Perovskites for ultrafast active terahertz photonics

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**[PEROVSKITES FOR ULTRAFAST ACTIVE TERAHERTZ
PHOTONICS]**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

[2020]

[PEROVSKITES FOR ULTRAFAST ACTIVE TERAHERTZ PHOTONICS]

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2020

Statement of Originality

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Authorship Attribution Statement

The thesis contains material from 3 papers published in the following peer-reviewed journal where the author's contributions are listed below:

Chapter 3 is published as Manu Manjappa, Ankur Solanki, **Abhishek Kumar**, Tze Chien Sum, and Ranjan Singh, "Solution-Processed Lead Iodide for Ultrafast All-Optical Switching of Terahertz Photonic Devices," *Advanced Materials*, vol. 31, no. 32, p. 1901455, 2019, doi: 10.1002/adma.201901455.

The contributions of the authors are following:

- Manukumara Manjappa and I performed the experiments and done the terahertz characterization.
- Manukumara Manjappa and I fabricated the metamaterial samples.
- Ankur Solanki has done the perovskite thin film fabrication, characterization and deposition on metamaterial samples.
- Prof Ranjan Singh and Prof Tze Chien Sum supervised the whole project and edited the manuscript drafts.

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The author's contributions are following:

- Abhishek Kumar, Ankur Solanki, Prof Ranjan Singh and Prof Tze Chien Sum conceived the idea.
- Abhishek Kumar designed the experiments and performed all the terahertz measurements and theoretical analysis.
- Yogesh and Abhishek fabricated the metamaterial samples.
- Ankur Solanki prepared all the perovskite thin films and performed the characterization
- Sankaran Ramesh performed the transient PL measurement.
- Abhishek, Manu and Piyush performed the analysis in THz measurements.
- Prof Ranjan Singh and Prof Tze Chien Sum supervised the overall work.
- Abhishek wrote the manuscript drafts and all other co-authors provided their feedback to improve it.

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The author’s contributions are mentioned below:

- Abhishek Kumar Prof Ranjan Singh conceived the idea.
- Abhishek Kumar performed the THz measurements and performed the analysis with the help of Manukumara Manjappa.
- Anish Priyadarshi, Sudhanshu Shukla and Lew Jia Haur prepared the perovskite samples and done the characterization of film quality.
- Prof Ranjan Singh and Prof Subodh G. Mhaisalkar supervised the overall project.
- Abhishek Kumar wrote the manuscript with the inputs from all other co-authors.

23-11-2020

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Abstract

In the electromagnetic spectrum terahertz (THz) frequency that lies between conventional electronics and photonics is vital due to its uniqueness and high potential for many disruptive applications such as security, high-resolution imaging, ultrasensitive sensors and high-speed wireless communication for the sixth generation (6G). THz waves hold the potential to boost the key performance of many existing technologies thus, the emergence of THz photonics is inevitable. Hence, it is of paramount importance to develop the technology that provides unprecedented control on terahertz waves. The difficulties to control the properties of THz waves using natural existing materials led to the development of artificial composite materials known as metamaterial (MM).

Metamaterial (MM) offers a simple and effective platform to develop the terahertz technologies owing to its scalable and on demand optical property that could be tuned. Active control of metamaterial response enables realization of THz functional devices. More importantly, the ability to control THz waves at ultrafast time scale is extremely crucial for developing next generation high-speed wireless communication. Integrating dynamic material such as semiconductors with MM offers a possible solution. However, for commercial large-scale deployment a cost-effective high performing functional solution is desired for advance manipulation of THz waves in emerging THz technologies.

This thesis aims to address these questions and provides a possible route to develop cost effective, easily integrable and high performing ultrafast THz photonic devices by integrating solution processed perovskite with metallic THz

metamaterial (MM) structures. In the development of ultrafast active THz devices, the natural progression is to introduce multifunctionalities in active metamaterial for advance manipulation of THz waves. In this context, strong interaction of perovskite thin film with confined THz electric field offers a viable route to tune the carrier dynamics which is key to the foundation for next generation multifunctional active metamaterials.

In this thesis, solution processed perovskite has been explored to develop ultrafast THz photonics device. Fano resonant metamaterial structures owing to strong THz electric field confinement were employed to integrate with perovskites. The high photoconductivity and ultrafast free carrier dynamics in perovskite thin film enabled near unity modulation of THz electric field at ultrafast timescale. The existence of self-assembled quantum well (QW) in 2D perovskite provides an additional channel for the photoexcited free carrier to relax at ultrafast time scales (~ 20 ps) which is fastest in the family of solution processed semiconductors. We demonstrated 2D perovskite integrated hybrid metadvice at rigid as well as flexible platform that showed modulation of THz waves at ~ 50 GHz modulation speed.

In the future prospect of the thesis we provide an outlook to achieve wavelength dependent response of active THz metadvice through integration of perovskites with silicon. The large band gap tunability, ease of integration and ultrafast carrier dynamics of perovskite opens a new paradigm to develop multifunctional ultrafast active THz photonic devices for advance manipulation of THz waves.

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Chapter 1	13
Introduction: Theory and Overview	13
1. 1 Why terahertz frequencies are important: A motivation behind closing the “ <i>terahertz gap</i> ”	14
1.2 A brief history of THz technologies.....	16
1.3 Metamaterial	19
1.4 Metamaterial: A perfect platform for THz	28
1.5 Research gap in active THz photonics and motivation of the thesis.....	29
1.6 Fano resonance in terahertz metamaterials.....	30
1.7 Dynamic metamaterial in THz frequency	34
1.9 Why Perovskite for THz applications?	38
1.10 Scope of the thesis.....	39
1.11 References.....	42
Chapter 2	46
Simulation, Characterization technique and Fabrication.....	46
2.1 Electromagnetic Simulation of terahertz metamaterial	46
2.2 Terahertz time domain spectroscopy (THz-TDS).....	55
2.3 Optical Pump Terahertz Probe spectroscopy (OPTP).....	66
2.4 Sample fabrication	68
2.5 References.....	70
Chapter 3	73
Solution-processed Lead iodide for Ultrafast Terahertz Photonic devices.....	73
3.1 Introduction.....	73
3.2 Terahertz time resolved spectroscopy (TRTS) of PbI ₂ thin film	76
3.3 PbI ₂ integrated hybrid metadvice	78
3.4 Effect of thickness on ultrafast dynamics.....	88
3.5 References.....	91
Chapter 4	93
Excitons in 2D perovskites for ultrafast terahertz photonic devices	93
4.1 Introduction.....	93
4.2 Structural and optical characterization of 2D perovskite thin film.....	96

4.3 Integration of 2D perovskite with metamaterial	106
4.4 Active flexible metadvice	114
4.5 References.....	119
Chapter 5	122
Ultrafast THz photo physics of solvent engineered triple-cation halide perovskite	122
5.1 Introduction.....	122
5.2 Why mixed cation perovskite?.....	123
5.3 Optical pump terahertz probe (OPTP) of mixed cation/anion perovskite.....	123
5.4 References.....	130
Chapter 6	133
Conclusion and Future direction	133
6.1 Future works	135
6.2 References.....	139
Appendix A	140

Chapter 1

Introduction: Theory and Overview

The remarkable properties of electromagnetic waves have led the development of many disruptive technologies and changed the life in an unimaginable way. This has always motivated to develop a platform that provides unprecedented control on the electromagnetic waves. In the EM spectrum, “terahertz (THz)” which lies between the electronics and photonics realm was largely unexplored due to the lack of the natural material that responds to the THz region. At lower frequencies (less than a few hundred of GHz), the motion of free electrons characterizes the EM devices, and generally known as *electronics*. The output power of EM waves decreases with increasing the frequencies as a consequence of mainly following factors: (i) carriers saturation velocity, that typically falls in the range of 10^5 m/s (ii) maximum electric field supported by the device before breakdown. These majorly limits the source power to sub-milliwatt level for 300 GHz and few microns level for frequencies near to 1 THz^[1]. While on the other hand, the *photonics* realm of EM spectrum that spans optical and ultra-violet wavelength region shows a decrease in output power with a decrease in frequencies. The main reason behind this is the lack of natural materials that satisfy the bandgap requirement for photonic sources. In contrast, the terahertz electric field oscillations are too fast for conventional high-speed *electronics* devices to respond and at the same time their energy is too low to provide efficient *photonics* devices. This has hindered the technological advancement in terahertz technologies for

efficient generation, detection, manipulation and control of terahertz waves thus known as “*terahertz gap*”, as shown in Figure 1.1.

Figure 1.1: Electromagnetic spectrum highlighting the spectral region of “Terahertz (THz) band”.

1. 1 Why terahertz frequencies are important: A motivation behind closing the “*terahertz gap*”

Despite of suffering from the technological gap the terahertz frequency region has attracted considerable attention owing to its diverse range of disruptive applications ranging from high-resolution imaging, spectroscopy, sensing to high-speed wireless communications^[1-4] which bring the researcher from both the electronics and photonics world to come together to bridge the technological gap for terahertz region.

The initial thrust for THz research was started in the field of astronomy and space research. This is because, most of the abundant molecules found in comets, stellar and planets are carbon monoxide and oxygen, and these have unique spectral fingerprints that fall in THz frequency

region^[5]. Slowly, THz spectroscopy became an important tool for material characterization owing to its noninvasive and low photon energy (~ 4.1 meV) nature. THz time-domain spectroscopy (THz-TDS) has been intensively employed to unravel the carrier dynamics of many important materials like 2D materials (graphene, WSe₂, MoS₂), high-temperature superconductor and semiconductors (GaAs, perovskites, Ge and many more)^[6-8]. The ability to capture directly both the amplitude and phase at individual frequencies in THz-TDS without employing Kramers-Kronig relation allows to extract the frequency dependent complex optical constants of materials.

As THz waves can penetrate most dielectric and non-polar liquids thus it is very useful for applications like security screening, food and pharmaceutical quality control monitoring, and medical diagnosis^[1, 9]. Its harmless interaction with human tissue owing to low photon energy (in the range of meV) has allowed the use of THz waves for a wide range of applications such as skin cancer detection, bio and drug detection.

In recent years information and communication technology (ICT) has been seen to be benefited by terahertz technology due to the availability of huge spectral bandwidth that offers high-speed wireless communication, high volume data processing, and satellite communication^[3, 10]. THz frequency has been envisioned as the next frontier for high-speed wireless communication for beyond 5G communication: 6G communication^[11, 12]. With the current implementation of 5G networks underway, the pursuit for 6G wireless communication has already begun. 6G wireless communication is expected to provide *terabit per second (Tbps)* data rates, which will lead to novel applications such as a fully connected cyber-physical world (internet of everything), wireless data centers, massively multicore processors, and will foster the Industry 4.0 revolution. Carrier waves operating at THz frequencies are vital for achieving the desired data rates of 6G

communication due to huge spectral bandwidth. Figure 1.2 showcase the potential applications of THz waves that span from spectroscopy to ICT, medical, defense, and security sectors. Thus, it is imperative to develop the technology that will bridge the gap between electronics and photonics i.e. THz-gap.

Figure 1.2: An overview of disruptive applications of THz waves ranging from wireless communication, imaging, sensing to material characterization.

1.2 A brief history of THz technologies

The research to develop the terahertz sources and detector started in early 1960. However, it experienced the first boost when a powerful terahertz source was developed using HCN laser^[13]. Roughly at the same time, the advent of ultrashort pulsed laser accelerated the generation and detection of terahertz waves using a photoconductive antenna (PCA) and nonlinear crystals like ZnTe^[14, 15]. The generation of terahertz waves using nonlinear crystal via optical rectification

started in 1970's. Later between 1975-82 the generation of terahertz was demonstrated using Auston switch. It was the combination of ultrashort pulsed laser and electrooptic sampling which opened up a new spectroscopic modality, *terahertz time domain spectroscopy* (THz-TDS) in 1989^[16].

The success of semiconductor-based laser in the visible and near-infrared frequency region has always motivated the researcher to develop similar technology for THz frequencies. However, the lack of appropriate interband materials pushed the researcher to develop an artificially engineered material that could generate THz waves. The pursuit of developing efficient

THz sources led to the first demonstration of quantum cascade laser (QC) in 1988^[17, 18]. This was one of the remarkable discoveries that boosted THz research activities. Since then significant research has been done in the development of QC lasers. Currently, the QC laser has a broad frequency range of operation that can emit THz waves from 0.8-5 THz^[19]. However, one of the major problems with QC laser was its inability to operate at room temperature. That prevented the QC lasers from finding the place directly into the commercial applications. But owing to its high resolution spectral and high output power many investigations even in recent time going to improve the functionality. For example, the recent work in 2012 has shown the operation of QC laser at 200 K^[20]. Very recently the topological Valley Hall crystal-based THz QC has been demonstrated where the topologically protected Valley Hall cavity has been utilized which is more robust and immune from back scattering^[21]. Despite of not being operating at room temperature, the future of QC laser is healthy. It is still a high power ($> 1\text{W}$)^[22] THz source that serves many applications such as high-resolution imaging^[23-25].

The potential of terahertz waves for wireless communication was first demonstrated by Gebbie in 1970. It was the lack of appropriate source, detector, and modulators that halted the application of terahertz waves for wireless communication. However, looking at the current trend of data consumption, particularly in the wireless domain, there is a huge demand to develop a wireless system that could support tens to hundreds of *gigabits per second*. To accommodate this demands the obvious route is to increase the carrier frequency towards a higher node. The current 5G communication is using up to 100 GHz as a carrier frequency. But 5G is not an ultimate solution to communicate the gigantic volume of data at a near-instant time scale. Thus, for the next generation wireless communication: i.e. 6G communication, the terahertz wave is inevitable. Hence, foreseeing the bright future of terahertz-based communication, global intense research effort has been started in recent few years. Researchers have taken photonics-based route to demonstrate the high-speed terahertz wireless communication^[3, 10, 26]. In this approach uni traveling carrier photodiode (UTC-PD) is employed as a THz source. The added advantage with the photonics-based approach is that a mature developed modulation technology can be used to implement an advanced modulation scheme for the THz wireless communication. To showcase the potential of THz waves for high-speed wireless communication a photonics-based THz wireless system with an operating frequency 120 GHz has been successfully demonstrated data transmission of 4K video streaming at a distance of 100 m^[27, 28]. Also, the recent development in semiconductor IC technologies allowed to develop the low cost, miniaturized terahertz system that brings the terahertz technologies one step closer towards consumer operation^[29, 30]. In this direction, the electronics-based source like resonant tunneling diode (RTD) is viable that can emit terahertz waves with output power up to 1 mW. The development of RTD has opened up a new avenue for portable terahertz sources that could easily integrate

with existing silicon-based technologies. In summary, the journey of terahertz technologies is witnessing rapid development that is inspired and accelerated by its disruptive applications. These technological advancements will bridge the gap between *electronics* and *photonics* which is known as “*terahertz gap*”

1.3 Metamaterial

Metamaterial, an artificially engineered structure with exotic and tunable materials properties has emerged as a new frontier of science involving physics, chemistry engineering, and material science. The advent of metamaterials has opened a new paradigm for controlling electromagnetic waves. Just after the first experimental demonstration of metamaterials, the scientific community quickly realized that the potential of metamaterials is unprecedented.

In general, the property of bulk material is essentially derived from its chemical elements. People have always intended to control and tune the optical properties of materials. For instance, slight doping of silicon enhances the conductivity by an order of magnitudes that led to the foundation of the whole semiconductor industry. Similarly, the recent nanoscience and technology have always targeted to better understand the material properties starting from the atom to the molecule level. All these efforts have been put to enhance the applications using materials.

In this context, metamaterial emerged as a new frontier for technologies. It offered an entirely new route to further enhance the capability to design the material properties at will. As compared to natural existing materials, the physical and optical properties of metamaterials are not primarily dependent on chemical compositions rather it derives its properties from the geometry of meta-atoms.

