication technology.¹⁰³

Similar to THz radiation, infrared radiation possesses non-ionizing and non-invasive properties which is also suitable for infrared thermal imaging¹⁰⁴, in particular the detection of heat-related body condition.¹⁰⁵ Infrared spectroscopy has been developed as an essential tool for characterization and analysis of samples in their solid, liquid and gaseous states.¹⁰⁶ It has also been crucial for the study of protein molecules.^{107, 108} With metamaterials, the weak vibrational modes of molecules are amplified by electromagnetic fields that are confined at the metasurfaces.⁸⁴

In summary, THz and infrared regimes cover the range of useful frequencies where health, security and communication technologies are essential to improving the quality of lives of humankind. This is also the range of frequencies which we are best suited to integrate our work with, given the availability of equipment and measurement systems.

1.5 Organization of thesis

The main focus of this thesis is to investigate, enhance and exploit the fascinating features (high sensitivity, intense electromagnetic field confinement and high- Q) offered by Fano

resonant metasurfaces in the electromagnetic spectrum, which spans from THz to infrared frequencies.

In chapter 1, the discovery of metamaterials and scattering phenomenon of Fano resonance were introduced. The prospects of Fano resonance in various applications were also elaborated to illustrate the attractiveness of its features.

In chapter 2, the operating mechanism of fabrication processes such as thermal evaporation and focused ion beam (FIB) fabrication were explained in detail. Scanning electron microscope built with the FIB system was also covered. In addition, two main spectroscopy methods using such as ultraviolet/visible/near-infrared (UV/VIS/NIR) microspectrophotometry and optical-pump terahertz-probe (OPTP) spectroscopy were employed for the measurement of NIR and THz metasurfaces sample respectively.

In chapter 3, we devised a model based on an exponentially decay function that can be used to explore the universal behaviour of high- Q Fano resonance in the entire electromagnetic spectrum. Moreover, further probing of this behaviour has enabled us to graph a calibration plot that is useful for scalable metadevices.

In chapter 4, we inverted the unit cell configuration of asymmetric double bars and obtained an enhanced Q -factor of Fano resonance in the near-infrared regime as compared to non-inverted unit cell configuration. We showed how multipole analysis can be employed to provide qualitative and quantitative analysis of the contributions of multipoles toward linewidth narrowing in complementary Fano resonant metasurfaces which resulted in the enhanced Q -factor.

In chapter 5, we exploited the high- Q and sensitive nature of Fano resonance to materialise an ultrafast and flexible metaphotonic device in the THz regime. We presented a universal

strategy to achieve ultrafast photoswitching which is based on trapped-assisted recombination sites due to structural defects from thermal evaporation of single-element germanium above our Fano resonant metasurfaces. Kapton substrate is used to form a flexible metaphotonic device.

Lastly, in chapter 6, we come to a closure of the thesis where the conclusion presents and overview representation of the results and discussion. We also suggests possible future works based on Fano resonance by utilizing all-dielectric metamaterial structures, and two-dimensional (2D) materials (such as MoS_2) which has been an increasingly hot topic in the community.

As we look at the above-mentioned chapters, we will grasp a better appreciation of the motivation behind the work in Fano resonance.

2 EXPERIMENTAL TECHNIQUES

This chapter is divided into two sections which cover the experimental techniques that were used to fabricate the metamaterials and characterisation methods that were performed in the infrared and terahertz frequencies regime. The fabrication techniques mainly employ a top-down fabrication process in which focused ion beam and photolithography were used for nanofabrication and microfabrication of metamaterials respectively. Scanning electron microscope verifies the quality of the fabricated metamaterials before measurements are taken. The characterisation of the metamaterials in the infrared and terahertz regimes were performed using microspectrometer and optical-pump terahertz-pump spectroscopy respectively.

2.1 Fabrication techniques

2.1.1 Thermal evaporation system

Thermal evaporation is a physical vapor deposition method that can be used to deposit thin metallic films. In terms of quality, it is fundamental for thin metallic films to be of highest purity, have low surface roughness and accurate thickness. Thermal evaporation provides a simple, convenient and efficient method to deposit thin metallic films onto substrates. In the thermal evaporation system (Univex 250), to achieve a good quality of thin metallic films, three main components play a crucial role: the vacuum system, thickness monitor and power supply. Figure 2.1 shows the inner chamber of the thermal evaporation system.

An evacuated vacuum chamber with a high-vacuum can be achieved with the help of a rotary vane vacuum pump and a turbomolecular pump. A rotary vane vacuum pump initiates the rough vacuum pumping up to approximately 10^{-4} mbar, before the turbomolecular pump takes over for high-vacuum pumping so that pressure value as low as 10^{-8} mbar is achieved.

Metal pellets are placed onto the trough of the resistive boat whose material element (e.g. carbon, molybdenum or tungsten) is based on the physical properties of the desired source. A power supply provides the current to be driven through the electrodes which are connected by the resistive boat. The resistive boat is heated to a very high temperature and metal pellets start to melt due to Joule effect. With the assistance of the thickness monitor, the rate of evaporation and thickness of the thin film can be monitored and adjusted accordingly using the power supply.

Figure 2.1. Inside of the thermal evaporation system. Labelled in the figure from top to bottom are the motorised stage holder, thermal shutter, quartz crystal thickness monitor, position of resistive boat and electrodes that are connected to a power supply (the vacuum pump and power supply are not shown inside).¹⁰⁹

Three basic steps take place in thermal evaporation: evaporation, transportation and condensation of source atoms. According to the Clausius-Clapeyron relation, evaporation

where k_B is the Boltzmann constant, T is the absolute temperature, P is the vapor pressure and d is the diameter of the atoms. It represents the average distance travelled by a source atom in a straight line before it encounters a collision with another atom in the vacuum chamber. At the same time, the motorised stage holder is continuously rotated to ensure uniformity of thin metallic film deposited on the substrate. Since the surface of the substrate is much cooler than the source atoms, energy is transferred to the substrate which results in the condensation of the source atoms, thus forming a solid layer of thin metallic film. Eventually, a quartz thickness monitor will automatically shut the thermal shutter when the desired thickness is obtained. The power supply is turned off to stop the evaporation process and the melted liquid solidifies.

The accuracy of the thickness determined for the thin metallic film is based on the piezoelectric sensitivity of quartz monitor crystal to the added mass, m_f .¹¹¹ The added mass onto the quartz crystal of mass, m_q changes the original resonant frequency value from f_q to f_f . The relationship between the added mass and the frequency shift ($\Delta f = |f_f - f_q|$) is,

$$\frac{m_f}{m_q} = c \frac{\Delta f}{f_q} \quad (13)$$

where c is a unity if the coverage of added mass over the quartz crystal is uniformly distributed.

The thickness of the film deposited, l_f is related to the frequency shift, Δf through known parameters and is calculated as,

$$l_f = \frac{N_q \rho_q}{\rho_f} \frac{\Delta f}{f_q^2} \quad (14)$$

where N_q (1.668×10^5 Hz cm) and ρ_q (2.648 g/cm³) is the frequency constant and density for AT-cut quartz crystal, and ρ_f is the density of the added mass.

2.1.2 Focused ion beam fabrication

Focused ion beam (FIB) fabrication is performed using Helios Nanolab 650. FIB is a well-established technique suitable for top-down fabrication of patterns or structures. It is an extremely versatile technique that has been employed in semiconductor industry for sample preparation and nanoscale processing of devices. As in all precise and clean fabrication, the requirement for a high-vacuum environment is mandatory, so that the path travelled by the ions or electrons from the gun to the sample is free of collision with air molecules. This is supported by a turbomolecular pump which is backed by a scroll pre-vacuum pump. As the name of the technique implies, ions are tightly focused into a beam which will strike onto the sample surface, either for imaging or milling purposes. Gallium (Ga^+) ions are preferred over electrons because they are 130,000 times heavier than electrons which gives a large momentum despite their low velocity. Consequently, Ga^+ ions can be well-controlled to remove materials at the nanoscale level. In addition, their low penetration depth and high interaction probability with the sample atoms promote ionisation and breaking of chemical bonds.

Gallium liquid metal ion sources (LMIS) are widely used in FIB system as they possess physical properties that are advantageous over other metals. They have a low melting temperature of 30°C (suitable for operation at room temperature) and low vapor pressure (applicable in high-vacuum), a long lifetime of 1500 hours which makes it the most stable LMIS (suitable for high-resolution imaging at low beam currents and enduring fabrication at high beam currents) and can be readily identified among other elements (low analytical interference). When gallium metal is melted, the balance of forces between surface tension

and electrostatic forces causes liquid gallium to form a Taylor cone at the tip of a metal-coated tungsten needle. Large negative voltage is applied between the needle and extraction electrode which causes the gallium atoms to ionise and be extracted by field emission. The Ga^+ ions are accelerated through a lens system composed of electrostatic lenses where the beam of ions is adjusted, aligned and focused with a beam diameter of approximately 7 nm, and scanned by a scan generator which feeds signal to the deflection system, before they strike the sample surface.

Figure 2.3. Illustration representing the principle of FIB milling.¹¹²

As depicted in Figure 2.3, bombardment of Ga^+ ions (orange beam) onto the sample surface sputters small amount of the sample atoms which causes implantation of Ga^+ ions or amorphisation of sample surface. In the process, secondary ions, sputtered atoms and secondary electrons are released, whereby secondary ions or electrons are detected by a secondary detector. Three parameters determine the FIB process: acceleration voltage, ion beam current and dwelling time.

A higher acceleration voltage equals to a higher beam energy, and the Ga^+ ions will have a higher momentum to strike the sample surface. More sample atoms will be sputtered from

the sample surface and the Ga^+ ions will penetrate the sample surface deeper. Thus, the acceleration voltage determines the penetration depth of the ions into the sample surface.