1.3.1 A brief history of metamaterial

The root of “artificial materials or metamaterials” can be found in 1898 when Jagadish Chandra Bose showed the polarization of microwaves using the twisted jute^[31]. Then after a decade in 1914, Lindman showed an “artificial chiral materials”^[32]. The concept of negative refractive index came after a long pause.

It was Veselago’s seminal work that again created the noise about metamaterials. In his seminal work, he showed the theoretical overview of left-handed materials (LHM). LHM is characterized as a material having simultaneous negative value of permittivity (ϵ) and permeability (μ). He showed a systematic analysis of the behavior of electromagnetic waves in LHM, that predicted exotic features like backward Cerenkov radiation and reversed Doppler shift^[33].

Despite of having theoretical framework for LHM, the works of Veselago and others went unnoticed for almost 30 years due to the lack of experimental evidence. It was Sir John Pendry, who demonstrated negative permittivity (ϵ) and permeability (μ). The demonstration of negative permittivity came in 1996 using a thin wire medium, followed by the demonstration of negative permeability in 1999 by using the well-known split ring resonator (SRR) as magnetic element^[34, 35]. Using both the concepts of negative ϵ and μ , in 2000 Smith et al. experimentally showed the first negative refractive index artificial material^[36].

Since then, the research in metamaterial has seen an unprecedented rise. Many exotic phenomena have been shown such as negative refractive^[37-40], super-lensing^[41-43], cloaking^[44, 45], perfect absorbers^[46, 47] and transformation materials^[48, 49]. However, all these pioneering works are based on passive metamaterials. Although, passive metamaterials have provided a route to engineer the optical properties of materials on demand, but their dynamic tunability is missing. For many

potential applications the dynamic control on the material properties is desirable that has given the birth of “*active metamaterial*”.

In the quest of developing active metamaterial, the first work came in 2006, where Padilla et al.^[50] demonstrated dynamic control of electric response of SRR through photoexcitation of free carriers in the substrate. Followed by this Chen et al.^[51] showed electrical control of terahertz metamaterials using electric biasing. Since then, the field of active metamaterials has seen rapid growth and expanded the horizon of metamaterials applications. In active metamaterial most of the work includes the dynamic control by means of optical, electrical, thermal and mechanical^[8, 50-52]. Each has their own advantages and limitations. For the development of ultrafast devices, the optical control is viable as it provides fast tunability.

1.3.2 Overview of metamaterial

In general, the isotropic materials are characterized by their effective permittivity (ϵ) and permeability (μ), where ϵ contains the properties corresponds to electric field while μ corresponds to magnetic field. The ϵ and μ of most of the natural materials are defined with reference to free space as: $\epsilon_r = \epsilon/\epsilon_0$ and $\mu_r = \mu/\mu_0$, where ϵ_r and μ_r are the relative permittivity and permeability of material respectively, ϵ_0 and μ_0 are the free space permittivity and permeability respectively. The refractive index of material can be written as: $n = \sqrt{\epsilon_r \mu_r}$. Figure 1.5 shows the classification of isotropic materials based on their ϵ and μ in the $\epsilon - \mu$ space. The first quadrant characterizes as positive ϵ and μ . Most of the natural existing dielectric materials fall in this region. They are also called as right-handed material (RHM). According to Maxwell's equation the electric field $\mathbf{E}$, the magnetic field $\mathbf{H}$, and the propagation direction $\mathbf{k}$ form right-handed triplet as shown in Figure 1.5. The second quadrant characterizes as negative permittivity

($\epsilon < 0$) and positive permeability ($\mu > 0$). Most of the plasmonic materials such as gold (Au), silver (Ag) in visible and ultra-violet frequencies fall in this region. The materials fall in this region support evanescent decay fields. The third quadrant which characterizes as $\epsilon < 0$ and $\mu < 0$ is known as left-handed material (LHM) that supports many exotic phenomena such as negative refractive index, backward propagating waves, and many more. No known natural materials fall in this quadrant. The artificially engineered materials by selectively designing the permittivity and permeability to negative value lie in this quadrant. For this quadrant, the triplet **E-H-k** follow left-hand rule. The fourth quadrant ($\epsilon > 0$ and $\mu < 0$) is known as magnetic plasma, which supports evanescent waves. Only few ferromagnetic materials at sub-GHz frequencies fall in this region.

Figure 1.3: Material parameters space characterized by permittivity (ϵ) and permeability (μ).

After looking at the classifications of materials based on their ϵ and μ , we talk about a new form of material: *metamaterial*. A metamaterial (MM) is an artificially designed material that attains its properties from its sub-wavelength sized unit structure rather than its constituent materials. The sub-wavelength sized unit cell is called as “*meta-atoms*”. The meta-atoms of MM are typically arranged in the periodic fashion on dielectric substrate. As depicted in Figure 1, the periodicity of meta-atoms is much smaller than the wavelength of the incident light, thus allowing the incoming light to see the MM system as an effective homogeneous medium. The total electromagnetic response from the MM system is considered as collective response of the constituent unit cells. Thus, by tuning the geometrical parameters of the unit cell, the EM response of MM can be tuned. This remarkable feature of MM allowed to realize many exotic electromagnetic phenomena such as negative refractive index and inverse Doppler shift.

The EM response of MM is characterized by effective permittivity and permeability which is derived from the homogenization of the sub-wavelength structures by averaging the local fields^[53, 54]. At the early days, negative-refractive index material or LHM used to be considered as metamaterials as predicted by Vesalago in 1968^[33]. In contrast, the material falls in the third quadrant of Figure 1.5 used to be considered as metamaterial. But nowadays, the term metamaterial is used not only to address the LHM rather it has a much broader scope than LHM. In a more general way, any artificial EM materials that derive its optical properties like ϵ and μ from the constituent periodic inclusions are referred as metamaterial. Thus, for the classification shown in Figure 1.5, today metamaterials denote any artificial effective medium that can belong in any of the second, third and fourth quadrant.

Figure 1.4 Periodic arrangement of metamaterial (MM) array illustrating the periodicity (p) is much less than the wavelength of incident EM waves. Inset shows the unit cell of MM, where l is the side length, w is the width and g are the width of gap.

Next, we talk about the two most common types of unit cells that comprise metamaterials and allow to demonstrate negative ϵ and μ . These are magnetic split ring resonator (mSRR) and electric split ring resonator (eSRR). By changing the geometrical parameters of these unit cells, the range of operating frequency can be tuned.

Magnetic Split-Ring Resonator (mSRR)

The most popular unit cell design for metamaterial is the split ring resonator (SRR). The early demonstration of artificial magnetic material by Sir Pendry^[55] at microwave frequencies the design of “magnetic atom” was mSRR as shown in Figure 1.5. The mSRR constitutes from non-magnetic conducting sheets on a dielectric. The effective material response of mSRR are shown in Figure 1.5b, c that solely depends on the SRR geometry. To quantify the frequency dependent complex permeability its mathematical expression can be written as:

$$\mu_{eff} = 1 + \frac{F \omega^2}{\omega_0^2 - \omega^2 - i\gamma\omega} = \mu_{eff}^1 + i\mu_{eff}^2 \quad (1.1)$$

where, ω_0 is the resonant frequency, F and γ are geometrical and damping constants respectively. To quantify the resonance strength the quality factor (Q) is defined as $Q = \frac{\omega_0}{\gamma}$ where γ characterizes the bandwidth of the resonance. From equation 1, it is clear that at high Q of the resonator near the vicinity of ω_0 the real part of μ_{eff} will be negative. To get more intuitive picture, we consider mSRR as inductor-capacitor (LC) resonator, where the inductance (L) arises from the circulating current in the periphery of mSRR and capacitance (C) comes from the dielectric gap of the split ring. The resonance frequency of the SRR can be given as $\omega_0 = \sqrt{1/LC}$. When a time varying magnetic field polarized perpendicular to the plane of mSRR is incident (Figure 1.5a), it induces a circulating current that causes accumulation of charges with opposite polarity at the split gap. This induces strong field confinement across the split gap as shown in Figure 1.5e. Below the resonant frequency, ω_0 , the currents in the loop are in phase with the incident field that results in a positive response that also manifests as positive permeability (μ). But at the proximity of resonant frequency, ω_0 , the currents in the loop lag thus results as negative response that manifests as negative value of permeability (μ).

Figure 1.5 Split ring resonator (SRR) (a) Array of SRR with periodicity is much less than ($a \sim \lambda_0/10$) the wavelength of incident EM wave. (b) Reflection (red solid line) and transmission (black solid line) spectra from the SRR (c) The extracted and simulated magnetic response of the SRR (d) Surface current distribution at resonant frequency (e and f) Simulated electric and magnetic field distributions at resonant frequency.

Electrical Split Ring Resonator (eSRR)

Figure 1.6 shows the most common eSRR. The frequency dependent permittivity of natural occurring material can be written using Drude-Lorentz relation:

$$\epsilon_{eff} = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 - i\gamma\omega} \quad (1.2)$$

where, ω_p is the plasma frequency given by

$$\omega_p^2 = \frac{4\pi n e^2}{m^*} \quad (1.3)$$

here, n is the carrier density, e is the electronic charge, γ is damping factor and m^* is the effective mass of electrons. In the case of artificial EM materials, the n and m^* are related to geometrical parameters thus provides great flexibility to tune the ϵ_{eff} as compared to natural materials. The schematic of electric SRR is shown in Figure 1.6a. One of the major advantages of this structure is that the plane EM wave can be incident normal to the planar SRR with electric field polarized perpendicular to the split gap as shown in Figure 1.6a. Similar to magnetic response the effective permittivity of eSRR can be given as:

$$\epsilon_{eff} = \epsilon_{inf} + \frac{F \omega^2}{\omega_0^2 - \omega^2 - i\gamma\omega} = \epsilon_{eff}^1 + i\epsilon_{eff}^2 \quad (1.4)$$

where, ϵ_{inf} is the frequency independent dielectric constant, F is geometrical factor, ω_0 is resonance frequency. Similar to μ at the vicinity of resonance frequency, the real part of ϵ will result in a negative value. Figure 1.6b, c and d show the simulated surface current, electric field and magnetic field confinement in eSRR at the resonant frequency.

Figure 1.6 Electric SRR (eSRR) (a) Array of electrically coupled LC resonators. The EM waves is incident normal to the surface of the eSRR. (b, c) Simulated electric and magnetic distribution at resonant frequency (d) Surface current distribution at resonance frequency (e) The extracted and simulated electric response of eSRR.

1.4 Metamaterial: A perfect platform for THz

So far, we have seen that, metamaterials can provide a flexible and versatile approach to tune the optical properties by changing the geometrical parameters of unit cell. One of the major advantages of MM structure is its scalability whereby changing the size of unit cell the response of MM can be tuned from microwave to optical frequency. For THz frequencies (0.1 - 2 THz or 150 - 3000 μm), the length scale required to achieve resonance response is on the order of microns (~ 10 -100 μm). The size of these features allows to successfully use the conventional micro photolithography technique resulting in low cost and highly efficient means of production.

As discussed in the previous section, the SRR structure near the vicinity of resonance frequency may lead to negative permittivity and permeability. In the THz frequency where most of the natural existing materials do not show proper response, the MM offers to control both the electric and magnetic response of THz waves. More importantly, these artificial materials offer the benefits to dynamically control the material response as well as spectral selectivity. Both of these are paramount important for the development of THz based applications like communication, sensing, and high-resolution imaging.

1.5 Research gap in active THz photonics and motivation of the thesis

THz frequency has just started witnessing rapid development. Still, many efforts are going to develop cost and power effective THz sources and detectors. In parallel to this it is also paramount important to develop the technologies for advanced manipulation of THz waves such as spectral selectivity, polarization filter, reconfigurable beam steering, and spatial-temporal control. To develop these functionalities MM is a perfect platform owing to its structural simplicity and on-demand optical properties tunability. In the context of active THz device, the integration of active materials like semiconductors, phase change materials and superconductors have shown a promising future. However, to bring this into the practical applications many parameters such as cost, ease of integration, performance efficiency, and tunability need to be carefully addressed. The research of active THz photonics is still in its early stage. In the timeline of the development of active THz photonics the very next step is to develop cost effective, ease of integrable and high functional THz devices. *And the natural progression in the development of active metadvice is to achieve multifunctionalities without changing the structures passively.* Also, tuning the operational frequency of active metadvice is missing.

Most active metamaterial operates in the narrowband frequency region owing to the resonant properties of MM. Thus, it is paramount important to develop spectral tunability along with temporal control. The works in this thesis address the prospect to develop cost-efficient and high-performance ultrafast THz metadvice. The results presented in the thesis will led the path for the development of ultrafast THz photonic devices on rigid as well as flexible platform. In addition to this, the prospect of tuning the carrier dynamics of perovskite thin film by interacting with a strongly confined THz electric field is presented. This is important to develop the multifunctional active THz metadvice as it allows to tailor the MM properties in the temporal domain. Further, as a future outlook, we presented the device architect to realize wavelength-dependent active THz metadvice. For this particular study, the halide perovskite is an ideal candidate owing to its tunable bandgap and absorption coefficient which allows using the various optical pump with different wavelengths. In the thesis, we utilized the Fano resonant metamaterial to demonstrate for the demonstration of ultrafast THz switching.

1.6 Fano resonance in terahertz metamaterials

The flexibility of tuning the EM response of metamaterial (MM) by changing the geometrical parameters of meta-atoms has provided unprecedented control on EM wave manipulation. As a result of this many exotic phenomena like super lens, invisible cloaking, transformation optics and novel biosensors have been demonstrated^[43, 45, 46]. In addition to this, at the same time MM structures have shown to emulate number of basic optical phenomena such as electromagnetically induced transparency (EIT) ^[56, 57] and slow light^[58]. One of the interesting and application rich optical phenomena emulated by MM structure is Fano resonance. In the context of photonics, the origin of the appearance of Fano resonance is related to the constructive

and destructive interference of narrow discrete resonance with a broad linewidth resonance that serves as a continuum. To put into a perspective, the spectrum overlap of broad and narrow resonance leads to the Fano resonance. However, the concept of Fano resonance was first introduced in quantum physics to explain the asymmetrically line shape of ionization spectral line^[59]. Since the wave interference is not specific to the quantum world, many classical systems have been identified to exhibit Fano resonance. The emergence of Fano resonance is not only restricted to the photonics rather many other areas of physics such as atomic and solid-state physics have also witnessed the existence of Fano resonance^[60]. Various solid-state systems for example 2D electronic waveguide, Aharonov-Bohm (AB) have shown Fano resonance^[61]. The uniqueness of Fano resonance is that it manifests as asymmetry spectral shape in transmission or absorption spectra that mathematically can be explained by the following expression:

$$T(E) = \frac{1}{1 + q^2} \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \quad (1.5)$$

where ε is the reduced energy equal to $(E - E_0)/\Gamma$, E_0 and Γ are energy and width of resonance respectively, q is the coupling strength which also quantifies the degree of asymmetry of spectra. For example, $q \sim \pm \infty$ characterizes the Lorentzian line shape while $q = \pm 1$ refers to maximum asymmetry in spectra. Fano resonance is important as it offers a diverse range of potential applications such as highly sensitive sensors, low-threshold lasers, enhanced Raman scattering, and nonlinear effects, thus it is useful to understand the physics behind the emergence of Fano resonance. In the classical mechanics framework, Fano resonance can be explained by using a coupled harmonic oscillator. The equation of motion for the damped coupled oscillators shown in Figure 1.7a can be written as:

$$\frac{d^2x_1}{dt^2} + \gamma_1 \frac{dx_1}{dt} + \omega_1^2 x_1 + g x_2 = f_1 e^{i\omega t} \quad (1.6)$$

$$\frac{d^2x_2}{dt^2} + \gamma_2 \frac{dx_2}{dt} + \omega_2^2 x_2 + g x_1 = 0 \quad (1.7)$$

where γ_1 and γ_2 are the damping constants for first and second oscillators respectively, g is the coupling constant. The steady solutions of these equations are

$$x_1 = c_1 e^{i\omega t} ; x_2 = c_2 e^{i\omega t}$$

where, the complex amplitudes are given by:

$$c_1(\omega) = \frac{(\omega_2^2 - \omega^2 + i\gamma_2\omega)f_1}{(\omega_1^2 - \omega^2 + i\gamma_1\omega)(\omega_2^2 - \omega^2 + i\gamma_2\omega) - g^2} \quad (1.8)$$

$$c_2(\omega) = \frac{g f_1}{(\omega_1^2 - \omega^2 + i\gamma_1\omega)(\omega_2^2 - \omega^2 + i\gamma_2\omega) - g^2} \quad (1.9)$$

The amplitude of c_1 and c_2 are plotted in Figure 1.7 band d, where the position of resonance corresponds to the real part of complex eigenmodes of equations 2 and 3. For frictionless second oscillator i.e. $\gamma_2 = 0$ it is clear from Equation 4 that $c_1 = 0$ at $\omega = \omega_2$. This condition leads to the sudden change in phase for the first oscillator at $\omega = \omega_2$ as can be seen in Figure 1.7c. From the phase plots of both the oscillators (Figure 1.7 c and e) it is clear that the first oscillator is out of phase with the second oscillator at $\omega = \omega_2$ which leads to the destructive interference. Here in this system, the first oscillator can be consider as broad continuum as it is driven by continuous external force while the second oscillator can be consider as discrete mode thus at the frequency $\omega = \omega_2$ the interference leads to the asymmetric spectra which is known as Fano resonance.

Schematic of coupled damped oscillators with a driving force f_1 applied to one of them.

Figure 1.7 Classical picture of Fano resonance in coupled oscillator system (a) Artistic sketch of the two coupled damped oscillators where one of them is driven by external force f_1 . (b and d) Amplitude of the first and second coupled oscillator respectively (e and f) Phase acquired by the first and second oscillators in the coupled system respectively^[62].

In the context of MM structure, the emergence of Fano resonance in MM structure allows high-density electric field confinement. This is useful for studying light-matter interactions for example plasmon-phonon coupling and enhancing the nonlinear effect. In addition to this, the high sensitivity of Fano resonance towards external perturbations make it an ideal candidate for ultra-sensitive sensors.

For THz frequencies, the planar MM structures that support Fano resonance are vital for the development of THz-based imaging, sensors, and communication systems. Many 2D materials have spectral signature of phonon modes in THz region, thus the interaction of such 2D materials with highly confined THz electric field would be interesting in unraveling the dynamics of photon-phonon quasi particles.

In the scope of this thesis, we have taken the advantage of Fano resonance in planar THz metamaterial to demonstrate ultrafast THz photonic devices. Fano resonance has been used as a

tool to quantify the ultrafast features of THz photonic devices. The unique asymmetric spectral shape is the signature of Fano resonance. In MM there are multiple ways to achieve the Fano resonance. Following the first demonstration of Fano resonance in the asymmetric split ring arrays in microwave frequency^[56], there have been many demonstrations based on breaking the structural symmetry of split-ring resonator. The detailed discussion on the excitation of Fano resonance in planar THz split-ring resonators is given in chapter 3.

1.7 Dynamic metamaterial in THz frequency

To add the active functionality in MM, the inclusion of dynamic materials with MM offers a promising route. In this section, we present the potential of solution-processed perovskite as dynamic material for ultrafast THz photonic devices.

1.7.1 Solution-processed semiconductor an effective route for ultrafast THz devices

1.7.1a An overview of Halide perovskite vs conventional semiconductor

In modern days nanophotonics as well as optoelectronics and photovoltaics, the conventional semiconductors like silicon (Si), gallium arsenide (GaAs) and germanium (Ge) have shown remarkable performance. They have laid the foundation for many disruptive applications. In recent years, a new family of semiconductors named as “*halide perovskites*” have emerged and shown promising potentials for many applications ranging from optoelectronics, photovoltaics to nanophotonics due to their unique electronic and optical properties (Figure 1.8). As compared to

conventional semiconductor perovskite shows inverted band structure^[63] as shown in Figure 1.7. That means in comparison to conventional semiconductors for example GaAs, the valence and conduction band of perovskite shows opposite orbital characteristics. For example, the conduction band of GaAs has *s* orbital character, whereas the valence band has *p* orbital character. While on other hand, the valence band of perovskite has *s* orbital character whereas the conduction band has *p* orbital character. This is because the valence band of perovskite is mainly comprised with lead's (Pb) *s* and X (i.e. halide) *p* anti bonding character whereas the conduction band is composed of Pb *p* bands as shown in Figure. The advantage of having *p* orbital character in the conduction band is having high density of states in the lower conduction band owing to less dispersive nature of *p* orbital. Thus, halide perovskites have a stronger interband transition dipole moment that yields a high absorption coefficient and high quantum efficiency.

In addition to unique electronic band structure, the reversible bandgap tunability, supporting stable excitons at room temperature, morphology engineering, and large scale ease of fabrication at low cost, these are the added remarkable properties of perovskites that makes them important and alternative promising options of materials for next-generation optoelectronics, photovoltaics, nanophotonics, and ultrafast photonic devices. Below we briefly discuss the promising potential of perovskite in various applications.

Figure 1.7 Band structure comparison of conventional semiconductor with halide perovskite (a) Artistic sketch of the band structures of silicon (Si) and gallium arsenide (GaAs) (b) Sketch of band structure of halide perovskite illustrating broadband and reverse tuning of bandgap via changing anions. Dashed parabolic curve shows the existence of excitons in perovskite at room temperature.

1.7.1b Photovoltaics:

In photovoltaic application silicon-based solar cells are well established at the commercial level and used as sustainable energy sources. At wafer-scale both the polycrystalline and monocrystalline silicon-based solar cells show remarkable ambience stability, heat resistivity and good photoconversion efficiency. However, the major disadvantage of this silicon-based solar device is poor absorbance owing to the indirect bandgap of silicon. To boost the absorption requires an increase in active layer that increases the cost and puts a constraint in creating flexible thin-film photovoltaic devices. On other hand, GaAs offer high absorption coefficient due to their direct bandgap, better carrier lifetime and mobility, and low nonradiative energy losses. But its high cost of production puts a major constraint for large-scale translation thus not a feasible option at commercial scale.

In contrast, the halide perovskites offer optical properties close to GaAs i.e. high absorption coefficient, and excellent electronic properties such as high electron mobility and photoconversion efficiency ($> 20\%$)^[64] that is favorable for thin-film photovoltaics application. In addition to this, the major advantage offer by perovskite is its low production cost without involving complex manufacturing processes. The wet chemistry and roll-to-roll techniques make it possible to create cheap, flexible, and effective photovoltaics devices.

1.7.1c Lasers and LEDs:

Perovskites have shown excellent performance as light emitting devices (LEDs). Perovskite-based LEDs have shown the efficiencies higher than 20%^[64-66] owing to their direct bandgap, strong excitons, high defect tolerance, and excellent color tunability features.

Also, the perovskite lasers based on microdisks, nanowires, and nano grating have shown low-lasing thresholds, high defect stability, and spectral tunability^[67]. In contrast, the pure silicon and GaAs require additional doping or integration with quantum wells to perform as laser. However, we should acknowledge that silicon and GaAs based sources widely used in telecom wavelengths, where no compositions of halide perovskites are yet available.

1.7.1d Nonlinear optics:

In recent years there are many reports that shows the excellent nonlinear properties of halide perovskites^[68, 69]. Among the various perovskite family, the lead-free perovskites such as CsGeI₃ and MAgGeI₃ have shown giant second harmonic generation with χ^2 value exceeding 150 pm V⁻¹, which is comparable to GaAs and far better than silicon^[70]. Also, third-harmonic generation with third order susceptibilities χ^3 exceeding 10⁻¹⁷ m² V⁻² has shown in perovskites^[70, 71].

1.7.1e Integrated photonics:

Due to bandgap tunability and high refractive index, perovskite can be a potential option to develop integrated photonics devices. The bandgap tunability offers unprecedented opportunities for the reconfigurable photonic devices which is not possible with conventional semiconductors like Si and GaAs. In addition, the ease of fabrication and process of perovskite-based nanowire, nano-disks, nano grating, and metasurfaces offer a cheap and convenient route for futuristic nano circuitry. However, we want to stress that the perovskite cannot overrule the existing developed and advanced silicon-based platform for on-chip integrated photonics rather it offers an additional alternative option for futuristic photonic devices owing to its excellent and tunable optical properties.

1.9 Why Perovskite for THz applications?

In the quest for the development of ultrafast THz photonic devices, the active metamaterial is vital. More particular, the dynamic material based active metamaterials have shown unprecedented performance. For the candidate of dynamic materials, many semiconductor options are available such silicon (Si), germanium (Ge) and gallium arsenide (GaAs). Among all these conventional semiconductors each has their own advantage and disadvantages such as Si-based active metamaterial can be CMOS compatible but require complex fabrication processes. Ge based active metamaterials are ultrafast in nature but require high pump fluence to switch ON and OFF the resonance^[72]. Similarly, GaAs based active metadvice is good for ultrafast low pump switching but requires complex fabrication process. In addition to these liquid crystals^[73], superconductor^[8], graphene^[74], VO₂^[75] and micro-electromechanical system (MEMS)^[76] also provides an effective route for realizing THz photonic devices.

On the other hand, halide perovskite presents itself as a potential candidate for ultrafast THz photonic devices owing to its excellent electronic and optical properties and ease of fabrication process and integration with metamaterials. This also allows to translate the perovskite based active metamaterials to realize at flexible platform too that opens up a new avenue for flexible THz photonic devices. Here we highlight a comparison between conventional semiconductors and halide perovskite in Table.

Table 1: Comparison of different dynamic material based active THz metadvice.

Materials	Speed	Stimuli	Modulation amplitude	Integrated with flexible platform
Silicon on sapphire (SOS) ^[77]	~ ms	200 $\mu\text{J}/\text{cm}^2$	100 %	No
GaAs (Gated) ^[51]	~ kHz	16 V	50 %	No
GaAs (photoexcitation) ^[50]	~ 1 ns	2 $\mu\text{J}/\text{cm}^2$	55 %	No
VO₂ ^[75]	50 ms	40.5 K	~ 10 %	No
Superconductor (YBCO) ^[8]	~ ps	100 $\mu\text{J}/\text{cm}^2$	70 %	No
MEMS ^[76]	30 kHz	16 V	56 %	No
Ge ^[72]	~ ps	~ 1500 $\mu\text{J}/\text{cm}^2$	90 %	Yes
Perovskite ^[78]	ps-ns	~ 10 $\mu\text{J}/\text{cm}^2$	100 %	Yes

1.10 Scope of the thesis

The area of photonics has seen rapid growth where significant efforts have been done in understanding the fundamental as well as technological counterpart of electromagnetic waves. In the electromagnetic spectrum, terahertz frequencies remained unnoticed till decades. However, the vision of many disruptive applications such as high-speed wireless communication, high-resolution imaging, sensing and spectroscopy has forced the researcher from both the world of

electronics as well as photonics to come together to elevate the field of terahertz research. Metamaterial has played a significant role in fueling the terahertz research. It offers a simple and efficient platform to potentially develop applications in the diverse field of technology such as sensing, high volume data processing, wireless communication, and light-matter interactions.

This thesis aims to develop solution-processed semiconductor-based ultrafast terahertz photonic devices. The control and manipulation of THz waves at ultrafast time scales is of great interest for the basic as well as from technological aspects. Numerous interesting phenomena such as altering the carrier dynamics due to strongly confined THz electric fields and quantum well assisted excitonic effects at room temperature are effectively probed and discussed in the scope of this thesis. The results presented in the thesis offer useful insight in light-matter interactions and opens up an exciting and efficient way to develop THz photonic devices. The focus of the thesis is not only to integrate dynamic material with metamaterials rather it also includes the investigation of the effect of strongly confined THz electric field on the carrier dynamics of the semiconductor. We for the first time unravel the dynamics of excitons in 2D perovskite using time-resolved THz spectroscopy.

So far in this chapter, the overview and technical concepts of the MMs have been briefly discussed. Further, a comprehensive comparison of solution-processed halide perovskite with conventional semiconductors is also presented.

In chapter 2 we presented the detail of numerical tools that have been utilized to characterize the optical properties of MM. Further, a detailed outlook of THz generation and detection for photoconductive antenna and ZnTe crystal-based THz systems is presented. It also includes a

brief description of optical pump terahertz probe (OPTP) spectroscopy as it has been intensively used in the latter part of the thesis.

Chapter 3 presents the ultrafast optical characterization of lead iodide (PbI_2) followed by its integration with terahertz Fano resonator metamaterial. This chapter discusses the all-optical ultrafast switching of the THz electric field. Further, at the end of this chapter PbI_2 thickness dependent carrier dynamics are presented and showed that thickness indeed an important parameter for dynamic materials-based active metadevices. And at the end, this chapter concludes with altering the carrier dynamics of PbI_2 thin film using the Purcell effect.

Chapter 4 includes the investigation of excitons as well as free carrier dynamics of 2D perovskites using OPTP spectroscopy. For the first time using time-resolved THz spectroscopy, we unravel the dynamics of excitons. Thanks to the quantum well structure of 2D perovskite that enables the formation of stable exciton at room temperature as well as provides an additional relaxation channel for the free electrons to relax back at ultrafast timescale. We leveraged the ultrafast properties of 2D perovskite to develop ultrafast THz photonic devices by integrating 2D perovskite with MM at rigid as well as a flexible platform.

The study presented in chapter 5 is important as it gives an insight on the carrier dynamics of perovskite thin-film fabricated using various method. The results revealed that the choice of solvent used in the fabrication of perovskite thin film is important as it affects the morphology as result carrier dynamics. Thus, to utilize the perovskite thin film for various optoelectronic applications these findings are vital.

Finally, in chapter 6, we presented the conclusion of each chapter and given a future outlook to develop a multifunctional active THz device for next-generation applications like high-speed wireless communication and THz interconnects.

1.11 References

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Chapter 2

Simulation, Characterization technique and Fabrication

This chapter overviews the basics of the numerical tool that has been extensively used to simulate the electromagnetic response of the metamaterial (MM). Section 2.1 describes the steps involved in modeling the metasurface using CST Microwave studio. To characterize the metamaterial resonance spectra, we used the latest version of CST 2019. Section 2.2 discusses the theoretical details of terahertz time domain spectroscopy (THz-TDS). The detailed discussion on Photoconductive antenna (PCA) and ZnTe crystal-based THz-TDS are given in sections 2.2a and 2.2b respectively. Section 2.3 sketches the theoretical and experimental outline of an optical pump and terahertz probe (OPTP), which is the heart of this thesis. Section 2.4 discusses the fabrication procedure, which is utilized for fabricating the metamaterial (MM) structures.

2.1 Electromagnetic Simulation of terahertz metamaterial

This section describes the principle and techniques involved in numerical simulation to characterize the electromagnetic response of metamaterial (MM) resonators. Numerical simulation provides an ideal platform to design, optimize and analyze the electromagnetic response of metamaterial structures. We used a commercially available software named Computer Simulation Technology Microwave studio (CST-MWS). It solves the integral form of Maxwell's equation using Finite Integral Technique (FIT) and Finite element method (FEM)

based on the selected solver. The Maxwell's equation in integral form in a medium of volume “V” containing charge density “ ρ ” and current density “ $\vec{J}$ ” can be written as:

$$\begin{aligned}
\oint_S \vec{D} \cdot d\vec{S} &= \int_V \rho dV \\
\oint_S \vec{B} \cdot d\vec{S} &= 0 \\
\oint_l \vec{E} \cdot d\vec{l} &= \int_S \left(-\frac{\partial \vec{B}}{\partial t} \cdot d\vec{S}\right) \\
\oint_l \vec{H} \cdot d\vec{l} &= \int_S \vec{J} \cdot d\vec{S}
\end{aligned} \tag{2.1}$$

where, $\vec{D}$, $\vec{E}$, $\vec{B}$ and $\vec{H}$ are the displacement current, electric field, magnetic field and magnetizing field, respectively.