The ion beam current controls the number of ions that will be focused onto the sample. At low ion current, small amount of Ga^+ ions sputter secondary electrons and ions that can be used as an imaging channel. More often, low ion current is used to obtain a better resolution and cause lesser damage to the sample. At high ion current, more Ga^+ ions are focused which transfer energy to the sample atoms at the surface, resulting in ionisation and breaking of their chemical bonds. Therefore, materials are removed by milling or physical sputtering of ions. As such, high ion current will be used if the sample is required to be milled at a faster rate, but it produces a poorer resolution.

Dwelling time refers to the amount of time the ion beam will stay focused at a sputter point. A longer dwelling time implies that the focused ion beam will remain at a specific sputter point longer before it scans to the next sputter point.

In summary, a higher acceleration voltage with a higher ion beam current and a longer dwelling time imply that the sputtering rate of FIB will be much more intense and faster, but this results in more damages done to the sample surface. Under unfavourable conditions, Ga^+ ions are redeposited onto the sample surface and cause contamination. An approach to effectively remove these contaminants is to perform plasma processing using a plasma cleaner.¹¹³ Therefore, a good balance of the acceleration voltage, ion beam current and dwelling time should be established based on the requirements of resolution imaging and milling altogether.

2.2 Characterization methods

2.2.1 Scanning electron microscope

In our dual-beam FIB instrument (Helios Nanolab 650), the FIB comes integrated with scanning electron microscope (SEM). As depicted in Figure 2.4, the electron column of the SEM is situated at normal to the plane of the sample surface, while the ion column is tilted at an angle of 52° from the electron column. This allows simultaneous monitoring, imaging and ion milling at the same spot on the sample surface. During milling, the sample is tilted towards the ion column so that the ion beam strikes the sample surface at normal incidence.

Unlike FIB, SEM utilizes a beam of focused electrons to perform high-resolution imaging under a high-vacuum environment. A high-vacuum environment reduces scattering of secondary electrons which are detected as signals, and thus improves the resolution. A beam of electrons is accelerated from the electron gun and travel through a series of electromagnetic lenses and apertures in the electron column which alters their path, provides focusing and magnification. The electron beam scans systematically over the surface of the sample and forms the SEM image made up of signal generated from each point on the surface.

Depending on the power of the accelerating voltage, the signal generated will affect the resolution of the image. For a higher accelerating voltage, the electron beam penetrates the sample even deeper and the interaction volume increases. Despite generating a higher signal, more backscattered electrons are emitted due to elastic scattering, which increases the brightness and blurs the structural details of the sample surface in secondary electron imaging.

Figure 2.4. Typical configuration of FIB-SEM system.¹¹²

SEM image is generated mainly from the secondary electrons that comes from the inelastic scattering with the sample atoms. Due to their low energies (<50 eV), secondary electrons emitted from the surface are detected which provide information about the topography of the surface. Backscattered electrons (with energy >50 eV) come from the primary electron beam which are electrons emitted back from the surface of the sample, and they provide information about the contrast of the surface.

Compared to FIB imaging, SEM is better in terms of high-resolution imaging and its less damaging effects on the sample. According to the de Broglie expression, the de Broglie wavelength, λ of a particle is related to the momentum, p of a particle through the Planck constant, h and is written as,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}} \quad (15)$$

where K is the kinetic energy, m is the rest mass of a particle. For an electron with a kinetic energy of 1eV and rest mass of 9.11×10^{-31} kg, the de Broglie wavelength is 1.23 nm. The

resolution of image obtained from electrons compared to ions is several thousand times smaller. Therefore, to obtain the optical images of our samples, the function of SEM in Helios Nanolab 650 is employed for imaging and checking the FIB outcome of our nanostructured patterns.

2.2.2 Ultraviolet/Visible/Near-Infrared microscopic spectrophotometer

The optical system utilizes a double beam type single monochromator Czerny-Turner (CT) mount (Figure 2.5) that covers a broad range of wavelength with the help of two planar diffraction gratings: 1200 lines/mm and 300 lines/mm for UV/Vis and NIR regions respectively. Both deuterium (D_2) and halogen (W) lamps provide the light sources for wavelengths ranging between 200 to 350 nm and 330 to 2700 nm respectively.

Figure 2.5. Optical system for MSV-5200 with a CT monochromator.

In the monochromator, a broadband spectrum input is converted into a narrow band output using a Czerny-Turner mount. The filter limits the bandwidth of the light entering the monochromator. The focused light from the light source enters through an entry slit and is collimated by a collimating mirror. Parallel light rays travel towards the diffraction grating and are dispersed by the grooves on the grating into different wavelengths. A series of closely

spaced wavelengths are reflected to the focusing mirror and refocused as they are directed towards the exit slit at different positions. The selection of exit wavelength is determined by rotating the diffraction grating as different wavelengths reflect at different angles. Only one monochromatic light corresponding to the diffraction angle of the diffraction grating will exit the monochromator.

The monochromatic light passes through a polarizer and an aperture, then to a beamsplitter which splits the path of the light into two beams. The polarizer is based on Glan-Taylor prism and the control of polarization angle between -90° to $+90^\circ$ is fully automated. One beam becomes the reference beam, while the second beam becomes the measurement beam, hence functioning as a double beam instrument. The measurement beam travels either the reflectance (by reflecting off a beamsplitter) or transmittance path and forms an image on the sample by the condensing mirror at the sample position. The measurement beam passes through a second aperture located before a second polarizer and is detected by either a photomultiplier tube (PMT) or a lead sulphide detector (PbS det.) that covers a spectral range of 200 to 900 nm or 750 to 2700 nm respectively. The detector is selected by moving the mirror and provides detection of the beams based on the specification. The reference beam is also detected by similar detectors which compare their intensities and send a signal proportional to the ratio of their intensities to a computer that controls the microscopic spectrophotometer.

Reflectance path is desirable for our experimental condition due to the reflective nature of the thin gold film, which provides us with a better signal in terms of intensity. For all measurements, normal incidence was used, and the reflectance of the substrate was first measured to act as a baseline reference. Subsequently, reflectance results obtained from

measurements of metastructures fabricated above similar substrate were normalized with the baseline reference, to get the true optical response of the metastructures.

2.2.3 Optical-pump terahertz-probe spectroscopy

Microscopic spectrophotometer only covers the frequency range between the UV and NIR. For terahertz measurement, we employed the optical-pump terahertz probe (OPTP) spectroscopy system as illustrated in Figure 2.6 which is a ubiquitous technique that provides spectral information and carrier dynamics of semiconductors and THz metamaterial system.

Figure 2.6. Optical setup of the OPTP spectroscopy system.

The excitation source is an amplified femtosecond laser that generate optical beam that consists of pulses with wavelength of 800 nm and pulse width of 35 fs, at a repetition rate of 1 kHz. The optical beam travels to a beamsplitter which splits the optical beam into a pump beam and a probe beam. The pump beam is directed to a variable delay stage where the delay of the pump beam can be controlled during the excitation of the sample. The probe beam goes to another beamsplitter which splits the probe beam into two beams for generation and detection of pulsed THz radiation.

The intense ultrashort laser pulse hits a <110> zinc telluride (ZnTe) nonlinear crystal and its electric field changes the electromagnetic field inside the crystal. Consequently, electrons or ions oscillate sinusoidally and their displacement from the average position causes the crystal to generate a direct current (DC) polarization which is known as optical rectification (second-order nonlinear effect). According to the nonlinear Maxwell's equation, the local terahertz field, $\tilde{E}$ is proportional to the second-order time derivative of the second-order nonlinear polarization, $\tilde{P}^{NL}$ that is induced by optical rectification and is written as,^{114, 115}

$$\nabla^2 \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{P}^{NL}}{\partial t^2}, \quad (16)$$

where n is the linear refractive index, c is the speed of light and ϵ_0 is the permittivity of free space. As such, the time-varying polarization of the nonlinear crystal drives the electric field and charges are accelerated. It follows from Larmor formula¹¹⁶ that any charges accelerated are able to form a source to generate electromagnetic radiation. In our case, difference-frequency generation of different frequencies component determined by the bandwidth of the femtosecond laser pulse results in electromagnetic radiation generated in the THz region.

An optical chopper is placed after the THz radiation to synchronise the lock-in amplifier to obtain a better signal-to-noise ratio. An optical pump beam hits the sample at the sample position and the photo-initiated changes in the optical properties of the sample are probed by a delayed THz pulse. Non-equilibrium carrier dynamics of the material sample are probed which reveals the photoconductivity and carrier relaxation time.

Figure 2.7. THz and optical pulses are collinearly propagating towards the ZnTe crystal detector.

The THz pulse is detected by another ZnTe nonlinear crystal via electro-optic sampling based on the Pockels effect (refractive index of the medium is modified as a consequence of the applied electric field). At the same time, a delay probe pulse whose group velocity is equal to the phase velocity of the THz pulse are phased matched and they propagate collinearly into the ZnTe nonlinear crystal as shown in Figure 2.7. This is necessary because the delay probe pulse has a pulse width of 100 fs which is spatially much shorter than the pulse width of THz pulse which is 1 ps. The delay time of the delay probe pulse is varied by another variable delay stage that allows the entire profile of the THz pulse to be mapped in the time domain.

The electric field of the THz pulse induces a birefringence to the ZnTe nonlinear crystal and the linear polarization of the delay probe pulse is rotated as it interacts with the THz pulse. The phase difference, $\Delta\phi$ of the x - and y -polarization components of the delay probe pulse through the ZnTe nonlinear crystal of length L is written as,¹¹⁴

$$\Delta\phi = (n_y - n_x) \frac{\omega L}{c} \quad (17)$$

where n_x and n_y are the refractive indices along x - and y -directions respectively in the principal-axis under the presence of THz electric field E_{THz} , ω is the optical frequency and c is the speed of light.