One of the significant added advantages of using CST-MWS is its enrich CAD environment that allows designing the MM structure in a simple way. In addition to this, CST-MWS contains a wide range of materials library which includes frequency-dependent complex permittivity of many commonly used materials like silicon, quartz etc. It also provides the freedom to define a broad range of user-defined materials with frequency-dependent dispersion. The predefined model such as Drude and Lorentz can also be used by defining the appropriate parameters require like scattering rate, plasma frequency etc.

CST offers mainly two types of solvers to characterize the MM structures: these are *frequency domain solver* and *time domain solver*. Although, both give similar output results but the implementation of both is specific to the problems. The frequency-domain solver is more appropriate for the structures with the resonant response, while on the other hand, time domain

solver is suitable for large structures with the broadband spectral response. The S-parameters obtained from time domain solver depends on the Fourier transformation, thus when sharp resonance exists, the Fourier transformation in time domain solver will give inaccurate results. In my work to characterize MM resonators, we used *frequency domain solver*. To capture the resonant behaviour of system *frequency domain solver* is good at it solves the Maxwell's equation at each frequency for the given range while on the other hand to capture the broadband feature time domain solver is preferred. For resonant systems to capture the performance of systems near the resonant frequencies, the time duration in *time domain solver* needs to sufficiently long that costs high computational time. Hence, to characterize the MM structures, we opted the *frequency domain solver*. The details of the simulation flowchart are shown in Figure 2.1.

Figure 2.1: The illustration of different steps involve in the simulation using CST microwave studio.

2.1.1 Meshing in CST

In simulation meshing play an important role, it decides the accuracy and simulation speed. In CST different solver utilized different meshing elements, for e.g. the *frequency domain solver* uses tetrahedral mesh while *time domain solver* uses hexagonal mesh elements. The frequency domain solver calculates the solution for a single frequency at a time.

Figure 2.2: (a) Illustration of meshing in CST. First structures get divided into small grids with continuity at the interface. (b) Hexahedral mesh element. The optimization of Δx , Δy , and Δz is required to achieve better accuracy. (c) There exists a trade-off between accuracy and simulation time. (d) In the optimization process, to achieve better accuracy for broadband simulation, the minimum frequency in the given range of frequencies need to be mesh with minimum 10 mesh elements.

For each frequency sample, the linear equation system is solved either by iterative solver or sparse direct solver. The solution for each frequency consists of S-parameters, field distribution and derived parameters. In order to get the accurate results, the solver requires consistent meshing specially at the interface of the different medium as shown in Figure 2.2 in red and green color.

How meshing works: - To solve the Maxwell's equation numerically the entire geometry is divided into a small volume and to do so different solver uses different types of mesh element which is called "mesh cell". For example, *time domain solver* uses hexahedral mesh where the computational volume is discretized by using variable sized rectangular cuboids as shown in Figure 2.2b. While frequency domain solver utilizes tetrahedral mesh elements. In both the cases the in discretized form each mesh elements represents the small volume where electric and magnetic field are computed. Thus, more the number of mesh elements the more accurately field gradient will be captured but at the cost of high computational time. There exists a trade off between accuracy and computational time (Figure 2.2c). To optimize this the time step at which signal propagates into the computational domains need to be optimized. The time step of the signal depends on mesh element size according to Courant stability condition as:

$$\Delta t_{max} < \frac{1}{u_{max}} \left[\frac{1}{\Delta X^2} + \frac{1}{\Delta Y^2} + \frac{1}{\Delta Z^2} \right]^{-1/2} \quad (2.2)$$

where, u_{max} is the maximum phase velocity and ΔX , ΔY and ΔZ are the change in length of mesh cell in x, y and z-direction respectively. From Equation 2.2 it is clear that to maximize the time step the smallest mesh cell need to be large. While on the other hand, the largest mesh cell size is also an important parameter. The mesh size cannot be arbitrarily large as it will induce

numerical dispersion i.e. each frequency propagates with slightly different velocity in mesh cell. Thus, to minimize this dispersion and ensure uniform frequency response, the shortest wavelength of the sample must be spatially sampled by at least 10 mesh cell per wavelength as shown in Figure 2.2d. Hence, the size of the larger mesh size is constrained by the shorter wavelength (higher frequency).

To get the desire mesh consistency between multiple surfaces, CST combines the common surfaces or edges of multiple geometries to single as shown in Figure 2.3a. This process is called “non-manifold”. And then, mesh the edges and faces. Based on this surface meshing, the volume meshing is generated by combining different nodal points of faces (Figure 2.3b). once the initial volume mesh created, its quality improvement is the next step. In CST adaptive mesh refinement is a powerful tool to achieve good mesh quality. It ensures an accurate numerical solution. It runs the simulation for short time and improve the meshing from run to run. Before running the simulation, it is a good strategy to first start with coarse mesh and use adaptive mesh refinement tool to improve the meshing.

Figure 2.3: Mechanism of meshing in CST (a) Two different colored rectangle shows objects with different material properties. CST combines multiple geometries with common interface. It

is called non-manifold. In the next step the meshing of common edges or surfaces occur followed by volume meshing. **(b)** Illustrates the steps involve in the meshing as shown in (a).

After the adequate quality of meshing, CST shows the meshed structure in mesh view option. Here, to avoid the simulation artifact the we keep the number of cells per wavelength 10 as shown in Figure 2.4.

Figure 2.4: Schematic after mesh adaptation using tetrahedral mesh grids in frequency domain solver. The metallic part of the resonators is shown in yellow color and the thick substrate is shown in blue. For better accuracy of the simulation results we select 10 mesh cells per wavelength.

2.1.2 Boundary conditions

Unit cell and periodic boundary conditions are used to model an infinite array of unit cell in XY plane. The field at opposite periodic planes are related by the complex factor. In CST it is determined by the *phase shift*. Thus, the electric field at different point is given by:

$$E(x_0 + dx) = E(x_0) e^{i\phi_x}$$

$$E(y_0 + dy) = E(y_0) e^{i\phi_y}$$

where, ϕ_x and ϕ_y are the *phase shift* in x and y direction respectively. In the Z direction, the boundary condition is “open” as it is the propagation direction of light. In order to prevent the interference from the fringing field, the boundary condition for $Z_{\max}$ (+Z) must be “open (add space)” as shown in Figure 2.5.

Figure 2.5: Boundary condition applied in frequency domain simulation. The inset shows the applied boundary condition in the z-direction. Zmin is assigned as open and Zmax is assigned as open add space to emulate the feature of far field excitation.

2.1.3 Interpretation of simulated data

After the simulation, the transmission and reflection spectra are calculated using S-parameters, that relates the input and output waves via scattering matrix (as shown in Figure 2.6). Mathematically for two ports system it can be written as:

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (2.4)$$

where, a_i represents the incident wave to port i and b_j represents the reflected wave from port j . The elements in S-matrix S_{pq} are complex in nature which contains both the information of amplitude and phase. Here subscript “ q ” represents the excitation port (i.e. input port) while “ p ” represents the output port. Thus, S_{11} represents the ratio of the amplitude of wave reflects from port 1 to the amplitude of signal incident on port 1. Mathematically, all the elements of S-matrix can be calculated using:

$$\begin{aligned} S_{11} &= b_1/a_1 ; S_{12} = b_1/a_2 \\ S_{21} &= b_2/a_1 ; S_{22} = b_2/a_2 \end{aligned} \quad (2.5)$$

Figure 2.6: S parameters for the two-port network.

The calculated S-parameters in CST is complex and contain both the information of amplitude and phase. The expression given above in the matrix equation is for two ports. In addition to S-parameters, CST also offers to calculate the electric/magnetic field and charge distributions at each frequency that is vital to analyze the resonant and non-resonant behaviour of MM.

2.2 Terahertz time domain spectroscopy (THz-TDS)

Terahertz waves are characterized as low photon energy waves. Terahertz time domain spectroscopy (THz-TDS) is unique from other spectroscopy techniques as it directly measures the transient electric field rather than its intensity. This section gives an overview of THz-TDS followed by detailed discussion of two majorly used THz-TDS system which are Photoconductive antenna (PCA) based THz-TDS and ZnTe (zinc telluride) nonlinear crystal-based THz-TDS.

2.2.1 THz-TDS: An overview

THz spectroscopy typically covers the frequency spans ranging from 0.1-10 THz^[1]. THz time domain spectroscopy means the generation and detection of THz pulse in a synchronized and

coherent manner^[2]. In other words, THz-TDS is an efficient technique for generation and detection of broadband coherent THz radiation. Other spectroscopy techniques such as vector network analyzers or IR-Vis-UV spectroscopy performs frequency domain measurement via frequency sweeping. While Fourier-transformed infrared spectrometers (FTIR) indirectly measure the time domain via interferometry^[3].

In contrast, THz TDS offers direct access to the amplitude and phase of the THz electric field that makes it unique. It allows to capture many useful information such as complex optical constants of material without using Kramer-Kronig transformation relation. In the context of material characterization, it is extremely useful, as the free carriers either reflect or absorb the THz radiation. THz-TDS has been intensively utilized for the characterization of topological insulators (TI)^[4, 5], superconductors^[6, 7], phase change materials^[8] and 2D materials^[9, 10]. In addition to this, THz-TDS has broad prospect for various real-life applications such as virus detection^[11], food-quality inspection^[11] and security scanning^[12].

An ultrafast femtosecond laser with a pulse width ranging from 100-10 *fs* plays a crucial role in THz-TDS as it utilizes for both the generation and detection of THz waves. Section 2.2.2 and 2.2.3 present the detailed discussion of PCA and ZnTe based THz-TDS, respectively. Since the THz electric field has a time duration of few picoseconds, thus it requires a fast and sensitive detection technique. The electronic circuit-based detector lacks such fast sensitivity and high time resolution. Thus, it requires a special detection technique. One of the ways to reach sub-picosecond resolution is by using an optical technique where an ultrafast laser pulse can be used to generate and detect the transient THz field.

Concept behind detecting the THz pulse: Capturing the time-domain spectra of THz field can be seen as sampling unknown THz field with a known femtosecond laser pulse. The femtosecond laser pulse that samples the THz electric field is known as “read-out pulse”. Usually, in the THz-TDS, the convolution of short readout pulse and long THz pulse is being detected. To perform coherent detection, the optical read out and THz pulse must arrive simultaneously. Figure 2.7.a shows the schematic of the experimental setup to capture the full-time domain THz pulse. The femtosecond laser pulse split into two parts by beam splitter. One part being used for THz generation thus send to the emitter and other part used for coherent detection of THz wave. To achieve the time delay between optical and THz pulse, a mechanical delay stage is used with micrometer precision thus picosecond resolution in time domain. The different colors marked in Figure 2.7.a represents the various time instance of the delay stage, and the corresponding amplitude of THz electric field is shown in Figure 2.7.b. Thus, by moving the delay stage with smaller steps full THz time domain electric pulse mapped out.

Here two important points to be noted:

- a. Femtosecond laser and THz pulse must arrive simultaneously.
- b. The width of optical pulse must be significantly shorter than THz pulse.

Figure 2.7: Sampling of THz pulse (a) Schematic of the experimental setup to capture the temporal profile of THz pulse (b) An example of THz pulse recorded at different time delay.

The measured THz transient signal after performing Fourier transformation yields complex-valued frequency domain spectrum that can be written as amplitude and phase form as:

$$E(t) \xrightarrow{\text{Fourier transform}} \tilde{E}(\omega) = E(\omega)e^{-i\phi(\omega)} \quad (2.6)$$

This is the most important and unique property of THz-TDS. It allows to calculate both amplitude as well as phase of THz pulse which is not possible from other spectroscopic methods. The retrieval of the complex electric field helps to calculate the complex permittivity and conductivity of the sample.

THz radiation can be generated and detected through several mechanism^[13-16]. Here, we mainly describe the two most common approaches of THz-TDS: (a) Photoconductive antenna (PCA) and (b) ZnTe based THz-TDS system.

2.2.2 Photoconductive antenna (PCA) based THz-TDS

PCA based THz-TDS is one of the most widely used THz spectroscopy systems with high signal-to-noise ratio ($\sim 10000:1$)^[17, 18]. The generation and detection of THz is based on photocarrier transport process. An antenna is used to generate and detect the THz waves. The commonly used antenna architect contains parallel metallic microstrip lines fabricated on photoconductive substrate (low-temperature GaAs). The schematic of PCA-based THz-TDS is shown in Figure 2.9.

2.2.2a THz generation from PCA

An ultrafast optical pulse with a high repetition rate ((1 kHz)) is used for the generation and detection of THz pulse. Figure 2.8 shows the schematic of PCA based THz spectroscopy setup. The optical laser pulse (in Figure 2.8 Femtosecond laser pulse, 800 nm) is divided into two parts using beam splitter. One part of beam is directed to the emitter antenna while the second beam is utilized for THz detection. The emitter PCA consists of two metallic electrodes on low semiconducting substrate as shown by dashed circles in Figure 2.8. In our setup the PCA antenna was fabricated on GaAs substrate owing to high electronic mobility and ultrafast photocarrier relaxation^[19]. One part of the femtosecond pulse incident on the antenna with photon energy higher than the bandgap of the semiconductor substrate (E_g for GaAs 1.424eV^[20] and $E_{800nm} \sim 1.51$ eV) results in generating a transient photocurrent. Upon laser illumination, there exists a rapid rise in transient current followed by a longer decay due to finite carrier lifetime. These transient photocurrents induces the time-varying surface currents ($J(t)$) which are accelerated by applying DC voltage across the electrodes of antenna which in turn emits THz radiation^[21-23]. Mathematically, the photogenerated current density ($J(t)$) can be written as:

$$J(t) = N(t) e \mu E_b \quad (2.7)$$

where, E_b is the electric field produced by biasing electrodes with DC voltage, $N(t)$ is the photoinduced free carrier density, e is the electronic charge and μ is the mobility of electrons. To achieve large current density ($J(t)$), high electronic mobility is favorable. In Eqn.2.7, we neglect the contribution of holes owing to its low mobility as compared to electrons. The strength of radiated THz electric field is given by i.e. E_{THz} ^[24]:

$$E_{THz} = \frac{Ae}{4\pi\epsilon_0 c^2 z} \frac{\partial N(t)}{\partial t} \mu E_b \quad (2.8)$$

where, A is the optically illuminated area in the semiconductor substrate located between the electrodes, ϵ_0 is the vacuum permittivity, c is the speed of light and z is the distance between the emitter and far-field probe. To achieve high bandwidth, the lifetime of free carriers must be short (in the range of picoseconds), thus substrate with ultrafast free carrier dynamics are always preferable. Low temperature gallium arsenide (LT-GaAs) is one of the commonly used substrates for PCA emitter. Also, the strength of THz electric field is directly proportional to the electron mobility of the substrate. Thus, high mobility substrates are an ideal choice for fabricating PCA emitter. In this regard, LT-GaAs substrate is perfect candidate owing to high electronic mobility ($\sim 8500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ^[20]) and ultrafast carrier relaxation ($\sim$ few picoseconds^[19]). The polarization of emitted THz radiation is along the biased field direction. This information is vital to detect the THz radiation using PCA (described in section 2.2.2b). One important point must be noted here that, significant part of the energy of THz radiation is emitted during the rise of photocurrent and most of the energy is coupled to the substrate rather than air, this the reason why a hemispherical silicon lens is attached to the substrate opposite to the dipole antenna as shown in left dashed circle in Figure 2.8.

Figure 2.7: Schematic of Photoconductive antenna-based THz-TDS. The inset shows the zoomed part of THz emitter and detector section.