The refractive indices along x - and y -directions in the principal-axis of ZnTe nonlinear crystal with an electro-optic coefficient r_{41} , where n_o is the refractive index at optical frequency are written as,

$$n_x = n_o - \frac{1}{2}n_o^3r_{41}E_{THz} \quad (18)$$

$$n_y = n_o + \frac{1}{2}n_o^3r_{41}E_{THz} \quad (19)$$

A quarter waveplate introduces a $\frac{\pi}{2}$ phase shift and converts the polarization of the delay probe beam from linear to circular (or slightly elliptical under the influence of an electric field). The electric field, amplitude and delay of the THz pulse at a variety of delay times are acquired when the Wollaston prism acting as a polarization beamsplitter splits the circularly polarized delay probe beam into two orthogonal linearly polarized beams which are detected by a balanced detector.

The intensities of the two orthogonal linearly polarized beams at the balanced detector are written as,¹¹⁷

$$I_x = \frac{I_0}{2}(1 - \Delta\phi) \quad (20)$$

$$I_y = \frac{I_0}{2}(1 + \Delta\phi) \quad (21)$$

where I_0 is the initial intensity of the delay probe beam.

The balanced detector evaluates the intensity difference, I_s between the two orthogonal linearly polarized beams which is directly proportional to the applied THz field amplitude,

$$\begin{aligned}
 I_s &= I_y - I_x \\
 &= I_0 \Delta\phi \\
 &= \frac{I_0 \omega L}{c} n_O^3 r_{41} E_{THz} \propto E_{THz}
 \end{aligned} \tag{22}$$

The obtained values of THz electric field amplitude, $E_{THz}(t)$ are time-dependent and fast Fourier transform (FFT) is performed to transform the values into frequency-dependent THz electric field amplitude, $E_{THz}(\omega)$ for further computation,

$$E_{THz}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} E_{THz}(t) dt \tag{23}$$

In OPTP spectroscopy, two separate sets of reference and sample measurements are needed to obtain the transmission spectrum of the sample. The transmission spectrum of the sample is determined by taking the ratio between the frequency-dependent THz electric field amplitude through the sample, $E_{SAM}(\omega)$ and the reference, $E_{REF}(\omega)$:

$$T_{SAM}(\omega) = \left| \frac{E_{SAM}(\omega)}{E_{REF}(\omega)} \right| \tag{24}$$

2.3 Summary of equipment main specifications

SYSTEMS	Power / Source	Vacuum level	Detectors employed
Thermal Evaporation (Univex 250)	TDK-Lambda, Genesys™	> Mid 10 ⁻⁷ mbar	Inficon SQM-160 Rate/Thickness monitor
FIB / FESEM (Helios NanoLab™ 650)	Ga ⁺ liquid metal ion source (1,000 hours)	< 2.6 × 10 ⁻⁶ mbar (after 24 h pumping)	Everhart-Thornley SE detector (ETD)
UV/NIR/VIS Microspectrophotometer (Jasco MSV-5200)	Deuterium lamp (200 – 350 nm) Halogen lamp (330 – 2700 nm)	Room condition	Photomultiplier tube (200 – 900 nm) Peltier-cooled PbS (750 to 2700 nm)
Optical-pump Terahertz-probe spectroscopy	Titanium: Sapphire laser (800 nm, repetition rate - 1 kHz, pulse duration - 35 fs)	Room condition	ZnTe nonlinear crystal emitter and detector

3 SYSTEMATIC STUDY OF Q -FACTOR IN TERAHERTZ TO NEAR-INFRARED FANO RESONANT METASURFACES

3.1 Introduction

In recent years, the field of plasmonics and metamaterials have enabled a seemingly new and innovative direction in the optics and photonics community, promising the conceptualization of subwavelength inventions with advanced and exceptional functionalities.^{11, 19, 118} The occurrence of strong light-matter interactions in metallic nano- to micro- structures is beneficial for applications in sensors,^{80, 84, 119-121} absorbers,^{122, 123} nanolasers,¹²⁴ photoswitches⁸⁹⁻⁹³ and slow-light devices.⁴⁶ However, metallic subwavelength structures entail extremely high losses due to absorption, especially at higher frequency regime of the electromagnetic spectrum where the energies are transferred into optical and acoustic phonons.²³ Radiative and non-radiative losses render the operation of metamaterial devices inefficient and hence impractical. As such, several solutions were proposed to reduce the inherent losses dominant in metamaterials which involve replacing metals with highly doped semiconductors¹²⁵ or superconductors,¹²⁶ or to compensate losses by integrating metamaterials with optical gain medium.^{87, 127}

Apart from introducing new plasmonic materials or optical gain into the system, geometric tailoring of the subwavelength structures offers an additional platform to mitigate radiative losses through Fano resonance. Fano resonance suppresses the radiative losses in Fano resonators and the overall losses are mainly contributed by non-radiative losses due to

resistive heating (especially at high frequencies). In metals, free conduction electrons are constantly moving in random motion among the cloud of positive lattice ions. When the free conduction electrons collide with the lattice ions or another free electron, energy is lost non-radiatively to the environment in the form of heat due to resistive heating in metallic Fano resonators. However, at low frequencies, Drude metals have a higher conductivity and so non-radiative losses can be reduced which leads to radiative losses contributing as the main loss mechanism. In summary, the sharp asymmetric lineshape of Fano resonance is more prominent at terahertz frequency as compared to infrared frequency due to lower non-radiative losses.

Albeit the abundance of discussion on Fano system, there remains a void in the systematization of the Q -factors for different asymmetry parameters in complementary structures across the near-infrared (NIR) to terahertz (THz) regime. It has been observed in several works that the Q -factor of Fano system decays exponentially with increasing asymmetry parameter.^{41, 53, 66} However, the similarity in the decay trend of the Q -factor ubiquitous in Fano system has received less attention and remains an essential part of understanding the implications of radiative and non-radiative losses. Hence, if a standard system of decay trends under different situations could be developed, it could serve as a guide for appropriate optimization and fabrication of scalable and functional metamaterial-based devices.

In this work, we performed numerical calculations on a complementary asymmetric dipole bars, and by proportionally scaling the dimensions we induced Fano resonance at different frequency regimes ranging from NIR to THz. The Q -factors at different regimes were evaluated and fitted with an exponential decay function to extract the decay constants. Our results further show that for the smallest asymmetry parameter, the decay constant of the Q -

factor obtained as a function of the Fano resonance frequency from NIR to THz regime is the largest. We also observed that the decay constant of the Q -factor obtained as a function of asymmetry parameter is largest at the NIR Fano resonance frequency and then decreases (with saturation) towards THz Fano resonance frequency. Both distributions display similar trend which tends towards an exponential decay behaviour.

3.2 Numerical simulation

For the choice of simplicity, but not limited to this design of metamaterial structure, we evaluated the Q -factors of complementary asymmetric dipole bars to elucidate the behaviour of Q -factors from NIR to THz regime. In Figure 3.1, the dimensions of a unit cell of the asymmetric dipole bars in THz regime are illustrated as follow: Both periods, p_x and p_y of the unit cell is $70\text{ }\mu\text{m}$; the width w and gap between the dipole bars g are each $14\text{ }\mu\text{m}$; the long bar length l is fixed at $42\text{ }\mu\text{m}$ and the short bar length s varies from 10 to $42\text{ }\mu\text{m}$ which evolves the unit cell from asymmetric to symmetric structure. The thickness of the aluminium metal is kept constant at 40 nm . Subsequently, taking the dimensions of the asymmetric dipole bars in the THz regime as a reference, the dimensions of the asymmetric dipole bars from NIR to mid-IR regimes are reduced proportionally by 100 and 10 times, respectively. In all cases, the asymmetry parameter of the Fano resonators is defined as the ratio between the difference in the length of long and short dipole bars to the length of the long dipole bar, $\alpha = \frac{l-s}{l}$.

Figure 3.1. Schematic illustration of the asymmetric dipole bars with the dimensions enlarged proportionally from NIR to THz regime. The electric field and magnetic field are polarized along the y - and x - axis respectively, and k_z is the propagation direction of the incident plane wave source.

Numerical simulations based on Finite-Differential Time-Domain (FDTD) technique were performed using commercially available electromagnetic simulation software, Computer Simulation Technique (CST) Microwave studio using the frequency domain solver. Unit cell boundary conditions were imposed in the periodic directions of x and y , and the incident plane wave source is excited from the Z_{max} direction with the electric field polarized along the symmetry axis of the asymmetric dipole bars as shown in Figure 3.1. Throughout the interested regions of the electromagnetic spectrum, the quartz substrate is modelled as loss free and assigned with a permittivity of 2.25. The aluminium is modelled as a lossy metal in the THz regime with DC conductivity of $\sigma = 3.56 \times 10^7 \text{ S/m}$, and permittivity values of aluminium in the optical regime were taken from the data measured by Palik.¹²⁸

3.3 Results and discussion

Figure 3.2. Simulated reflectance spectra of the asymmetric dipole bars at different regimes of the electromagnetic spectrum – NIR to THz (right to left). Coloured solid lines represent the Fano lineshape fitted to equation 3, described in Chapter 1.2 at different asymmetry parameters.

In Figure 3.2, the simulated reflectance spectra of the asymmetric dipole bars show that the symmetric dipole bars produce a broad dipole resonance accompanied by a lattice resonance at the higher frequency of each frequency regime. The broad dipole resonance at 264 THz is more pronounced in the NIR regime. For asymmetric dipole bars, the length of the short bar, s is reduced relative to the length of the long bar, l . When the symmetry of the dipole bars is broken, two resonances are observed from the spectrum: the Fano resonance is distinct as a sharp asymmetric lineshape at a lower frequency, associated with the background of the broad dipole resonance. A further decrease in the length of the short bar will increase the asymmetry parameters from 0 to 0.762, and a noticeable blue-shift of the Fano resonance is observed.