2.2.2b THz detection using PCA

The detection process using PCA is the reverse of the generation process. At the detector side, the second optical pulse generates free carriers which recombine in the absence of incidence THz pulse. Once the THz pulse focused in the active region of PCA with polarization parallel to the dipole, THz electric field acts as bias and sweep the free carriers across the photoconductive gap and generates photocurrent (J) across the electrodes which is given as:

$$J = N e \mu E(\tau) \quad (2.9)$$

where N is the photocarrier density μ is electronic mobility, and τ is the temporal delay between the optical probe and THz pulse. Since the lifetime of free carrier is much shorter than the THz pulse duration, thus the magnitude of generated photocurrent represents the amplitude of THz electric field at an instant. This process is called photoconductive sampling. At last, by varying the time delay between THz and optical laser pulse, the entire waveform of THz pulse can be recorded. In this process, the amplitude of generated photocurrent is very low typically on the order of nanoampere thus current amplifier is used to amplify the photocurrent. To probe the full waveform of THz electric field in time domain, τ is varied using mechanic delay stage as shown in Figure 2.8.

2.2.3 ZnTe based THz-TDS

This is also one of the most intensively used THz-TDS system. As compared to PCA based THz-TDS, the output of THz pulse is high in nonlinear crystal-based THz-TDS, which is vital for many nonlinear spectroscopic applications. Nonlinear crystal is the key component for the generation and detection of THz waves via a nonlinear optical process. In general, nonlinear crystals uses amplifier laser system with high pulse energy for generating the THz waves. Thus, it can also be utilized to develop a robust optical-pump terahertz probe (OPTP) spectroscopic systems which is described in section 2.3.

A suitable nonlinear crystal should have a high transparency in both the optical and THz regime to avoid the energy dissipation. In addition to this, to facilitate the high conversion efficiency, its electrooptic coefficient must be sufficiently large. A number of materials satisfy these requirements, that includes dielectric crystals e.g. LiNbO₃, LiTaO₃, semiconductors e.g. ZnTe, GaAs, spintronics based emitter e.g. FeNi. In our studies, we employ ZnTe crystal-based THz-

TDS which further served as OTP setup as well. A major factor that degrades the performance of nonlinear crystal is the optical phonon absorption which typically falls in the THz region and restrict the bandwidth of the THz generation. For example, ZnTe has optical phonon mode at 5.3 THz.

2.2.3a Generation process

The generation of THz from ZnTe crystal involves a nonlinear process which is known as optical rectification. In this process, high intense optical beam induces a polarization in a nonlinear medium. The most commonly used nonlinear crystal is ZnTe. It is noncentrosymmetric crystal that has large 2nd order nonlinear susceptibility ($\chi^2 = 1.6 \times 10^{-7}$ m/V) and high electro-optic coefficient $r_{41} = 4.04$ pm/V^[25]. There are many parameters such as thickness, the orientation of crystal, wavelength and intensity of incident beam that affects the efficiency of THz generation from the ZnTe crystal. In the generation process, an ultrafast optical pulse (35 fs in our case) interacts with the crystal that induces the transient polarization with the low frequency that radiates transient electromagnetic field, whose frequencies span the THz region.

The optical rectification process requires second-order frequency mixing. Given that $E(t)$ is the electric field of the incident optical pulse, thus the second-order polarization induced inside a nonlinear crystal is given by:

$$P^2(t) \propto \chi^2 E(t)^2 \quad (2.10)$$

where, χ is the second-order susceptibility of ZnTe crystal. Since the femtosecond optical pulse contains many frequencies, by assuming only the two frequency components i.e.

$$P^2(t) \propto \chi^2 [E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-2i(\omega_1 + \omega_2)t} + 2E_1 E_2^* e^{-2i(\omega_1 - \omega_2)t} + c.c.] + 2\chi^2 [E_1 E_1^* + E_2 E_2^*] \quad (2.11)$$

here c.c. represents the complex conjugate. The polarization expression contains second harmonics of E1, E2, sum-frequency and difference frequency. In optical rectification only the difference frequency component i.e. E ($\omega_1 - \omega_2$) will be useful. Mathematically, the far-field radiated THz electric field is related to the second-order derivative of second-order polarization:

$$E_{THz}(t) \propto \frac{\delta^2 P^2(t)}{\delta t^2} \quad (2.12)$$

2.2.3b Detection process

The ZnTe based THz-TDS utilizes linear electro-optic (EO) effect or Pockels effect to resolve the amplitude of subpicosecond transient THz electric field. It is the reverse of the optical rectification process. This effect is related to the local change in optical birefringence (i.e. different refractive index for light polarized in different axes of the crystal) of a crystal-induced by the THz electric field. The change in birefringence induces the polarization change in low intense optical probe pulse as shown in Figure 2.10. Modulating the probe laser pulse inside the EO crystal is the basics behind the THz detection in EO sampling.

Figure 2.9: Schematic of free space electro-optic detection using ZnTe crystal.

In the presence of THz electric field, the co-propagated optical probe pulse experiences phase delay due to induced birefringence that results in polarization change of probe pulse after passing through the crystal. Generally, the optical probe pulse with linear polarization is incident to the ZnTe crystal. That acquires modification in polarization due to birefringence of crystal and become elliptically polarized. This change in polarization is recorded via polarization-sensitive balanced detection. Figure 2.9 shows the schematic of THz detection using ZnTe crystal. In the absence of THz pulse, the polarization of optical pulse does not change and remains linear which by using the combination of QWP (quarter wave plate) and Wollaston prism that splits the circularly polarized light into orthogonally polarized light with equal intensities is detected by balanced detector. The output signal of the balanced detector is the intensity difference of two orthogonally polarized beam (Figure 2.9), which is zero in this case. While on the other hand in the presence of THz pulse, the polarization of optical probe pulse changes that results in nonzero signal in the balanced detector for the scheme shown in Figure 2.9. Thus, by recording the change in signal strength, we record the instantaneous amplitude of THz pulse i.e. E_{THz} . Hence, by adjusting the time delay between the optical probe and THz pulse, entire THz wavefront can be sampled.

2.3 Optical Pump Terahertz Probe spectroscopy (OPTP)

Figure 2.10 depicts the ZnTe crystal-based THz-TDS experimental setup integrated with optical pump, which serves as OPTP spectroscopy setup. An amplifier laser pulse (pulse width 35 fs, central frequency 800 nm) is split into two parts using a 70:30 beam splitter where the transmitted beam is utilized in the generation and detection of THz pulse. And the reflected beam is utilized as pump beam for photoexciting the sample in OPTP. This beam as per requirement can also be frequency-doubled to generated 400 nm optical pump beam using BBO crystal as shown in Figure 2.10.

Figure 2.10: Schematic of Optical Pump Terahertz Probe (OPTP) system using ZnTe crystal based THz system.

The transmitted beam (70 % from beam splitter) from the beam splitter is further split into two parts using 90:10 beam splitter, where the transmitted beam from the second beam splitter

incident on ZnTe crystal for THz generation via above mentioned optical rectification process while the reflected beam is used to map the THz pulse via electro-optic process as discussed above. At the emitter side, THz pulse diverges with propagation which is collimated using parabolic mirror followed by focusing to the sample using another parabolic mirror as shown in Figure 2.10. Thus, the combination of two pairs of parabolic mirrors is used to guide the THz beam from emitter to sample to the detector. At the detector end, the THz is detected using above mentioned EO detection process. By varying the delay stage THz time domain signal is mapped out, which further in the post processing step Fourier transformed to extract the frequency spectrum and phase. Another important point in the OPTP is the time matching of optical pump beam with THz beam as it offers to capture the time-resolved dynamics. Thus, by varying the time delay between optical pump beam and THz probe beam, we can scan the dynamics of species such as free carriers, excitons or copper pairs with picoseconds time resolution.

For OPTP setup, we utilized ZnTe based system owing to the high peak power of laser pulse in amplifier laser. The laser pulse of an amplifier laser has average power 6W with 1 kHz repetition rate and 35 fs pulse width that outputs approx. ~ 170 GW of peak power of pulse. On the other hand, for PCA based THz system, we use oscillator laser that has 1 W average pulse power with 80 MHz repetition rate and 12 fs pulse width that outputs approx. 1MW peak power laser pulse. An oscillator laser is ideal for PCA based THz system as the peak laser pulse power is low that does not spoil the PCA while on the other hand, an amplifier laser with high peak pulse power will damage the PCA thus it is not suitable. In principle, we can build OPTP setup with PCA and oscillator laser but at the cost of low peak pulse power which put limitations in pump-probe measurement as for carrier dynamics, high peak power is required. Also, the high THz output

power in ZnTe system is an added advantage for developing OPTP in ZnTe based THz system.

To calculate the peak pump power, we used the following formula:

$$Peak\ laser\ power = \frac{Power_{average}}{Pulse\ width \times Repetition\ rate} \quad (2.13)$$

2.4 Sample fabrication

As we discussed in Chapter 1 that, the electromagnetic response of metamaterial is attributed to the resonant excitation of each unit cell that constitutes the whole array. In principle, the unit cell can be made of metal, dielectric or both depending on the demand of operation. In the scope of this thesis, the metamaterial structure used is fabricated using standard cleanroom fabrication processes. For THz frequencies, the dimension of unit cell structures is in micron length scale thus standard photolithography technique is suitable. Figure 2.11 shows the processes involved in the fabrication of metallic resonators. This is a single step lithography. The detailed fabrication steps are following:

1. The substrate (in our case z-cut quartz) are cleaned using acetone solvent in the ultrasonic baths followed by washing from isopropyl alcohol (IPA) to remove the traces of acetone. Then these cleaned substrates are dried using dry nitrogen to remove the moisture.
2. In the next step, a positive photoresist (AZ5214E) is deposited on the substrate using spin coating technique. The parameters of spin coating (4000 rpm for 40 seconds) are optimized to achieve the desired thickness of photoresist 1.5 μm . Later, the coated photoresist is baked on a hot plate at 105⁰C for about 60 seconds.

3. Now in the mask aligner MJB04, we aligned the mask of the desired pattern of resonator structures, then UV light is illuminated. To get better resolution of pattern, we use hard contact mode setting for the UV illumination in mask aligner.
4. In the next step, the photoresist coated substrate is soaked into the developer solution (AZ developer) for 30 seconds and then rinsed with deionized water. The developer solution dissolves the UV exposed area of photoresist, thus imprint the desired pattern on the photoresist as shown in Figure 2.11.
5. Now, we deposit the metal (in our case Aluminium) of thickness 200 nm on the substrate containing the patterned photoresist using thermal evaporation. To achieve better film quality, we keep the deposition rate very low ($\sim 0.5 \text{ \AA}/\text{sec}$).
6. In the final step, the metal deposited substrate is soaked into the acetone for lift-off where the undesired metal and photoresist film get remove from the substrate and left behind the patterned metal film.

Figure 2.11: Pictorial representation of photolithography steps involved for the fabrication of metamaterials.

2.5 References

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Chapter 3

Solution-processed Lead iodide for Ultrafast Terahertz Photonic devices

Solution-processed lead iodide (PbI_2) governs the charge transport properties in hybrid metal halide perovskites. Besides being a precursor in enhancing the photoconversion efficiency of solar cells, PbI_2 alone offers remarkable high photoconductivity and ultrasensitive photo response that has been unexplored yet. In this chapter, we present the photo physics of PbI_2 explored using time resolved terahertz spectroscopy (TRTS). As an application prospect, an ultrafast terahertz (THz) modulator (which is a key component for next generation high-speed wireless communication) has been demonstrated by integrating the PbI_2 with THz metamaterial. Further, at the end of the chapter, the influence of strongly confined THz electric field on the transient photo carrier dynamics of PbI_2 has been probed by varying the thickness in metamaterial system. Such control in tailoring the nonequilibrium dynamics of PbI_2 is very important in realizing a broad range of applications ranging from on-chip reconfigurable devices to ultrafast all-optical switchable photonic devices.

3.1 Introduction

The active control of metamaterial resonances is highly desired as it can facilitate myriad applications and unprecedented control on light-matter interactions. The dynamic tuning of phase, frequency and amplitude of the electromagnetic wave is the heart of the technological revolution. Since, THz lies between the electronics and photonics regime of the electromagnetic

spectrum and has been envisioned as a potential candidate for many disruptive applications like high-speed wireless communication^[1, 2], high-resolution imaging^[3, 4] and ultra-sensitive bio, chemical and gas sensors^[5]. However, to utilize the full potential of THz waves, the development of active devices for on-demand manipulation is vital. In this context, various approaches have been demonstrated such as: interfacing metamaterials with semiconductors like Si^[6], Ge^[7], phase change materials^[8], superconductors^[9] and micro-electromechanical systems^[10].

Nevertheless, in terms of enhancing practical applications and technological relevance, there has been a huge quest for tunable metadevices possess ultrafast switching speed, low threshold switching, cost-effective and ease of fabrication techniques. In this regard, solution-processed semiconductors present themselves as a potential candidate. Their remarkable and tunable optoelectronics properties allow them for a broad range of applications such as light-emitting diode, low threshold lasing, cost effective large area solar cells and highly sensitive photodiodes^[11-13]. Organic-inorganic perovskites is one of the key examples in the solution-processed family of semiconductors. Recently, in THz frequencies the integration of 3D perovskites (methyl ammonium lead iodide: $\text{CH}_3\text{NH}_3\text{PbI}_3$) has shown ultrasensitive reconfigurable metadvice^[14]. The ease of fabrication which just involve the spin coating on the metamaterial structures allow to realize the reconfigurable THz metamaterial even at flexible substrate. The integration of 3D perovskites with THz metamaterials have opened many avenues for practical applications, however, the major limitation of such devices is the stability. 3D perovskite has very low ambience stability. It degrades under the presence of moisture, which majorly hinder the practical applications. To mitigate this major limitation, motivated to investigate other alternatives which exhibit excellent optoelectronics properties with great ambience stability. Solution-processed lead iodide (PbI_2) offers the above-mentioned desired

properties. In organic-inorganic perovskite (for e.g. $\text{CH}_3\text{NH}_3\text{PbI}_3$) the inorganic component i.e. PbI_2 is the one which predominantly contributes the optoelectronics properties due to its rich chemical and photophysical properties.

PbI_2 is a direct bandgap semiconductor with bandgap 2.35 eV^[15], shows high photon absorption and photon-electron conversion efficiency thereby favouring for low threshold THz active devices. In contrast, it has shown to exhibit excellent optical properties as detector material with high stability, high efficiency and excellent charge transport properties^[16, 17]. However, in the context of PbI_2 most of the studies has been restricted to enhance the performance of perovskite-based photovoltaic devices as the presence of PbI_2 in perovskite films passivate the defects in grain boundaries thereby enhance the photoconversion efficiency (PCE) in solar cells^[18-20]. In this work, we experimentally probe the photocarrier dynamics and pump fluence dependent photoconductivity of solution-processed lead iodide (PbI_2) thin film using the time resolved terahertz spectroscopy (TRTS). We show that the PbI_2 thin film exhibits excellent photoconductivity and ultrafast carrier relaxation dynamics, which are further used to demonstrate a solution processed PbI_2 thin film coated sensitive and ultrafast tunable metasurface with a switching time of less than 150 ps. Furthermore, we observe the interactions between the confined THz electric field and the photoexcited free carriers in thin film, that results in Purcell modified recombination dynamics for varying thickness of the PbI_2 thin film spin coated on the metasurface. Consequently, the ultrafast switching time and the sensitivity of the active metasurface is tailored by varying the thickness of the spin coated PbI_2 thin film. Hence, our technique enables tailoring the nonequilibrium properties of semiconductor through Purcell enhanced fields using resonant metamaterials which is vital for the development of next generation multifunctional active THz devices.

3.2 Terahertz time resolved spectroscopy (TRTS) of PbI₂ thin film

The PbI₂ thin film is photoexcited with 400 nm ($E = 3.1$ eV) optical pump beam having energy higher than the bandgap ($E_g = 2.35$ eV)^[15], results in interband excitation of electrons from valance band to the conduction band. Terahertz is used to probe the relaxation dynamics of free carrier. Photoexciting the electrons with high energy photon excites the electron to higher energy states of the conduction band and generates nonequilibrium of electrons. Further these excited electrons arrange themselves as Fermi Dirac distribution due to thermalization. It occurs at femtosecond time scale which could not be captured by our spectroscopy technique due to resolution limitation. After thermalization these photo excited electrons relax to conduction band minima by either electron phonon coupling, or electron-electron scattering and further relax back to valance band via various relaxation channels such as bi-molecular recombination or monomolecular recombination^[21].

The change in THz transmission ($-\Delta T/T$) is used as a probe to monitor the free carrier relaxation dynamics which is shown in Figure 3.1a. The transient photoconductivity for various pump fluence is calculated using the thin film formula:

$$\Delta\sigma(t) = -\frac{\epsilon_0 c}{d} (n_{air} + n_{sub}) |\Delta T/T| \quad (3.1)$$

where n_{air} and n_{sub} are the refractive index of air and substrate (in this case quartz) respectively, c is the speed of light, ϵ_0 is the vacuum permittivity and d is the thickness of PbI₂ thin film, which is 160 nm for this case. The extracted transient photoconductivity at various pump fluence is shown in Figure 3.1b. With increasing the pump fluence the photoconductivity increases and gets saturates at higher pump fluence due to fully occupied density of states. The

important point to be noted here is that the free carrier relaxation dynamics is ultrafast in nature where the photoexcited electrons relax back within hundreds of picoseconds time scale which is three order of magnitude faster than 3D perovskites^[14]. This ultrafast feature is key for ultrafast THz active photonic devices.

Figure 3.1 Time-resolved ultrafast characterization of PbI₂ thin film (a) Differential terahertz transmission at various pump fluence for spin coated PbI₂ thin film sample. In the experiment the sample is photoexcited using 400 nm pump beam and change in THz amplitude is monitored to probe the dynamics of free carriers. The solid black line shows the bi exponential (Eqn. 2.) fit to extract the fast and slow relaxation components. (b) The extracted transient photoconductivity calculated using Eqn.1. for different pump fluence. The inset shows the peak value of photoconductivity as function of pump fluence. It shows the linear trend at lower pump fluence and gets saturated at high pump fluence.

To extract the relaxation time constants, we performed the global fitting of THz transient (Figure 3.1a) using bi-exponential function given as:

$$\left| \frac{\Delta T}{T} \right| = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (3.2)$$

where (τ_1 , τ_2) are the fast and slow relaxation time constants, respectively. The bi-exponential fitting allows to extract the contribution of slow and fast relaxation components. We tried to fit the THz transient using tri-exponential function too, but in the fitting parameters the value of two

different time constants came identical which suggest that bi-exponential function is the best fit for this. Further, to identify the nature of recombination, we performed fluence dependent dynamics, and the fitting revealed that the fast component “ τ_1 ” decreases from 12.8 ± 1 to 8.2 ± 0.6 ps by increasing the pump fluence (Φ) from 50 to 400 $\mu\text{J}/\text{cm}^2$. This decrease in time constant suggest that the fast relaxation process is Auger recombination, as Auger process is directly proportional to the number densities. Increasing the pump fluences increase the carrier densities which in turn facilitate the faster relaxation process via Auger recombination. Figure 3.1b shows the transient photoconductivity ($\Delta\sigma$) extracted using Eq. 1. The extracted photoconductivity value varies in the order of $\sim 10^3$ S/m which ensures the excellent photoconductive nature of PbI_2 thin film. Increasing the pump fluence increases the photoconductivity. Inset shows the peak of $\Delta\sigma_{\text{max}}$ as function of pump fluence which suggest that $\Delta\sigma_{\text{max}}$ increases linearly with pump fluence till 400 $\mu\text{J}/\text{cm}^2$ and starts getting saturated at higher pump fluence. Thus, operating below 400 $\mu\text{J}/\text{cm}^2$ ensures that there won't be any nonlinear effects in the PbI_2 thin film. The number 400 $\mu\text{J}/\text{cm}^2$ is not very specific, it may vary from thickness and morphology (i.e. film quality) of the film. After characterizing the ultrafast feature of PbI_2 thin film, we next integrate it with THz metamaterial to realize active control of THz waves which is essential for THz based applications.

3.3 PbI_2 integrated hybrid metadvice

The advent of metamaterials (MMs) has allowed the advance manipulation of THz waves such as amplitude, phase and polarization^[22]. MMs are topologically flat, functionally versatile and spectrally scalable. However, the optical properties of these MMs are static once they fabricated that put constraint for many applications. Thus, it of desire to tune the optical properties of MMs

actively by external means. In this section, we describe the active modulation of THz waves by integrating MM structure with PbI_2 thin film. The first part of section (i.e. 3.3.1) is devoted to THz MM that exhibits Fano resonance and its advantages. In the next section (3.3.2), we present all optical ultrafast active modulation of THz in PbI_2 spin-coated hybrid metadvice. Further, the effect of optical pump fluence and the effect of thickness of PbI_2 on Fano resonance modulation are investigated in section 3.3.3.

In the quest of developing active metadvice, many approaches have been demonstrated like mechanical^[10], electrical and integrating with semiconductors^[23, 24] and superconductors^[9]. Each of these approaches has its advantage and limitations and should be chosen appropriately depending on the required applications. For example, electrical and mechanical based active control exhibit slow switching speed so can't be used for high-speed modulator in communication scenario. Similarly, superconductor-based approach cannot be used for large scale applications due to cost restriction. Integrating the semiconductor offers vast range of options as we can choose the semiconductors smartly depending on the applications. Since, our aim is to develop high-speed THz modulators which could be used in next generation high-speed wireless communication, thus, the integration of PbI_2 with metamaterials opens up a potential avenue.

3.3.1 THz Fano resonator

In chapter 2, we discussed the basic physics of metamaterial. In this work, we choose asymmetric split ring resonator, which we call as terahertz asymmetric split ring (TASR) resonator throughout in this chapter. The TASR is a ring resonator with dual split capacitive gaps on opposite arms, and one of the gaps is displaced from the central position to create the

structural asymmetry as shown in Figure 3.3a. When a terahertz wave with the electric field polarized perpendicular to the gap incidence, a sharp asymmetric Fano resonance along with broad dipole resonance are excited as shown in Figure 3.2a. The Fano resonator consists of two near field coupled dipole resonators with broken structural symmetry, defined by the asymmetry parameter, ' d '. The broad dipole resonance of the individual resonator acts as the bright continuum which manifests as parallel surface currents at both the arms as shown in Figure 3.2b, while the broken symmetry encompasses the dark mode. When the dipole resonators are perfectly symmetric, Fano resonance ceases to exist (Red solid line, Figure 3.2a). Upon introducing the small structural asymmetry between the resonators, a sharp asymmetric line-shaped Fano resonance appears due to interference between sharp discrete resonance and much broader continuum-like dipole resonance as shown in Figure 3.2a, solid black line. The narrow linewidth of Fano resonance arises due to suppressed radiation mode. The structural asymmetry leads to weak coupling to free space which results in strong suppression of radiation losses. In addition to high Q the circulating surface currents are also the characteristic feature of Fano resonance which is shown in Figure 3.2b. With increasing asymmetry, the Fano resonance strength increases, while the quality factor decreases. Hence, at the optimal asymmetry of $d = 15 \text{ }\mu\text{m}$, the figure-of-merit in terms of resonance strength and terahertz field confinement is maximum. Hence, Fano resonators with $d = 15 \text{ }\mu\text{m}$ are chosen as the resonator design.

Figure 3.2: (a) Simulated transmission spectra for symmetric (red solid line) and asymmetric (black solid line) resonator. (b) Surface current distribution at Fano resonant and dipole frequency. At Fano resonance the surface current forms close loop that results as out of plane magnetic dipole. While at the other end, surface currents at dipole resonance frequency are symmetric in nature.

In our study, Fano resonance is selected owing to its high Q response that enables enhanced sensitivity to an external perturbation. The proposed metamaterial consists of a 2D periodic array of Fano resonators made of 200 nm thick aluminum (Al) on z-cut quartz substrate as shown in **Figure 3.3a**. The geometrical dimensions of the Fano resonator are as follows – square periodicity, $p_x = p_y = p = 75 \mu\text{m}$, length (l) = $60 \mu\text{m}$, width (w) = $6 \mu\text{m}$, gap (g) = $3 \mu\text{m}$ and asymmetry (d) = $15 \mu\text{m}$ as shown in the inset of Figure 3.3a.

3.3.2 Active modulation of THz in PbI₂ integrated hybrid metadvice

The artistic schematic of PbI₂ coated hybrid metasurface is shown in Figure 3.3a, where the PbI₂ is spin coated on the top of TASR fabricated on z-cut quartz. The optical image of PbI₂ coated hybrid metadvice i.e. PbI₂-TASR is shown in the inset of Figure 3.3a. The PbI₂ thin film covers the entire metasurface allowing it to uniformly influence the localized THz electric field in the

gap of metamaterials. An optical pump of wavelength 400 nm with photon energy 3.1 eV (higher than the bandgap of PbI_2 $E_g = 2.35$ eV) is incident on the PbI_2 coated hybrid metadvice. Upon photo excitation free carriers are excited in the PbI_2 thin film that alters the strength of confined THz electric field inside the gap of the resonator. This manifests as reduction in the Fano and dipole resonance amplitude with minimal red shift in their respective bare resonance frequencies.

Figure 3.3: PbI_2 coated hybrid THz metadvice (a) Artistic illustration of pump-probe excitation of PbI_2 coated hybrid metadvice. Left inset shows the unit cell of THz Fano resonator where $w = 6 \mu\text{m}$, $g = 3 \mu\text{m}$, $d = 15 \mu\text{m}$, and $p = 75 \mu\text{m}$. The inset at right hand side are optical image of fabricated PbI_2 coated metadvice sample. (b) Experimentally recorded terahertz

transmission at different pump-probe delay time from PbI₂ coated hybrid metadvice sample. The pump fluence of optical pump beam was kept 400 $\mu\text{J}/\text{cm}^2$ as it was enough to switch off the amplitude of Fano resonance completely. The inset shows the free carrier dynamics fitted with bi-exponential (red solid line) of PbI₂ thin film measured using time-resolved THz spectroscopy at 400 $\mu\text{J}/\text{cm}^2$. (c) Simulated electric field distribution in PbI₂ coated hybrid metadvice at different conductivity of PbI₂ thin film. 0 ps represents the case when pump is not arrived with probe pulse thus resulting as 0 S/m photoconductivity. At 6 ps, the pump and probe arrive at sample simultaneously resulting as high photoconductivity which quenches the Fano resonance that manifests as no electric field confinement. As the free carrier relax back to equilibrium the strength of confined electric field retrieves back.

We used the OPTP experiment setup (details are discussed in chapter 2) to characterize the metadvice. The ultrafast modulation characteristics are shown by the measured terahertz transmission spectra at different time instants of the pump-probe delay time (t_p) starting from the position, where pump beam has not yet arrived ($t_p < 0$ ps) to the complete recovery (steady) state of the system ($t_p \sim 150$ ps). Before the optical excitation (at $t_p < 0$ ps) of the PbI₂ sample, the structure exhibits the strongest Fano and dipole resonances (black line Figure 3.3b). Once the sample is photoexcited, the Fano resonance (near 0.7 THz) shows complete switch-off at $t_p = 6$ ps after the arrival of the optical pulse at the sample, where the photoexcitation of the PbI₂ is the maximum (red line Figure 3.3b). At the same time dipole resonance (near 1 THz) shows the amplitude modulation of nearly 50 %. Once the recombination of photocarriers in PbI₂ thin film reaches the steady state equilibrium ($t_p \sim 150$ ps), both the Fano and dipole resonance features are fully recovered to their original strengths, thereby showing profound and complete modulation of the Fano resonance feature of the metasurface (orange line Figure 3.3b). The pump fluence of optical beam was 400 $\mu\text{J}/\text{cm}^2$.

Figure 3.3c shows the simulated electric field at Fano resonant frequency for different photoconductivity of PbI₂. The electric fields are simulated using CST microwave studio under the unit cell boundary condition offered by the frequency domain solver (more details on the simulations are given in chapter 2). By tuning the conductivity of PbI₂, the strength of the

confined fields in the gaps is adequately controlled at the ultrafast time scales. To simulate the electric field confined at various photoconductivity of PbI₂ thin film, we used the experimentally extracted photoconductivity at pump fluence 400 $\mu\text{J}/\text{cm}^2$ as shown in Figure 3.1b (solid blue line). The ultrafast modulation of Fano resonance amplitude is reflected in the ultrafast switch-off and recovery of the confined electric fields present in the resonator gaps with respect to change in the conductivity of the PbI₂ thin film. Since the fields are sensitive to the screening effect from the photoexcited electrons, they are annihilated when the conductivity of the film is high $\sigma_{\text{PbI}_2} = 1940 \text{ S/m}$ ($t_p = 6 \text{ ps}$) (as can be seen in Figure 3.1b) and are recovered to their maximum strength in 150 ps (70 S/m).

3.3.3 Effect of optical pump fluence and thickness of PbI₂

Alongside the ultrafast modulation of the Fano resonance spectra, we study the influence of pump fluence and thickness of the PbI₂ thin film on modulation (M) depth of Fano resonance and sensitivity of the device. Before explaining the results, let's define the modulation depth (M). In rest of this chapter, the modulation depth (M) of the Fano resonance is calculated using the expression, $M = \frac{T_{np} - T_p}{T_{np}}$, where T_p and T_{np} are the amplitude of Fano resonance in the transmission spectra with and without pump respectively. Figure 3.4 shows the THz transmission spectra of PbI₂ coated hybrid metadvice, where the green solid line represents the no pump case while red solid line represents the presence of pump.

Figure 3.4: Terahertz transmission spectra at different pump-probe delay time. T_{np} and T_p are the amplitudes of Fano resonance representing the case of no pump and pump. It is used to calculate the modulation (M) depth.

Figure 3.5 a-c shows the pump fluence dependent spectra for PbI₂ coated metadvice for various thickness of PbI₂ thin films (160, 500 nm and 2.5 μ m). The black curve in all three plots represents the THz transmission spectrum through the bare metamaterial i.e. without PbI₂ coating. It shows the Fano and dipole resonances at 0.75 THz and 1.1 THz respectively. Upon spin coating with PbI₂ thin films of various thickness, the resonances show the reduced amplitude and redshift owing to change in the base conductivity and dielectric constants in the vicinity of the resonators. Under the pump incidence, amplitude of the Fano and dipole resonances decreases with increasing the pump fluence, which is also reflected as the increase in the modulation depth (M) of the corresponding resonances. Figure 3.5 d-f shows the modulation depths of Fano and dipole resonances for various thickness of PbI₂ in PbI₂-TASR. Figure 3.5d-f reveal that, Fano follows the exponential trend, while the dipole modulation exhibits linear response.

Figure 3.5: Thickness dependent sensitivity of resonance modulation for varying pump fluence. (a-c) Experimentally recorded THz transmission spectra of PbI₂-TASR-1, PbI₂-TASR-2, and PbI₂-TASR-3 respectively, where the thickness of spin coated PbI₂ thin films are 160 nm, 500 nm and 2.5 μm respectively. (d-f) The corresponding amplitude modulation depth (M) of Fano and dipole resonances.

To verify this behaviour, we performed numerical simulation using CST by varying the conductivity of PbI₂ thin film coated on the top of metamaterial. The simulated transmission spectra are shown in Figure 3.6 where we can observe that the Fano resonance is completely switch-off at the PbI₂ conductivity of 2000 S/m, whereas for the same conductivity the dipole resonance shows only 30% of modulation. To emulate the experimental spectra, we used experimentally extracted photoconductivity of PbI₂ thin film (as shown in Figure 3.1b). The extracted modulation depth from simulation are shown in Figure 3.6b which reveals the exponential and linear trend in modulation depth for Fano and dipole resonances. The observed exponential and linear response in the modulation of the Fano and dipole resonances highlight

the distinctive nature of their respective near-field confinement, where the strong field confinement for Fano resonance aids higher sensitivity in resonance switching.