Figure 3.3. Simulated electric and magnetic field distributions of the positive and complementary asymmetric dipole bars at asymmetry parameter of 0.190 which validate the Babinet's Principle for electromagnetic fields. The maximum electric and magnetic field strengths of the positive and complementary asymmetric dipole bars are (2.6×10^7 V/m and 5×10^4 A/m) and (1×10^7 V/m and 5.5×10^4 A/m), respectively. The white solid arrows indicate the direction of induced surface currents on the aluminium metal.

Unlike Fano resonance in positive structures, which appears as a sharp dip in the transmission spectrum, the Fano resonance of complementary asymmetric dipole bars appear as a sharp dip in the reflectance spectrum. Simulated electric and magnetic field distributions of the positive and complementary asymmetric dipole bars are shown in Figure 3.3 to better comprehend the spectral feature of the Fano resonance. In positive asymmetric dipole bars, strong enhancement of the electric field occurs at both ends of the dipole bars whereby the charges in each dipole bar flow opposite to one another, inducing anti-parallel surface currents which is representative of an electric quadrupole mode. In complementary asymmetric dipole bars, out-of-phase circular surface currents are induced outside each bar which excite the magnetic quadrupole mode, and electric fields are confined at the inner top

and bottom sides of each dipole bar, analogous to the magnetic field distribution in the positive asymmetric dipole bars. The destructive interference of the quadrupole mode (dark mode) with the dipole mode (bright mode) contributes to the origin of the Fano resonance. Similarly, the electric field distribution of the positive asymmetric dipole bars relates very well with the magnetic field distribution of the complementary asymmetric dipole bars. This behaviour demonstrates strong coherence with the Babinet's Principle for electromagnetic fields.⁵¹ In both positive and complementary asymmetric dipole bars, the direction of the flow of induced surface currents and position of the field distribution match very closely to the polarization of the electric field and magnetic field incident onto the metamaterial structures.

Since the dark mode is subradiant, radiative losses in Fano resonance are effectively suppressed which results in the narrow linewidth and high Q -factor. The Q -factors of the simulated reflectance spectra in the NIR to THz regime were evaluated from parameters obtained through fitting with the Fano resonance lineshape, equation 3 described in Chapter 1.2.

3.4 Exponentially decay behaviour of Q -factor

Figure 3.4. (a) Numerically evaluated Q -factor and, (b) FoM plotted against the asymmetry parameter. The decay of the Q -factors with increasing asymmetry parameter at different regimes was fitted with an exponential decay function.

In the context of this work, Q -factor is defined as the ratio between the resonance frequency and the full-width at half maximum of the resonance dip in the reflectance spectrum. As shown in Figure 3.4(a), the Q -factor at different regimes is plotted as a function of asymmetry parameter, α . The increase in the Q -factor from NIR to THz regime reveals that the radiative losses at the lower frequency as compared to higher frequency are more effectively suppressed. In addition, the size of the Fano resonators at NIR frequencies is less than half the resonance wavelength, which suggests that majority of the energy is stored as

kinetic energy and lost through electron scattering in metals at femtosecond scale.²³ Despite the higher Q -factor at lower asymmetry parameter, the performance of the Fano resonators is limited by the intensity of the Fano resonance dip. There exists a trade-off between the strength of the Fano resonance and the Q -factor. Therefore, a Figure of Merit (FoM) is proposed to quantify the amount of losses which can be reduced such that the strength of the Fano resonance is still well-defined with maximum field confinement.⁴¹ The FoM is defined as the product of the Q -factor and the resonant intensity, with the resonant intensity being the dip-to-peak amplitude of the Fano resonance frequency. As shown in Figure 3.4(b), the grey shaded area indicates the sector in which the performance of the Fano resonator is optimized for narrow linewidth and strong resonant lineshape across the NIR to THz regime.

Figure 3.5. Numerically evaluated Q -factor plotted against the Fano resonance frequency which is fitted with an exponential decay function. The inset shows the magnified view of the grey shaded area where the plots for higher asymmetry parameters are presented.

3.5 Calibration plots for scalability of metadvice

In conjunction with Figure 3.4(a), the Q -factor as a function of Fano resonance frequency across the NIR to THz regime was also plotted as shown in Figure 3.5 to fully visualize the decay trend of Q -factors under different situations. As expected, the Q -factor is larger at THz Fano resonance frequency, with it being highest at the lowest asymmetry parameter. It is evident from both Figures 3.4(a) and 3.5 that the decreasing trend of the Q -factor exhibits an exponential decay feature. Therefore, to visualize the decay trend of Q -factor against asymmetry parameter or Fano resonance frequency, a systematic study of the decay constants is investigated.

Figure 3.6. Decay constants (const.) evaluated from Q -factor against – (a) asymmetry parameter which is plotted against Fano resonance frequency, and (b) Fano resonance frequency which is plotted against asymmetry parameter.

Technically, Q -factor means the ratio between the amount of energy stored to the amount of energy lost through dissipation in the resonator system. Therefore, the decay constants that are obtained through exponential fitting under different asymmetry parameter and Fano resonance frequency describe the rate at which the energy retained is dependent on the geometrical and frequency factors respectively. An exponential decay function was fitted to various sets of Q -factor, and the decay constants obtained further demonstrate an exponential

decay behaviour as depicted in Figure 3.6. Both Figures 3.6(a) and 3.6(b) constitute as a set of standard system for tailoring and optimizing the dimensions of the Fano resonators which are complemented by Figures 3.4 and 3.5 as calibration plots. The calibration plots need to have information at the extremities of the interested frequency or asymmetry parameter so that any new data points can be interpolated from within the range of available data points. As an example, to find out the Q -factor of a Fano resonator near 150 THz with any asymmetry parameters, decay constant from Figure 3.6(a) is extracted and used to plot the Q -factor in any positions of Figure 3.4(a). Next, since the Q -factors are unknown, maximum and minimum Q -factors at 150 THz are obtained from the calibration plot of Figure 3.5 to allow full prediction on the behaviour of the Q -factor of a Fano resonators near 150 THz with varying asymmetry parameter. This works similarly for estimating the Q -factor of Fano resonators at a specific asymmetry parameter across the NIR to THz regime.

3.6 Conclusion

In conclusion, the universal behaviour of Fano resonance in symmetry-broken resonators is investigated in asymmetric dipole bars. Sharp asymmetric and strong resonant lineshape were observed with Q -factor of at least 20 from the near-infrared to terahertz regime. Positive and complementary structures follow closely to the Babinet's Principle for electromagnetic fields. A standard system based on exponential decay function has been developed to characterize the behaviour of Q -factor under varying asymmetry parameter or Fano resonance frequency. Decay constants obtained from the exponential fittings provide insights into the rate at which energy is stored under different conditions. This work will be more extensive if a larger superset can be established based on varying materials or geometries, and further evaluated based on their decay trends. The standard system is beneficial and useful for the realization of scalable and "smart" metadevices across a wide spectral range.

4 MULTIPOLE ANALYSIS OF NEAR-INFRARED FANO RESONANT METASURFACE IN AN INVERTED CONFIGURATION

4.1 Introduction

In the field of plasmonic metamaterials, various Fano resonant unit cell shapes and designs such as dolmen structures,^{34, 43, 129} ring/disk nanocavities,^{37, 130-132} heptamers^{38, 74, 75, 133, 134} and notably split ring resonators¹³⁵⁻¹³⁹ have been explored in great detail. An uncomplicated design composed of paired asymmetric double bars (ADBs) has also been studied for its Fano resonance^{63-65, 67, 140, 141} and electromagnetically-induced transparency properties.^{62, 66, 142, 143} *While computed charge distribution and field vectors are typically used as a visual mechanism to identify and attribute the origin of the Fano resonance in such structures, there has been little focus on quantitative and qualitative analysis of the role of the multipoles that contribute to the asymmetric line shape and the linewidth narrowing of Fano resonances in complementary nanostructures (paired asymmetric double slots in a thin plasmonic metal film).* Complementary nanostructures are interesting due to the enhanced mode volume as a result of the tight confinement of the electromagnetic fields in the narrow empty spaces of the nanostructures (portions without metal). Since the mode volume is higher in these nanostructures, the interaction of the Fano cavity with any other dynamic material medium would be extremely strong. As such, multipole expansion analysis is applied to this simple design as an illustration of the way in which it can enrich the understanding of symmetry-broken metamaterials in complementary designs.

Here, we introduce a comparison between complementary nanostructures of paired ADBs in so-called “Fano” and “iFano” configurations (iFano denoting a 180° inversion of one ADB relative to the Fano geometry – as shown in Figure 4.1), and report that in the iFano configuration, a larger figure of merit and quality factor can be achieved in the infrared regime, as compared to the Fano configuration. Numerical simulations attribute the origin of a broad dipolar resonance to the electric dipole, and the asymmetric Fano lineshape is a consequence of the electric dipole (E. dip) interacting with the magnetic quadrupole (M. quad) and the toroidal dipole (T. dip). Via a decomposition of the multipoles, we find that the magnetic quadrupole competes on the same scale as the toroidal dipole to narrow the linewidth of the resonance. In addition, the iFano configuration offers a spectral shift without the need to alter the periodicity or dimensions of the unit cell.

4.2 Methods

Figure 4.1. Asymmetric double bars (a) Dimensions of a single unit cell of paired ADBs in the iFano configuration (with scale bar). In experiment and numerical simulation, light is normally incident on the plane of the nanostructure with the electric field polarized along the y -axis and magnetic field in the x -axis. Scanning electron microscope (SEM) images of the complementary nanostructures in the (b, d) Fano and (c, e) iFano configurations with asymmetry parameters of 0.762 (b, c) and 0.286 (d, e). A perspective view of Fano (f) and iFano (g) configurations at an oblique viewing angle of 52° .