Figure 3.6 (a) Simulated transmission spectra for different photoconductivity of PbI₂ thin film. (b) The variation of modulation depths for Fano and dipole resonance are fitted with exponential and linear function. The rate constant for exponential fit is $\alpha = 0.003$ and slope of dipole variation is $b = 0.0019$

As shown in Figure 3.5d, for the PbI₂-TASR-1, where the thickness of PbI₂ thin film is $d_{\text{PbI}_2} = 160$ nm, shows near unity modulation at $\Phi = 400$ μJ/cm² pump fluence. The Fano modulation starts to saturate at 100 μJ/cm² owing to its exponential behaviour. While for PbI₂-TASR-2 and PbI₂-TASR-3 the where the thickness of PbI₂ thin films are 500 nm and 2.5 μm respectively, require high pump fluence to quench the resonances. The change in the depths of modulation (M) for Fano resonance with respect to pump fluence is fitted with an exponential function, $M_{\text{Fano}} = e^{-\alpha\Phi}$ where α is the rate constant and Φ is the pump fluence, whereas the linear change in dipole modulation is fitted using linear function, $M_{\text{dipole}} = a + b\Phi$ where, a is the intercept and b is the slope of the linear fitting. The extracted rate constants (α) for Fano modulation are 0.028, 0.009, and 0.004 for the PbI₂-TASR-1, PbI₂-TASR-2, and PbI₂-TASR-3 respectively

which affirms that the sensitivity and the rate of modulation are better for the PbI₂-TASR-1 i.e. metadvice with thinner PbI₂ film. The modulation depth for the dipole resonance in PbI₂-TASR-1 reaches as high as $M_{dipole} = 0.5$ at $\Phi = 400 \mu\text{J}/\text{cm}^2$, whereas for in PbI₂-TASR-2 and 3, the maximum achieved modulation for dipole even at high pump fluence: $\Phi = 900 \mu\text{J}/\text{cm}^2$ reaches 0.52 and 0.28 respectively. The slope of linear response for three metasurface is 0.0012, 0.0005, and 0.00025 for increasing thickness of PbI₂. The decreasing trend in slopes affirms the different sensitivity of photoswitching. In conclusion, these results affirm that modulation of metasurface resonances depend on the thickness of the spin coated PbI₂ thin film, where the thinner films aid ultrasensitive modulation at low pump fluences.

3.4 Effect of thickness on ultrafast dynamics

In section 3.2 we have investigated the ultrafast and high photoconductivity properties of bare PbI₂ thin film by using TRTS. Also, section 3.3 shows the influence of PbI₂ thin film thickness on the modulation depth of MM resonances. As a natural progression in the development of active metamaterial, it is important to develop multi functionalities where we can tune the properties of active device such as switching effect, threshold pump fluence for active modulation. In this regard, we observed the tunability of relaxation dynamics of PbI₂ thin film when coated on MM structure by varying the thickness of PbI₂ thin film. The interaction between the localized THz field and photoexcited electrons in PbI₂ thin film manifests as change in carrier dynamics for different thickness of PbI₂ thin film coated in metamaterial structure. Thus, we devote a dedicated section to discuss the effect of thickness of PbI₂ thin film on its relaxation dynamics when coated on MM structures.

Figure 3.7a shows the measured optical pump THz probe time dependent differential transmission ($|\Delta E|$) curves for the bare PbI₂ thin film having thickness $d_{\text{PbI}_2} = 160, 500 \text{ nm}$, and $2.5 \mu\text{m}$. The differential transmission of the THz probe is defined as $|\Delta E| = |\Delta E_{\text{no pump}} - \Delta E_{\text{pump}}|$. The experimental recorded spectra at $\Phi = 900 \mu\text{J}/\text{cm}^2$ show the identical response for all three thickness of PbI₂ that indicates the change in THz transmission through the bare thin film does not depend on the sample thickness, as they possess same optical penetration depths. This behaviour is consistent at other pump fluences too, where the thin films exhibit an identical value of $|\Delta E_{\text{max}}|$ with the increasing trend with pump fluence as shown in the inset of Figure 3.7a.

Figure 3.7 Effect of THz electric field on free carrier dynamics in different thickness of PbI₂ film (a, b) Transient differential ($|\Delta E|$) THz transmission from photoexcited samples, where (a) is the case of pristine PbI₂ thin film that does not show any change while (b) shows the spin coated PbI₂ thin film on TASR. The inset in their respective figures show the peak value of $|\Delta E|$ through pristine PbI₂ thin film i.e. PbI₂-TF and PbI₂-TASR. The thickness of PbI₂ film (d_{PbI_2}) was 160 nm, 500 nm and $2.5 \mu\text{m}$.

As the thin films of different thickness are spin coated on the metasurface (PbI₂-TASR), the samples exhibit a significant difference in the measured $|\Delta E|$ as shown in Figure 3.7b. For $\Phi = 900 \mu\text{J}/\text{cm}^2$, the absolute $|\Delta E_{\text{max}}|$ observed for the PbI₂-TASR sample is greater than the corresponding PbI₂ thin film of identical thickness. Each PbI₂-TASR sample with increasing

thickness of PbI₂ thin film exhibits a decrease in $|\Delta E_{\max}|$, thus signifies the film thickness dependent change in the THz transmission. Again, we want to highlight that for the given pump fluence “ Φ ” the value of $|\Delta E_{\max}|$ is high for 160 nm coated TASR as shown in the inset of the Figure 3.7b. This suggests the fact that TASR coated with the thinnest film are more sensitive towards external perturbation.

To unravel the reason behind the thickness dependent dynamics, we look into the THz field confinement in TASR. At Fano resonance frequency there exists THz electric field confined in the capacitive gap of the TASR as shown in Figure 3.3c. In addition to in-plane confinement, this electric field exponentially extends out of plane (i.e. in both directions perpendicular to the substrate). Thus, the interaction of this confined THz electric field acts as a probe in the OPTP measurement. Based on the interaction volume with PbI₂ thin film, the observed dynamics can be divided as surface dynamics and bulk dynamics. Similar strategy has been followed to isolate the surface carrier dynamics from the bulk dynamics in GaAs and InP thin film using THz nanoprobeing technique^[25]. For 160 nm PbI₂ thin film the interaction volume of THz probe is high compared to 500 nm and 2.5 μ m thick films thus the observed carrier dynamics in 160 nm coated thin film contains the bulk as well as surface dynamics as also discussed in^[25]. While on the other hand the carrier dynamics for 500 nm and 2.5 μ m PbI₂ thick film majorly contains the surface dynamics thus faster in nature as shown in Figure 3.7b. The thickness dependent ultrafast properties of PbI₂-TASR hybrid device can also be quantified by Purcell factor due to resonant nature of TASR. The Purcell factor for the metamaterial cavity can be calculated as $F_p = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \left(\frac{Q}{V}\right)$, where λ is the wavelength of confined electric field, n is the refractive index of thin-film, Q is the quality factor of metamaterial cavity and V is the cavity volume. For our TASR, the calculated Purcell factor F_p for Fano ($\lambda = 440 \mu\text{m}$) and dipole ($\lambda = 300 \mu\text{m}$)

resonances are 1080 and 6 respectively. The strong field confinement at Fano resonance frequency results to higher Purcell factor thus strong interaction with PbI₂ thin film and modifies the surface properties of the photoexcited thin film.

In conclusion, this chapter discusses about the photo-physics of PbI₂ thin film, where time-resolved THz spectroscopic measurement reveals the ultrafast feature of photo excited free carriers which relax back within 150 ps time scale. Further, integrating the PbI₂ thin film with TASR enable ultrasensitive and ultrafast THz modulators which is vital for the next generation THz wireless communication. PbI₂ integrated hybrid metadvice (PbI₂-TASR) exhibits near unity modulation of THz electric field at optical pump fluence ($\Phi = 400 \mu\text{J}/\text{cm}^2$) with 150 ps switching time speed. The thickness of PbI₂ plays an important role towards the sensitivity and ultrafast feature of PbI₂-TASR. The thinner PbI₂ film showed low threshold switching and high photoconductivity while on the other hand thick PbI₂ film exhibits faster switching speed owing to domination of surface dynamics detected by THz probe. The development of on-demand manipulation of carrier dynamics is of high interest to realize advance level functionalities of THz based devices. Thus, altering the ultrafast switching time of PbI₂-TASR hybrid metadvice by varying the thickness of spin coated PbI₂ film provides a novel platform to realize most-efficient, reusable, cost-effective, sensitive, and real-time tunable ultrafast all optical THz modulators. The design of optimized Q/V THz cavities could also play an important in altering the semiconductor dynamics quoted on it. In chapter X, we have discussed few strategies to design metadvice with on-demand altering the switching time, which is useful for next-generation high-speed THz wireless communication and THz based ultrasensitive sensors.

3.5 References

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Chapter 4

Excitons in 2D perovskites for ultrafast terahertz photonic devices

In chapter 3, we discussed about PbI_2 based all-optical ultrafast terahertz (THz) metadvice, which showed 150 ps (~ 6.7 GHz) switching speed at $\Phi = 400 \mu\text{J}/\text{cm}^2$ optical pump fluence. This remarkable ultrafast control on THz waves opens the avenue for the development of the solution-processed semiconductor based ultrafast THz metadvice. However, the development of ultrafast THz devices is still at the heart of many practical applications such as high-speed wireless communications. To give a perspective, in the wireless communication, modulators are the key component that decides the data transfer speed. Thus, switching the THz electric field with GHz modulation speed restrict the data transfer rate in *gigabits per second* range. Thus, switching the THz waves with high-speed will enhance the data transfer speed.

In this chapter, we will discuss 2D perovskite-based ultrafast terahertz photonic devices, where the ultrafast feature arises due to self-assembled quantum well structures in 2D perovskites. Further, we unravel the photo-physics of 2D perovskite including free carriers and exciton dynamics using time-resolved THz spectroscopy (TRTS).

4.1 Introduction

In recent years, organic-inorganic hybrid three-dimensional (3D) perovskites have seen unprecedented rapid development owing to their outstanding optoelectronic properties such as

larger diffusion lengths, excellent charge carrier mobilities, bandgap tunability, high optical gain, and nonlinear response along with low fabrication cost^[1-5]. However, their instability in ambient conditions hinders their large-scale applications^[6, 7]. In contrast, 2D Ruddlesden Popper (RP) perovskites offer better opportunities compared to their 3D counterparts^[8, 9]. Their excellent ambient stability, along with abundant tunable optoelectronic properties and high quantum efficiency, makes them ideal for a wide range of electronic and optical applications^[10-13]. In the recent times, RP perovskites have shown excellent efficiency for light-emitting diode (LED)^[8, 14]. The existence of self-assembled quantum wells (QWs) due to alternative arrangement of organic and inorganic atomic layers provides an additional relaxation pathway for the photoexcited free carrier to relax back at ultrafast time scales, that makes them a perfect candidate for ultrafast active photonic devices^[5, 15, 16]. Since past few decades, there has been huge demand for ultrafast tunable devices at terahertz (THz) frequencies owing to their wide range of disruptive applications ranging from imaging, sensing and high-speed wireless communications^[17-20]. To achieve unprecedented control over THz waves, metamaterials (MMs) have been extensively used due to their structural simplicity and tunable optical properties^[21, 22]. Furthermore, integrating the MMs with semiconductors offer a unique platform to dynamically control and manipulate the THz waves.

Recently, many developments have focused on developing the active MMs by integrating with dynamic materials such as liquid crystals^[23, 24], semiconductors^[25-28] (e.g. Si, GaAs etc), superconductors^[29], graphene^[30], and microelectromechanical systems^[31] where the intrinsic properties of MMs can be modulated by external stimuli such as voltage bias, optical light, electrical bias, and temperature. However, among these approaches translating them for large scale practical applications require either huge cost investment or advance level fabrication.

Thus, solution-processed semiconductors are a viable alternative that provides ease of integration with diverse range of optoelectronics functionalities. On the other hand, split ring resonators are the most commonly studied meta-atoms owing to its structural simplicity and ease of tuning optical parameters by structural reconfiguration^[32]. In this study we employed, asymmetric split ring resonator that exhibits high field confinement due to excitation of non-radiative mode which is known as Fano resonance owing to its asymmetric line shape in the transmission spectra^[33-35]. In chapter 3 we discussed about the terahertz split ring resonator (TASR) and its surface current characteristic for different resonances. Thus, we opted TASR due to Fano resonance and its strong sensitivity towards the surrounding medium as a metadvice for studying the 2D perovskite based ultrafast THz devices.

In this chapter, we report a facile ultrafast THz photonic device by integrating 2D perovskites with THz metamaterial for advanced manipulation of THz waves. The existence of QWs in the 2D perovskite thin film offers stable excitons at room temperature. Thus, the presence of QWs provides an additional relaxation channel to the photoexcited free carrier that manifests as ultrafast relaxation. The synergic relation between 2D perovskite with scalable metamaterials offer an efficient active metamaterial with enhanced optical features. In this work, we explore the free carrier as well as exciton dynamics using time-resolved THz spectroscopy (TRTS). Furthermore, we demonstrate an ultrafast active metadvice using solution-processed 2D perovskite thin film spin coated over TASR. Here, we achieve 93% modulation of Fano resonance amplitude, showing ultrafast switching times of 20 ps (i.e., ~ 50 GHz modulation speed) which is fastest for the solution processed semiconductor-based hybrid metadvice.

4.2 Structural and optical characterization of 2D perovskite thin film

The general formula for Ruddlesden-Popper (RP) perovskites family is $(\text{RNH}_3)_2\text{A}_{n-1}\text{M}_n\text{X}_{3n+1}$ where RNH_3 is an organic cation; A is monovalent organic cation; M is a divalent metal cation, X is a halide anion and n represent the number of $[\text{MX}_6]^{4-}$ octahedral layers sandwiched between organic cation layers. Since the density of QWs decreases by increasing the layers of 2D perovskites (n). Thus, as control reference we used $n = 1, 2$ and ∞ (i.e. 3D perovskite). The chemical formula for $n = 1, 2$, and ∞ are $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$ or $((\text{PEA})_2\text{PbI}_4)$, $((\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2)_2(\text{CH}_3\text{NH}_3)\text{PbI}_7$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ respectively. The AFM image for all these films were measured to confirm the good quality of the films and presented in **Appendix A**. Structurally, in pure 2D perovskite film the two-consecutive lead iodide octahedral layers $[\text{MX}_6]^{4-}$ are separated by two layers of large organic spacer cations, which are held together via weak Van der Waals forces. The octahedral structure of lead halide leads to the low energy barrier for the charge carriers while poor conductivity of organic spacer leads to the high energy barrier and thus form the QW structure as shown in Figure 4.1a. While $n = 2$ contains stacks of organic and inorganic layers supporting both in-plane and bulk transport of charge carrier. In 3D, each layer of $[\text{MX}_6]^{4-}$ octahedral connected with six neighbors at halogen atoms that forms a network where small organic cations located at the void of the network^[5] as shown in Figure 4.1c.

Figure 4.1 Charge transport in different dimensioned perovskite (a) shows the in-plane charge transport in 2D perovskite. The out of plane movement of free carriers is restricted due to insulating organic barrier. (b) in mixed 2D and 3D perovskite both the in-plane and out of plane motion of free carrier are allowed. (c) 3D perovskite facilitates the charge transport through bulk.

The existence of QWs structure in 2D perovskites makes it unique in the solution-processed semiconductor family. Excitons are formed with high binding energy ($E_b = 0.1\text{-}0.5\text{ eV}$)^[9] in 2D perovskite due to low dielectric screening from the surrounding organic ligands and electrons and holes get confined within the 2D inorganic lattices^[36]. Due its unique structural arrangement, 2D perovskite offer unique spatial redistribution of photogenerated species that is vital for the development of multifunctional active metadvice. By changing the 2D perovskite layer the charge carrier dynamics can be altered. For instance, Blancon et al. showed that there exists an “*edge states*”^[37] at the interface of perovskite layers for $n > 2$ as shown in Figure 4.2a. The unique feature of these “*edge states*” is that it provides a direct pathway for dissociating excitons into longer-lived free carriers. Such dissociated free carriers are expected to be protected from nonradiative decay channel thus contribute to the photocurrent in solar cells or radiative recombination for LED applications. The presence of these edge states alters the carrier dynamics from fast recombination to slow recombination, thus the integration of different layered 2D perovskite i.e. with different n can enable active THz metadvice with various range of switching speed ranging from picosecond to nanoseconds. In addition to this unique feature the presence of QWs aids the ultrafast

relaxation to the photo excited free carrier. In this study we have taken the advantage of this remarkable feature of 2D perovskite for ultrafast THz photonic devices.