Figure 4.1(a) illustrates a generic unit cell of the metamaterial nanostructure used in the present study, which comprises four slots (two complementary ADBs) in a thin gold film. In

the ‘Fano’ configuration the ADBs have the same orientation, while in the iFano configuration, one ADB is rotated by 180° with respect to the other. The period of the unit cell is fixed at $p_x = 1400$ nm and $p_y = 700$ nm, the long bar length is fixed at $l = 420$ nm with width, $w = 140$ nm, and the x -separation between ADBs within the unit cell is fixed at $g = 80$ nm. Within the double bars, the long and short bars are separated by a distance, $d = 140$ nm. The asymmetry of the nanostructures was controlled by varying the lengths of the short bar, from 420 nm to 100 nm. The asymmetry parameter is defined as the ratio of the difference between the length of the long (l) and short (s) bars to the length of the long bar, $\alpha = \frac{l-s}{l}$. Figure 4.1(b-e) shows SEM images of fabricated complementary Fano and corresponding iFano configurations for asymmetry parameters of 0.762 and 0.289 respectively. Experimental samples were fabricated in a 40 nm gold thin film evaporated onto a quartz substrate at a rate of $0.2 \text{ \AA/s}$. Each array of complementary nanostructures has dimensions of $40 \text{ }\mu\text{m}$ by $40 \text{ }\mu\text{m}$ and is fabricated by focused-ion beam milling (FEI Helios Nanolab 650 DualBeam operating at 30 kV and 24 pA). The reflectance spectra of fabricated nanostructures were measured using a microspectrophotometer (Jasco MSV-5200) with y -polarized incident light. Numerical simulations were carried out using commercial finite-difference time-domain Maxwell solver software (Lumerical FDTD) assuming plane wave illumination polarized in the y -direction. Periodic boundary conditions were imposed in the x - and y - directions; perfectly matched layers were set in the z -direction so that any incident waves do not reflect at the boundaries but are strongly absorbed. The optical constants of gold were taken from Johnson and Christy¹⁴⁴ and the refractive index of the quartz substrate was set to 1.5.

4.3 Observation of linewidth narrowing in “iFano” configuration

Figure 4.2. Comparison of reflectance spectra in Fano and iFano configurations.

Measured (a, b) and simulated (c, d) reflectance spectra of the complementary Fano (a, c) and iFano (b, d) configurations for a selection of asymmetry parameters. The dips of the Fano resonances are marked with arrows in the corresponding line colour. Colour maps of simulated reflectance against wavelength and asymmetry parameter for the (e) Fano and (f) iFano configuration. In these figures, the black arrow highlights, by way of example, the linewidth of the Fano resonance for $\alpha = 0.524$. The white dashed line illustrates the tuning extent of resonance wavelength tuning over the range of asymmetry parameters considered.

The reflectance spectra measured for y-polarized incident light propagating normal to the plane of the nanostructures are shown in Figure 4.2(a-b). They clearly illustrate that in both configurations, the Fano resonance red-shifts with decreasing asymmetry accompanied by linewidth narrowing. For a pair of *symmetric* double bars in both configurations, the resonance broadens and resembles a simple dipole resonance at around 1300 nm. In contrast, for non-zero asymmetry parameters, the broad dipolar resonance evolves into a Fano resonance centred at around 1400 nm for the iFano configuration at the highest level of asymmetry ($\alpha = 0.762$) - a wavelength that is markedly shorter than the resonance wavelength of the Fano configuration, at around 1600 nm. Numerically simulated reflectance spectra, shown in Figure 4.2(c-d) are in excellent agreement with the experimentally observed optical response, with the slight discrepancies in resonance wavelengths being attributed to imperfections incurred during the fabrication process (i.e. deviations from the ideal rectilinear geometry assumed in modelling) and differences in the optical constants of materials used in the simulations. It is evident from Figure 4.2(e-f) that for a given value of the asymmetry parameter, the linewidth of the iFano configuration is narrower than the Fano configuration. The blue-shift of the entire spectrum from the Fano to iFano configuration is a result of a decrease in the electromagnetic coupling between the in-plane modes of the long bars in the latter case.²⁹

4.4 Enhancement of Q -factor in “iFano” configuration

Figure 4.3. (a) Measured and (b) simulated Q -factor and FoM of the complementary Fano and iFano configurations as functions of asymmetry parameters.

Quality factors of the plasmonic system were evaluated for both configurations at their respective resonances. Quality (Q) factor is a dimensionless parameter which determines the extent of radiative and non-radiative losses in the plasmonic resonator. It is calculated here as a ratio between the resonance wavelength, λ_0 and the full-width at half maximum, $\delta\lambda$ of the resonance dip in the reflectance spectra, $Q = \frac{\lambda_0}{\delta\lambda}$. A plasmonic system is less damped when the Q -factor is higher, and the system can store more energy. As shown in Figure 4.3, measured and simulated Q -factors for the Fano configuration increase with decreasing asymmetry to values of 34.9 and 45.7 respectively at $\alpha = 0.048$. From simulations, the Q -

factor of the iFano configuration reaches 75.4 at $\alpha = 0.048$, a value more than 1.5 times (50%) larger than the corresponding Fano configuration. However, at these small values of the asymmetry parameter, experimental Q -factors cannot be evaluated due to the weakness of the resonance, which appears as a shoulder as opposed to a defined dip in the reflectance spectrum (Figure 4.2(b)). Another parameter which characterises the overall performance of the Fano resonance is the figure of merit (FoM), defined as the product of the Q -factor and the peak-to-peak resonant intensity. The FoM parameter is crucial as it considers the trade-off between the quality factor and the intensity of the Fano resonance. Typically, the Q factor of a Fano resonant system decreases as the resonance intensity increases when the asymmetry in the system is increased. From Figure 4.3, the measured and simulated FoM in both configurations suggest that the system has optimum performance near $\alpha = 0.4$ and 0.3 respectively. We observe reasonable agreement between the measured and simulated trends in both the Q -factor and FoM of the Fano and iFano configurations.

4.5 Influence of multipoles on linewidth narrowing

To better understand the nature of the optical responses in different configurations and its influence on the linewidth narrowing, numerical calculations were performed using a multipole expansion of the electromagnetic fields. The calculated induced current densities in the nanostructures were used to compute the scattering power of several multipoles, which can be represented in the x, y, z Cartesian coordinate frame as follow:¹⁴⁵⁻¹⁴⁷

$$\text{Electric dipole moment: } P_\alpha = \frac{1}{i\omega} \int J_\alpha d^3r, \quad (25)$$

$$\text{Magnetic dipole moment: } M_\alpha = \frac{1}{2c} \int (r \times J)_\alpha d^3r, \quad (26)$$

$$\text{Toroidal dipole moment: } T_\alpha = \frac{1}{10c} \int [(r \cdot J)r_\alpha - 2r^2 J_\alpha] d^3r, \quad (27)$$

Electric quadrupole moment:

$$Q_{\alpha\beta} = \frac{1}{i2\omega} \int \left[r_{\alpha} J_{\beta} + r_{\beta} J_{\alpha} - \frac{2}{3} (r \cdot J) \delta_{\alpha\beta} \right] d^3r, \quad (28)$$

Magnetic quadrupole moment:

$$M_{\alpha\beta} = \frac{1}{3c} \int [(r \times J)_{\alpha} r_{\beta} + (r \times J)_{\beta} r_{\alpha}] d^3r, \quad (29)$$

where c is the speed of light, J is the induced current density, and $\alpha, \beta = x, y$ and z .

Figure 4.4. The scattering power of the major multipoles evaluated from the induced current densities of a unit cell in Fano (dotted lines) and iFano (solid lines) configurations for an asymmetry parameter of 0.289. The magnetic dipole and electric quadrupole contributions are negligible and therefore not shown.

In both configurations, the analysis reveals that the appearance of the broad resonance for paired symmetric double bars can be attributed to an electric dipole which oscillates in phase with incident electromagnetic waves. As the length of the short bar starts to decrease, the symmetry of the nanostructures is broken, resulting in the excitation of the Fano resonance.

In the asymmetric case, crucial higher-order contributions come from the toroidal dipole and magnetic quadrupole alongside the fundamental electric dipole as illustrated in Figure 4.4 (magnetic dipole and electric quadrupole contributions by comparison are negligible). In general, the electric dipole is highly radiative and couples easily with the driving field. Although the electric dipole plays a determinative role in the appearance of the Fano resonance, the higher-order contributions of the toroidal dipole and the magnetic quadrupole cannot be neglected. As the asymmetry between the double bars is introduced in both configurations, there is an increase in their contributions, and together they interact with the electric dipole to form an asymmetric Fano resonance. The consequence is the narrowing of the linewidth of the resonance wavelength and a higher Q -factor obtained as compared to the symmetric system.

4.6 Competition between magnetic quadrupole and toroidal dipole

Figure 4.5. Evaluating the multipoles in Fano and iFano configurations. (a) The sum of the scattering powers of the major multipoles evaluated from the induced current densities of a unit cell in the metamaterial and (b) The difference between scattering powers of the magnetic quadrupole and the toroidal dipole, is evaluated at the resonance wavelength (reflectance dip), as functions of asymmetry parameter for the Fano and iFano configurations.

A closer look at the total contributions of the scattering power by the multipoles at resonance reveals that the sum of the scattering power due to the electric dipole, magnetic quadrupole and toroidal dipole in the Fano configuration is greater than in the iFano configuration, as shown in Figure 4.5(a). This accounts for the higher Q -factor observed for the iFano

configuration as compared to the Fano configuration. To understand the individual roles of the toroidal dipole and magnetic quadrupole, we evaluated the difference between their scattering powers and found that for all values of the asymmetry parameters, there is a larger difference in the iFano configuration as compared to the Fano configuration. In both configurations, as shown in Figure 4.5(b), below an asymmetry parameter of $\alpha = 0.35$, the difference between the scattering powers of the toroidal dipole and magnetic quadrupole starts to diverge. This corresponds to the point at which the Q -factor in Figure 4.3(b) increases more rapidly with decreasing asymmetry parameter in the iFano configuration as compared to the Fano-configuration. This indicates that the response of the magnetic quadrupole dominates the toroidal dipole in the iFano configuration. In the Fano configuration, the toroidal dipole slowly suppresses the response of the magnetic quadrupole and the difference starts to reduce. As a result, we can conclude that with regards to the linewidth narrowing of the Fano resonance, the magnetic quadrupole plays a significant role in the resonant line narrowing while the toroidal dipole competes with the magnetic quadrupole to broaden the resonance in complementary paired ADBs system. With the iFano configuration, we can increase the dominance of the magnetic quadrupole and narrow the linewidth to improve the Q -factor. Moreover, by simply inverting one ADB in the paired ADB unit cell, it is possible to blue-shift the near-infrared resonance by as much as 200 nm ($\sim 12.5\%$), providing for facile spectral tuning without a change of structural dimensions.

4.7 Conclusion

In conclusion, multipolar decomposition provides an informative and broadly applicable approach to the analysis of resonant modes in complementary plasmonic metamaterial structures. For the complementary paired ADB metamaterial arrays presented in this work, such analysis demonstrates that the optical response of the nanostructures is mainly due to interactions between the electric dipole, magnetic quadrupole and the toroidal dipole. The

plasmonic systems in ‘Fano’ and ‘iFano’ configurations (‘i’ denoting the geometric inversion of part of the unit cell) are similar but for an iFano configuration, the contribution of the magnetic quadrupole is enhanced relative to the toroidal dipole, which results in the linewidth narrowing of the Fano resonance. The achievable Q -factor in the iFano configuration is enhanced by as much as 1.5 times compared to the Fano-configuration. Aside from enhancing the Q -factor, it is notable here that the inverted configuration also provides a mechanism to widen the tunability in the infrared spectral range without a need to change the shape or dimensions of the metamaterial unit cell - a behaviour that may be of particular use in optical and bio-sensing applications.

5 ULTRAFAST PHOTOSWITCHING IN THZ FANO RESONANT METASURFACE

5.1 Introduction

As compared to three-dimensional metamaterial structures, planar metasurfaces are constructed in two-dimensional plane and offer an easy access to the manipulation of electromagnetic waves as only two parameters (in x- and y- axis) have to be considered during the fabrication of metamaterial structures. In this regard, plasmonic split ring resonators (SRRs) have been extensively studied as basic meta-atom building blocks for metamaterials, across the wide-band spectrum from microwave to optical frequencies, because they have the ability to interact with both the electric and/or magnetic field of incident electromagnetic waves.¹ Indeed, in the terahertz regime most of all they offer a means to supplement the extremely limited range of naturally occurring terahertz materials.¹⁴⁸⁻¹⁵¹ By breaking the symmetry of SRRs, the non-radiative mode of the plasmonic system can be excited and this manifests itself as a Fano resonance.^{25, 28, 53, 138} Such resonances can exhibit high quality factors and strong electric field confinement suitable for various applications such as lasing spasers,⁸⁷ bio-sensors,^{73, 120} and slow-light devices.¹⁵²

The high sensitivity of Fano resonances to changes in the resonators' local (electromagnetic near-field) environment also favours their utilization in switchable and reconfigurable metamaterial devices.¹⁵³ Dynamic modulation of the local environment is often achieved by hybridizing the plasmonic structure with a dielectric medium such as a semiconductor,^{91, 154-163} chalcogenide or other phase-change media¹⁶⁴⁻¹⁶⁷ with relative permittivities that can be reversibly manipulated via external stimuli such as heat,¹⁶⁶⁻¹⁶⁹ light^{90, 91, 154-162, 165} or voltage

bias.^{93, 163} In terms of practicality and technological relevance, semiconductors (in which free carriers may be excited optically) are highly desirable, particularly in regard to integration with current microelectronic and optoelectronic device technology platforms.

Silicon^{91, 154-157} and gallium arsenide¹⁵⁸⁻¹⁶³ have been exploited in a variety of photonic metamaterial device structures, but germanium (Ge) as an indirect band gap semiconductor also holds considerable potential – it has a fundamental energy band gap (0.66 eV) which lies 0.14 eV below the direct band gap, and a large intrinsic carrier concentration, and high carrier mobility, as compared to silicon. To fully exploit the rich optical properties of Ge, several schemes to lower the indirect band gap have been introduced which include combining with other materials,^{170, 171} doping¹⁷² and strain engineering.¹⁷³ Strain engineering in particular can promote the formation of a population inversion and increase inter-band radiative recombination at the lowered indirect band gap, making Ge also a suitable candidate as an optical gain medium.¹⁷⁴ The integration of Ge into Si-based material platforms has enabled a wide range of mid-IR photonic devices such as low-loss waveguides and modulators.¹⁷⁵ For example, a GeSi-waveguide-based modulator operating at ultralow energy consumption was demonstrated with 0.2% of tensile strain.¹⁷⁶ An electrically pumped laser has also been realized via tensile straining of n-doped Ge such that direct recombination of electrons and holes occurs for lasing emission.¹⁷⁷ Ge also has the added advantage of complementary metal-oxide-semiconductor (CMOS) compatibility in microelectronics.¹⁷⁸ Even in ultrathin films, Ge presents a high absorption coefficient, which has seen it employed in photonic devices such as solar cells¹⁷⁹ and photodetectors.^{180, 181} The ultrafast carrier dynamics of crystalline Ge are particularly interesting, with recent studies employing ultra-broadband mid-infrared spectroscopy¹⁸² and ultrafast transient absorption spectroscopy¹⁸³ to probe the fast relaxation of photoexcited carriers. However, to our knowledge, Ge has not previously been engaged for ultrafast switching in planar photonic metadevices.

In previous design of switchable devices, ultrafast photoswitching of inductive-capacitive (LC) resonances in metamaterials has been achieved in ErAs/GaAs superlattices.^{158, 161} Superlattice structures possess periodic structures of two or more materials with large variation in their band gaps but similar lattice constants. In such structures, lattice matching is crucial for short carrier lifetimes. *In addition, the fabrication of a superlattice requires alternating between two or more materials, which can be complicated as many growth factors have to be taken into consideration. In previous demonstrations of photoswitching using GaAs¹⁶² and other semiconductors (Si on Sapphire),¹⁸⁴ the recombination time of the carriers is >1 ns (around three orders of magnitude slower as compared to the present study).* Here, we demonstrate and explore the dynamic response of thin film amorphous Ge as an active medium for ultrafast photo-induced switching of metamaterial resonances. In our device architecture, Ge is simply evaporated as single layer over the Fano-resonant metamaterial array. Unlike in superlattices, trap-assisted recombination sites due to structural defects in the non-crystalline Ge help to boost ultrafast carrier recombination. The fabrication is simple and cost-effective as it involves deposition of a thin film single element semiconductor material with no requirement for lattice matching. Such devices can function as ultrafast modulator or active filters. Our work could also pave and illustrate a path towards the realization of a variety of *flexible* electronic and photonic devices based on Ge.

In our study, a thin film of Ge is thermally evaporated onto the terahertz asymmetric split ring resonators (TASRs), which are fabricated on an ultrathin flexible Kapton film. An optical pump beam excites free carriers in the Ge and shunts the capacitive gaps of the SRRs, thereby changing the THz transmission of the array. A sub-picosecond decay constant (~670 fs) is observed, which we attribute to the presence of structural defects in the non-crystalline Ge acting as trap-assisted recombination sites. The metaphotonic device structure provides ultrafast optically-induced modulation of THz transmission amplitude by up to ~90%.

5.2 Methods

Figure 5.1. Optical images and transmission spectra of aluminium TASRs before and after deposition of germanium. Optical microscopy images of aluminium TASRs fabricated on a Kapton film (a) before and (b) after thermal evaporation of a 310 nm thick Ge coating. (c,d) Corresponding single unit cell images with the polarization of incident THz wave employed in characterization measurements illustrated in the former and the design dimensions of the TASR annotated in the latter. (e) Measured THz frequency transmission spectra for the aluminium TASR arrays with and without the Ge coating.

A planar array of TASRs was fabricated using standard photolithography techniques on a 25 μm thick Kapton film substrate: A positive photoresist of thickness 1.5 μm was spin-coated onto the surface of the Kapton film and soft-baked at 105°C, making it photosensitive. It was exposed to high intensity UV light through a mask defining the TASR pattern (an array size of 1 cm $\times$ 1 cm, with unit cell size $p_{x,y} = 75 \mu\text{m}$) and exposed regions were then dissolved in a developer solution, uncovering the underlying Kapton (but leaving it otherwise unaffected). A 200 nm layer of aluminium was then thermally evaporated onto the patterned substrate. The patterned photoresist layer (with its coating of aluminium) was then lifted off in an acetone solution, thereby leaving the desired aluminium TASR metamaterial array on

the Kapton substrate, as shown in Figure 5.1(a). A 310 nm thick film of Ge was subsequently thermally evaporated onto the planar TASR array (Figure 5.1(b)). The dimensions of the TASR are annotated in Figure 5.1(d): the side length s and linewidth w are 60 μm and 6 μm respectively; the capacitive gap size g is 3 μm – one of the gaps being at the midpoint of the top edge of the split ring, the other being on the bottom edge but offset by a distance $x = 15$ μm from the midpoint. The two arms of the split ring thus have different lengths, and we quantify the asymmetry of the design as the percentage ratio of the difference between ‘left’ and ‘right’ arm lengths (l_L and l_R) to the total length of both arms: $\alpha = \frac{|l_L - l_R|}{|l_L + l_R|} \times 100\%$. In experiments, incident THz radiation is polarized in the y -direction, parallel to the non-gap sides of the TASRs (as indicated in Figure 5.1(c)), to excite the resonators’ Fano resonance. As shown in Figure 5.1(e), the evaporation of Ge onto the Fano resonators red-shifts the Fano and dipole resonances. This is attributed to the increase in the relative permittivity of the local environment of the Fano resonators (i.e., the change from air to Ge).

5.3 Dynamic response of Ge on Kapton film

Figure 5.2. Schematic illustration of the flexible aluminium TASR/germanium metaphotonic device configuration for the OPTP spectroscopy: the planar TASR array was excited at oblique incidence by optical pump pulses and probed by THz pulses at normal incidence.

As a control sample to the Ge-coated terahertz metaphotonic device, we first characterized the dynamic response of thermally evaporated Ge thin film on Kapton in the absence of aluminium TASRs with a ZnTe crystal-based optical-pump/THz-probe (OPTP) spectrometer. The output beam from an amplified Ti:sapphire laser producing optical pulses with an energy of 4 mJ and width of ~100 fs, at a centre wavelength of 800 nm (photon energy 1.55 eV) and a repetition rate of 1 kHz, is divided at a beam splitter; the transmitted beam pumps a ZnTe crystal for THz generation and detection of THz radiation with which the transmission of the sample is measured at normal incidence, while the reflected beam is used to optically excite the sample at oblique incidence, as illustrated in Figure 5.2. The diameters of the spatially overlapping THz and optical beam spots on the sample are

respectively ~ 3 mm and ~ 10 mm, ensuring homogenous optical excitation of Ge over the area probed by the THz beam. The relative time delay between the terahertz and optical pulses was controlled by a delay stage. Fast Fourier transformation (FFT) of time-domain THz waveforms recovers frequency-domain THz spectra. Normalized transmission is then obtained as $T(\omega) = \frac{E_s(\omega)}{E_K(\omega)}$ where $E_s(\omega)$ and $E_K(\omega)$ are the measured THz spectra of the sample and of the bare Kapton substrate respectively; ω being the angular frequency.

Figure 5.3. Negative differential transmission $-\frac{\Delta T}{T_0}$ measured at the peak of the THz time-domain pulse signal as a function of optical-pump THz-probe pulse delay for a 310 nm thick thermally evaporated Ge film on Kapton at a selection of average optical pump powers [as labelled]. Experimentally measured data points are fitted with mono-exponential decay profiles convolved with the instrument response function; plots are vertically offset from each other for clarity [in all cases $-\frac{\Delta T}{T_0}$ is zero at delay times < 0 ps and returns to zero within < 15 ps after excitation].

Figure 5.3 shows the negative differential transmission $-\frac{\Delta T}{T_0}$ of Ge – the induced relative change in THz transmission (where $\Delta T = T - T_0$ is the absolute transmission change, T being the transmission of THz wave through the sample at a given moment and T_0 is that of the sample in the absence of optical excitation.) - as a function of the pump-probe time delay for a selection of average optical pump power levels. The magnitude of the induced change is maximized at a delay of 3 ps and increases linearly with pump power from 0.0314 at 200 mW (0.254 mJ/cm²) to 0.1329 at 1200 mW (1.524 mJ/cm²).

The dependence of $-\frac{\Delta T}{T_0}$ on pump power is consistent with the semiconductor to quasi-metal transition of Ge when subjected to optical excitation, which gives rise to an increase in photoconductive free carriers density. The relative change in the transmission exhibits a characteristic exponential decay: mono-exponential decay profiles convolved with the instrument response function are fitted to the experimentally measured data points in Figure 5.3, using the following equation:¹⁸⁵

$$-\frac{\Delta T}{T}(t) = e^{-\left(\frac{t-t_0}{IRF/2 \ln 2}\right)^2} \times \left(A_0 + A_1 e^{-\frac{t-t_0}{\tau_1}}\right) \quad (30)$$

where IRF is the full-width at half maximum of the instrument response function, A_0 is a constant, and A_1 is the amplitude determining the weight of the exponential function, t_0 corresponds to time zero of the exponential fit and τ_1 is the decay time constant, values of which are found to increase as a function of pump power as given in Table 1, from 450 fs at 200 mW to 700 fs at 1200 mW. As photoexcited carriers relax from the conduction to the valence band, defect states present within the band act as trap-assisted recombination sites and become overpopulated by the large number of carriers relaxing. As a result, the number of available trap-assisted recombination sites decreases, leading to the increase in decay time with pump power.¹⁸⁶ In the present case, the largest modulation of differential transmission,

with a decay time of ≈ 700 fs, is attained at the maximum available pump power of 1200 mW.

Pump power (mW)	200	600	1200
τ_1 (fs)	450 ± 2	520 ± 1	700 ± 2

Table. 1 Exponential decay time constants for the optically-induced change in THz transmission of thermally evaporated Ge at a selection of pump power levels derived from mono-exponential fittings (Eq. 1) to the dependences of negative differential transmission on pump-probe pulse delay shown in Figure 5.3.

5.4 Relaxation dynamics of Ge-functionalized metaphotonic device

We subsequently investigated the response and relaxation dynamics of the Ge-functionalized TASR metamaterial array. In comparison to the Ge thin film alone, the maximum induced change in THz transmission of the Ge functionalized metamaterial array occurs at a slightly longer time delay of 4.7 ps, due to the increase in the optical path length caused by the 200 nm thickness of the aluminium metal resonator array. The magnitude of the light-induced transient change in THz transmission is enhanced in the metaphotonic device by around 70% relative to Ge on Kapton ($-\frac{\Delta T}{T_0}$ reaches a peak value of 0.2268 at 1200 mW in the TASR metaphotonic structure as compared to 0.1329 for Ge in isolation). In keeping with the properties of Ge alone, the differential transmission of the metaphotonic device retains sub-picosecond decay time constants (670 ± 2 fs at 1200 mW, as illustrated in Figure 5.4).

Figure 5.4. Ultrafast response and relaxation dynamics of an aluminium TASR/germanium metaphotonic device. Negative differential transmission $-\frac{\Delta T}{T_0}$ at the peak of THz time-domain pulse signal as a function of optical-pump THz-probe pulse delay for an array of TASRs [on Kapton] coated with 310 nm of thermally evaporated Ge at an average pump powers of 1200 mW. Experimentally measured data points are with a mono-exponential decay fitting as per equation 30.

5.5 Active optical switching in transmission

Figure 5.5. Optical switching of Fano and dipole resonance. (a) Measured THz frequency transmission spectra of the Ge-coated metaphotonic device at various time delays (as labelled) between optical pump and THz probe pulses. (b) Color map showing THz transmission amplitude against frequency and pump-probe time delay over the entire ultrafast on–off photoswitching cycle. (The resolution of time delay is ≈ 160 fs, calculated from the step size ($25\ \mu\text{m}$) of the optical delay stage in the pump–probe path.)

The temporal evolution of the THz transmission spectra in the metaphotonic device under the influence of the optical pump is shown in Figure 5.5(a). The time delay given in Figure 5.5(a) represents the relative time delay in the arrival of the pump (optical beam) and the terahertz probe at the sample position, which is controlled using the pump-probe delay stage. For instance, a time delay of 4.7 ps implies that the terahertz pulse arrives 4.7 ps after the arrival of the pump beam (800 nm) at the sample surface. For each given time delay, the terahertz probe pulse is scanned subsequently through the sample and the substrate, which is converted into the frequency-domain using FFT. Between time delays of -2.5 ps to 4.7 ps, as the pump pulse impinges on the sample, a large density of the carriers is photoexcited to the conduction band. At 4.7 ps, a sharp spike in the magnitude of the differential transmission occurs, which indicates the maximum density of photoexcited carriers in the conduction band. Photoexcitation of carriers into the conduction band short-circuits the capacitive gaps of the asymmetric split-ring resonators, resulting in the synchronous suppression of the Fano and dipole resonances, and thereby strong modulation of transmission. As depicted in Figure 5.5(b), the temporal evolution of the Fano resonance recovers more slowly than the dipole resonance. Unlike the dipole resonance, which is less susceptible to changes in its local environment, the Fano resonance is still moderately modulated by the presence of carriers at a time delay of 7.3 ps. After this, relaxation of the carriers restores the original spectral response completely within ~17 ps.

5.6 Validation of experimental results

Figure 5.6. Spectral dispersion of THz transmission for the Ge-coated TASR metaphotonic device at a selection of average optical pump power levels [as labelled], at a fixed pump-probe time delay setting of ~ 4.7 ps for which the transient optically-induced change in THz transmission is maximized [as shown in Figure 5.4]. (b) Corresponding numerically simulated spectra, whereby photoexcitation of Ge at increasing optical power levels is represented by increasing levels of conductivity. Normalized resonance amplitude evaluated from the transmission spectra of (c) experimental and (d) simulation results (the inset shows the evaluation of resonance amplitude).

Figure 5.6(a) shows the spectral dispersion of transmission at a pulse delay time of 4.7 ps: With increasing optical pump power, the TASR Fano resonance (characterized by a transmission dip at 0.75 THz and peak at 0.86 THz) is increasingly suppressed as the density of free carriers photoexcited into the conduction band increases. The trend towards saturation is clear, with the resonance being almost completely eliminated at an average pump power

of 1200 mW. The normalized resonance amplitude (inset to Figure 5.6(d); defined as the difference between transmission levels at the THz peak and the THz dip of the Fano resonance, relative to the magnitude of this difference in the absence of optical excitation) is reduced at this point by ~90% as shown in Figure 5.6(c).

This modulation of Ge-functionalized TASR metamaterial transmission resonance is elegantly reproduced in numerical simulations performed using the CST Microwave Studio package combined with a frequency-domain solver based on the finite-differential time-domain (FDTD) methods. In this model, the Kapton film and Ge are ascribed fixed real relative permittivities of 2.97 and 16, respectively and aluminium is modelled with a Drude conductivity of $\sigma = 3.56 \times 10^7 \text{ S/m}$; “Unit cell” boundary conditions were imposed in the x - and y - directions (i.e. in the sample plane); and incident plane wave THz radiation was taken to propagate in the z -direction with the electric field polarised in the y -direction as indicated in Figure 5.1(c).

Figure 5.7. Extracted photoconductivity values of THz transmission through 310 nm of Ge thin-film on bare Kapton substrate as a function of frequency at a selection of average optical pump powers.

The photoexcitation of Ge was modelled as an increase in its DC-conductivity, as shown in Figure 5.6(b), from 0 S/m (corresponding to zero optical pump intensity) to 9000 S/m - a level at which the change in resonant THz transmission saturates, i.e. resonance amplitude falls to zero (indeed, the broad dipolar resonance upon which the TASR Fano resonance sits is also effectively suppressed at this conductivity level). To model the increase in the photoconductivity of the Ge with increasing pump powers, numerically fitted conductivity values were used in the simulation model (shown in Figure 5.7), and it correlates very well with the experimentally measured transmission amplitude, as shown in Figure 5.6(b). As the conductivity values increase from 0 S/m to 9000 S/m, the transmission amplitude of the Fano and dipole resonance is diminished. Due to the photoconductive nature of the Ge thin film overlayer on the entire metamaterial array, there is a strong synchronous modulation of both Fano and dipole resonances in the experimental results.

Figure 5.8. Simulated electric field distributions for the Ge-coated Al TASR Fano and dipole resonant modes for Ge conductivity values of 0 S m^{-1} and 2000 S m^{-1} , corresponding respectively to 0 mW and 600 mW optical pump power levels. Before and after optical excitation. Without and with pump excitation, the maximum electric field strength in the

TASR gaps for the Fano mode is 12.03×10^6 and 4.039×10^6 V m⁻¹ respectively; for the dipole mode the corresponding values are 5.032×10^6 and 2.77×10^6 V m⁻¹.

As shown in Figure 5.8, there is strong confinement of electric field in the capacitive split gaps of the asymmetric resonators associated with the Fano resonance mode. When the conductivity of Ge is increased from 0 S m⁻¹ to 2000 S m⁻¹, representing an optical pump power of 600 mW (0.762 mJ cm⁻²), there is a large reduction in field confinement within the split gaps and the Fano resonance is effectively switched-off. Small disparities between the zero-optical-pump experimental spectrum and the zero-conductivity simulated spectrum are attributed to manufacturing imperfections in the Al TASR array and defects in the Ge film, which are not accounted for in the numerical model.

5.7 Conclusion

In summary, we have demonstrated the ultrafast photo-switching and THz transmission modulation characteristics of a metamaterial device comprising an aluminium asymmetric split ring array hybridized with a thin Ge film as an active medium. Resonant THz transmission is optically modulated on the picosecond time scale, with a sub-picosecond decay constant that is attributed to defects present in the amorphous Ge, which act as trap-assisted recombination sites for the relaxation of photoexcited free carriers. The operational (resonant) frequency of the device may be tuned by metamaterial design across a broad infrared to terahertz spectral range for a variety of applications in ultrafast microelectronic and optoelectronic devices, and the device being fabricated on a Kapton film provides an added advantage of flexibility.

6 CONCLUSION AND FUTURE WORK

6.1 Conclusion

Fano resonant plasmonic metamaterials is an intense field in physics that have garnered huge research interests. As a prelude to the thesis, chapters 1 and 2 have introduced the origination and also showed the combined strengths of metamaterials and Fano resonance in developing metadevices that have far exceeded our expectations in science and technology. The metadevices are available to be fabricated and characterized using state-of-the-art research facilities and equipment, as explicitly introduced in chapter 3.

The evolution of materials from macroscopic to microscopic, and to nanoscopic scale has changed the perspectives view of the world that humans lived in. It is possible to grasp a nanoscale device in your hand which may seem so insignificant, and yet could pack the same amount of data as a device that are a million times larger. Not to mention, the performance and efficiency of the nanoscale device can even be on par. To design scalable metadvice, chapter 4 investigates Fano resonators of various sizes across the electromagnetic spectrum, ranging from THz to infrared frequencies. To this end, we have devised a calibration plot and model that is based on an exponentially decay behaviour of Q -factor which is critical to achieve practical metadevices.

As we continue to innovate and invent beyond imagination, it is also desirable to achieve high performance or high quality (Q) factor metadvice. Therefore, chapter 5 demonstrated an inverted unit cell configuration that is able to enhance the Q -factor of Fano resonance by as much as 1.5 times compared to the non-inverted unit cell configuration. The enhancement of Q -factor comes from the linewidth narrowing of Fano resonance. This observation was

supported by numerical calculations using multipole expansion of the electromagnetic field which attributed it to the changes in relative magnitude of magnetic quadrupole and toroidal dipole contributions.

In chapter 5, as proof of concept, an ultrafast optical switching metaphotonic device was realised using Fano resonant metasurfaces (split ring resonator) that were thermally evaporated with germanium. Trap-assisted recombination sites in evaporated germanium film expedited the decay process of photoexcited carriers and a sub-picosecond decay constant of 670 fs is obtained. Furthermore, Fano resonance is optically switched on and off, with a full recovery time of 17 ps. This validates the use of germanium (or other optical medium) integrated metaphotonic device to achieve ultrafast photoswitching capability.

In summary, our studies have shown the scalability and applicability of Fano resonant metasurface to designing of a prototype THz photoswitching device. We hope our work can facilitate further development of other Fano resonance-based devices in the wide frequencies range from THz to infrared. Without a doubt, we envisage that the scattering phenomenon of Fano resonance has great prospects and could be the cutting edge of modern technologies and devices.

6.2 Future work

6.2.1 All-dielectrics metasurfaces

The subject matter of this work has been on the development and implementation of Fano resonance in plasmonic metamaterials. With Fano resonance as a non-radiative mode, radiative losses in metamaterial system are significantly mitigated. However, at higher frequencies in the ultraviolet to optical visible regime, the presence of non-radiative losses dominates radiative losses.

Lately, it has been trending to replace plasmonic metals with all-dielectrics as they are low-loss and have a high refractive index which are the solution to overcome ohmic losses and heating.⁵⁸ All-dielectrics nanostructures offer robustness in the Fano resonance frequency as they are not sensitive to geometrical imperfections.¹³⁴ Furthermore, it has been shown that all-dielectrics are now able to cover all four quadrants of the permeability and permittivity plot (in Figure 1.1), hence promising wide applicability.⁵

6.2.2 Dealing with two-dimensional (2D) materials

Ever since the inception of graphene as a 2D material, along came another variation of 2D materials which is called transition metal dichalcogenide (TMD). 2D TMD earned its name due to a layer of transition metal atom being sandwiched between two layers of chalcogen atoms. 2D TMDs have an advantage over graphene because they have a direct band gap which is composed of two (or more) unequal electronic valleys in the spin-orbit split valence and conduction bands.^{187, 188} The enticing physical properties of TMDs include being thin, flexible and transparent to THz wave.¹⁸⁹ Compared to traditional semiconductors (such as silicon or germanium), 2D TMDs can be scaled down in accordance with the microelectronics or optoelectronics devices, and perform better as it does not encounter heat dissipation due to reduction in size.¹⁹⁰

6.2.2.1 Continuous wave (CW) - pumped THz optical modulator

Recently, molybdenum disulphide (MoS_2) has been employed in active terahertz optical modulator with demonstrations using a hybrid system of monolayer (ML) MoS_2 on germanium¹⁹¹ or silicon^{192, 193} substrate and metamaterials stacked with multilayer MoS_2 films on silicon.¹⁹⁴ However, these optical modulators are designed on semiconductor substrates which does not justify the effective enhancement by MoS_2 . A sapphire¹⁹⁴ substrate was introduced due to its zero contribution to conductivity, but ML MoS_2 showed negligible modulation. As a result, multi-layered MoS_2 was employed to demonstrate enhanced

modulation. Bulk MoS₂ combined with THz ASSRs on quartz substrate was also considered for its involvement in ultrafast optical switching and modulation.⁹²

Until now, there is no clear demonstration of ML MoS₂ for THz optical modulation. In addition, continuous wave laser pumping of ML MoS₂ is more preferred for practical applications and metamaterials could still be employed to enhance the modulation efficiency. As mentioned in the Ge-based metaphotonic device, Fano resonance is more sensitive than the dipole resonance due to the presence of a strong local field and narrow linewidth. Since the intense field of the Fano resonance is confined at the small spatial volume of the capacitive split gaps, it is easily perturbed by changes in its local environment and we observed a strong modulation of the Fano resonance. This is different from the case of MoS₂-Si heterostructure metasurface¹⁹³, whereby the strong resonance frequency is not modulated. Fano resonance is desirable for observing strong modulation and the modulation effect due to ML MoS₂ can be observed more clearly without using the catalytic effect support by silicon. Therefore, a *ML MoS₂ on Fano metasurface based THz optical modulator* is promising for future studies.

6.2.2.2 Valley-based optoelectronics

Due to broken inversion symmetry, strong spin-orbit coupling of electrons in ML MoS₂ splits the valence band into two unequal electronic valleys K and K' in the Brillouin zone. As a result, these two different valleys are able to distinctively interact with either right or left circularly polarized light and show opposite helicities.¹⁹⁵ A growing interests have been generated on the manipulation of (TMDs) valleys of opposite spin via electrical¹⁹⁶ or optical pumping below 90 K.^{195, 197} Their valleys can be selectively chosen to be populated with valley electrons to be exploited for data storage and information processing. It was shown that the valley-polarized photoluminescence of ML MoS₂ can be optically modified by introducing a super chiral near-field.¹⁹⁸

For metamaterials, the size, shape or arrangement of a unit cell has an effect on the optical properties of the metamaterials. Therefore, by introducing or varying the structural shape (e.g. asymmetry) of chiral metasurfaces, we can effectively change the field enhancement around the chiral metasurfaces. The tuning of the field enhancement will allow control of the population states of the electrons, hence achieving a *controllable ML MoS₂ based spintronics device*. These findings could possibly benefit data communication where more information can be controlled or processed faster and efficiently.

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