Figure 4.2 Various unique properties of 2D perovskite (a) shows the existence of edge states in 2D perovskite for $n > 2$. The existence of this edge states increases the lifetime of free carrier and protected from nonradiative decay. The detailed discussion is given in ^[37]. (b) The existence of quantum well (QW) in 2D perovskite where inorganic layers act as potential well and organic layers serve as potential barriers. (c) Comparison of free carrier dynamics (normalized) for 2D, mixed 2D and 3D and pure 3D perovskite. The presence of QW in 2D perovskite provides an additional relaxation channel for the photoexcited free carrier as compared to other alternative that manifests as ultrafast relaxation.

Figure 4.2b shows the schematic of QW structure formed by altering semiconductor inorganic layers and organic layers. The excitons are formed inside the QW with binding energy ranging from 0.1-0.5 eV^[9]. Photoexciting with optical pump beam with energy above the bandgap of perovskite generates free carriers. We employed Optical Pump and Terahertz Probe (OPTP) spectroscopic technique to monitor the free carrier relaxation dynamics. We discussed the detail of OPTP in chapter 2. Figure 4.2c shows the normalized free carrier dynamics measured using OPTP for 2D, mixed 2D -3D and 3D perovskites. Increasing “ n ” reduces the density of QWs thus the additional relaxation channel for photo excited free carrier reduces as result we observe slow relaxation while moving from 2D to 3D as shown in Figure 4.2c. All the samples were photoexcited above the bandgap ($E_{g, 3D} = 1.5$ eV, $E_{g, 3D-2D} = 1.8$ eV, $E_{g, 2D} = 2.2$ eV) with 400 nm ($E = 3.1$ eV) optical pump beam and THz waves used as probe to record the free carrier relaxation dynamics. Pumping the 2D perovskite above the bandgap generates free carriers and

excitons. We employed OTP to unveil the dynamics of free carriers as well as excitons. In OTP experiment the attenuation in the peak amplitude of THz waves is proportional to the real part of photoconductivity which mostly arise due to in-phase motion of free electrons with THz electric fields^[38, 39]. The free carrier dynamics is recorded by monitoring the change in peak amplitude of THz waves by varying pump delay time. A translational delay stage with micrometers spatial precision is used for inducing delay between pump and probe. The detailed experimental procedure of OTP measurements are discussed in chapter 2. In contrast, the presence of excitons or bound electrons induces a phase shift in THz waves which is proportional to the imaginary part of photoconductivity. Thus, by monitoring the change in THz amplitude at zero crossing of THz pulse gives the excitons dynamics^[38-40]. In order to validate that the presence of excitons in 2D perovskite induces phase shift, we recorded differential change in THz electric field as shown in Figure 4.3a. The phase shift in differential THz electric field ensures that each point has been phase shifted due to presence of excitons. Figure 4.3 shows the differential change in THz electric field (Red solid line) at $\tau_{\text{pump}} = 1.5$ ps. It is clearly evident that the present of excitons induced phase shift in the THz pulse thus monitoring the change in THz amplitude at zero crossing reflects the exciton dynamics.

Figure 4.3 Transmitted THz pulse from pristine 2D perovskite thin film. Blue solid line shows the THz pulse when perovskite thin film is not illuminated with pump beam. Red solid line shows the differential change in THz electric field (ΔE) recorded at pump probe delay time 1.5 ps. The shift in ΔE arises due to the presence of excitons that adds up phase. Thus recording the change in THz amplitude at zero crossing provides the exciton dynamics.

Further, to ensure that the phase shift in THz pulse is arising due to the presence of excitons, we present THz electric field (zoomed) transmitted through perovskites thin film at no pump and pump condition as shown in Figure 4.4. We highlight three points *a* (peak point), *b* and *c* (zero crossing), where we recorded the change in terahertz amplitude ($\Delta T = T_{\text{pump}} - T_{\text{no pump}}$) using pump-probe measurement, as shown in Figure 4.4. It is clear from the Figure 4.4 is the sign of ($-\Delta T$) changes from positive to negative. We want to stress that in the measurements, the phase of lock-in-amplifier was kept unchanged thus, the change in sign of ($-\Delta T$) measured at different THz pulse positions solely comes from the change in phase induced by the bound excitons in 2D perovskite.

Figure 4.4 Effect of phase change induced by exciton in THz amplitude where the change in sign of $(-\Delta T = T_{\text{pump}} - T_{\text{no pump}})$ changes from positive to negative from point “a” to “c”. The THz pulse shifts due to presence of excitons which induces the negative sign of $(-\Delta T)$ at zero crossing.

Figure 4.5a represents the 3D color plot of ΔT at different THz pulse position (shown as blue dots in Figure 4.5b). In 3D plot, the gradual change in color represents the change in sign of $(-\Delta T)$ from positive (measured at peak position, marked as (i) in Figure 4.5b) to negative (measured at zero crossing, marked as (iii) in Figure 4.5b). This change in sign of $(-\Delta T)$ can be clearly explained by Figure 4.4, where at peak point (point *a* in Figure 4.4a) the THz amplitude is modulated by free carrier (i.e. $T_{\text{no pump}} > T_{\text{pump}}$). Similarly, at point “b” there is no in amplitude modulation (i.e. $T_{\text{no pump}} = T_{\text{pump}}$) and at point “c” (i.e. $T_{\text{no pump}} < T_{\text{pump}}$). This occur due to phase shift in THz pulse owing to the presence of excitons. Thus, the presence of excitons set the sign of $(-\Delta T)$ to vary from positive to negative.

Figure 4.5 (a) 3D color plot of ΔT recorded at different THz delay position shows as blue dots in “b”. (b) Transmitted THz pulse recorded from non-excited 2D perovskite thin film. Blue dots represent the delay positions where change in THz amplitude (ΔT) are recorded which shows the change in sign from positive to negative while moving from point (i) to (iii)

Now we know that the presence of excitons imparts the phase shift in THz pulse. Hence using OPTP, we monitor the dynamics of both the species (free electrons as well as excitons) in 2D perovskite that is critical in terms of understanding the fundamental physics as well as device applications. Figure 4.6 shows the real and imaginary part of photoconductivity at various pump fluences recorded using time-resolved THz spectroscopy. The real of photoconductivity is recorded by monitoring the change in THz peak amplitude by varying the pump-probe delay time. The change in THz peak (ΔT_{peak}) amplitude is proportional to the free electrons number densities thus monitoring the change in ΔT_{peak} captures the free electrons dynamics. While on the other hand monitor the change in THz amplitude at zero crossing ($\Delta T_{\text{zero crossing}}$) (see zero crossing marked in Figure 4.3) mostly capture the dynamics of bound electrons or excitons as shown in Figure 4.6b. Mathematically the real and imaginary part of photoconductivity is written as:

$$\Delta\sigma_{real}(\tau) = \frac{-\varepsilon_0 c}{d} (n_{air} + n_{sub}) \frac{\Delta T_{peak}(\tau)}{T} \quad (4.1)$$

$$\Delta\sigma_{imag}(\tau) = \frac{-\varepsilon_0 c}{d} (n_{air} + n_{sub}) \frac{\Delta T_{zero\ crossing}(\tau)}{T} \quad (4.2)$$

where d is the thickness of perovskite film (in our case it is 60 nm), c is the speed of light, ε_0 is the vacuum permittivity, n_{air} and n_{sub} are the refractive indices of air and substrate (in our case substrate is quartz and THz refractive index is 2.1), T is the THz transmission through perovskite thin film at no optical pump, ΔT_{peak} and $\Delta T_{zero\ crossing}$ are the change in THz amplitude recorded at peak and zero crossing of THz pulse at different pump-probe delay time “ τ ”. The detail derivation of photoconductivity from experimentally recorded THz transients are given in **Appendix A (section A2)**.

For clarity the plots corresponding to different pump fluence are vertically offset in Figure 4.6. To understand the relaxation dynamics of photoexcited free carriers and excitons, THz transient dynamics at different pump fluences are fitted using bi-exponential decay function ($A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$), where τ_1 and τ_2 represent the time constants for the fast and slow processes, respectively. To include the instrument response, we convoluted the bi-exponential decay function with instrumental response function as shown:

$$y = c + \left[\left(A_1 e^{-\frac{x-x_0}{\tau_1}} \right) \left(1 - \operatorname{erf} \left(\frac{-\left(x - x_0 - \frac{s^2}{\tau_1} \right)}{s} \right) \right) \right] + \left[\left(A_2 e^{-\frac{x-x_0}{\tau_2}} \right) \left(1 - \operatorname{erf} \left(\frac{-\left(x - x_0 - \frac{s^2}{\tau_2} \right)}{s} \right) \right) \right] \quad (4.3)$$

where τ_1 and τ_2 are the lifetimes corresponds to fast and slow process respectively and A_1 , A_2 are their respective amplitudes, s is the erf (error function) parameter and x_0 , c are the axis offsets.

Figure 4.6 Transient real and imaginary THz photoconductivity ($\Delta\sigma$) at different pump fluences (a) Transient real photoconductivity recorded by monitoring the change in THz peak amplitude at various pump fluences. (b) Transient imaginary photoconductivity recorded by monitoring the change in THz amplitude recorded at zero crossing of THz pulse. For clarity the graphs at various pump fluences are vertically offsets. Black solid line in **a** and **b** represent the biexponential fit.

The extracted time constants for free electrons dynamics and excitons are shown in Table 1 and 2 respectively. In free carrier relaxation processes, the biexponential fit reveals that the initial fast

relaxation process is independent of pump fluences (~ 0.2 ps). The relaxation of photoexcited free carriers follows various pathways to relax back to the equilibrium. It includes trap-assisted monomolecular recombination, bi-molecular recombination and many-body Auger recombination. The detailed discussion on various type of recombination are presented in **Appendix A (section A5)**. In the context of 2D perovskites by examining the behaviour of time constants at various pump fluence, we identify the relaxation pathway. Since, the initial fast relaxation process is independent of pump fluence (~ 0.2 ps), thus we attribute this fast relaxation process to be phonon-mediated, as phonon-mediated relaxations are either independent of pump fluence or increase with pump fluence due to hot phonon effect^[41, 42]. While on the other hand the time constant for slow relaxation process decrease with pump fluence. We attribute this to be trap-assisted relaxation because the densities of traps decrease with increasing pump fluence. An important point to be noted here is that the slow relaxation time (τ_2) shows the ultrafast recovery, which falls in picoseconds time scales. This remarkable feature in 2D perovskite arises due to the presence of QWs that provides an additional relaxation channel for the photo excited free carrier. The free carriers get localized in the QWs due to quantum confinement and form an exciton.

Following the previous studies on 2D materials and transition metal dichalcogenides, to unveil the exciton dynamics in 2D perovskite, the measured imaginary part of photoconductivity is fitted using biexponential decay function. The extracted time constants are shown in Table 2. The fit reveals that both the decay time constant decrease with pump fluence. We attribute this as many body assisted Auger recombination, as Auger assisted recombination highly depends on carrier densities and becomes faster with an increase in pump fluences.

Table 1: Time constants of the free carrier dynamics extracted by fitting the real photoconductivity (Figure 4.6a).

Pump fluence ($\mu\text{J}/\text{cm}^2$)	t_1 (ps)	t_2 (ps)
300	0.23 ± 0.04	2.9 ± 0.2
400	0.18 ± 0.01	3.5 ± 0.4
450	0.26 ± 0.01	5.0 ± 0.1
500	0.17 ± 0.01	7.2 ± 0.9
550	0.20 ± 0.01	9.0 ± 2.0

Table 2: Time constants of the exciton dynamics extracted by fitting the imaginary photoconductivity (Figure 4.6b).

Pump fluence ($\mu\text{J}/\text{cm}^2$)	t_1 (ps)	t_2 (ps)
300	3.2 ± 0.4	70 ± 30
400	2.5 ± 0.2	60 ± 10
450	1.6 ± 0.3	31 ± 6
500	1.2 ± 0.3	28 ± 5
550	1.1 ± 0.2	24 ± 5

4.3 Integration of 2D perovskite with metamaterial

In the solution-processed semiconductor families, 2D perovskite exhibits ultrafast relaxation. We utilize this feature of 2D perovskite for ultrafast THz metadvice. For this study asymmetric split ring resonators (ASRR) are opted due to its structural simplicity and ability to exhibit Fano resonance. Fano resonance offers strong field confinement of terahertz electric fields showing high sensitivity towards external perturbations that make it perfect platform for study strong light-matter interaction. The ASRR structures are fabricated on a quartz substrate.

Photolithography was used to define the Fano resonant metamaterial structures. 200 nm Aluminium (Al) was thermally deposited and lifted off using acetone. The thin film of 2D perovskite is spin coated on the top of fabricated metamaterial. Figure 4.7a shows the optical image of 2D perovskite coated hybrid metadvice. The geometrical dimensions of Fano resonators are marked in the inset of Figure 4.7c. It has a square periodicity $P_x = P_y = P = 75$ μm , length (l) = 60 μm , width (w) = 6 μm , gap (g) = 3 μm and asymmetry (x) = 15 μm . Figure 4.7c shows the schematic of optical pump and terahertz probe of the 2D perovskite coated hybrid metadvice. 400 nm is used as optical pump beam due to having energy higher than the bandgap of 2D perovskite ($E_g = 2.4$ eV). Pumping the perovskite thin film above the bandgap instantaneously generates free carriers in the conduction band that undergoes via various relaxation channels to reach equilibrium.

Figure 4.7 Artistic illustration of the perovskite-coated hybrid metadvice (a) optical image of the fabricated metadvice (b) Schematic of the quantum confinement of free carriers within the quantum well (QW) structure of pure 2D perovskite. The quantum confinement leads to formation stable exciton at room temperature. (c) Schematic of optical pumping scheme illustrates the THz transmission measurement from 2D perovskite coated hybrid metadvice.

The free carrier relaxation dynamics in 2D perovskite is discussed in detail in the previous section. The photo excited free carriers increase the conductivity of perovskite thin film and decrease the terahertz transmission. To be more precise the conductive patch of perovskite thin film that lies in the capacitive gap of the ASRR quench the amplitude of Fano resonance. At the capacitive gap, the conductive patch of perovskite thin film connects both the metallic arms of ASRR that manifests as switching off the Fano resonance in the transmission spectra. Figure 4.8

summarize the above-mentioned concept. Figure 4.8a shows the schematic of optical pump excitation of 2D perovskite coated hybrid metadvice. The transmission spectra correspond to no pump and the presence of pump case are shown in Figure 4.8b. As mentioned above the increasing the photoconductivity of perovskite thin film shorts the capacitive gap of ASRR that manifests as switching off the Fano resonance as shown in Figure 4.6: red solid line. The switching behavior of Fano resonance can also be seen in terms of quenching of confined THz field as shown in the insets of Figure 4.8b. Such active control on THz field is of great interest, particularly in sensing and communication applications.

Figure 4.8 (a) Schematic of optical pump for 2D perovskite coated hybrid metadvice, where 400 nm is used as optical pump beam to photoexcite the free carrier in 2D perovskite thin film. (b) Simulated THz transmission from the system architect shown in a. Black solid line shows the Fano resonance which is simulated for $\Delta\sigma = 0$ and red solid line shows the Fano switching simulated for $\Delta\sigma = 3500$ S/m. Insets show the simulated THz electric field for both the cases where strong THz electric field is confined in the capacitive gap for Fano resonance case.

The optical characterization of 2D perovskite coated hybrid metadvice was done using ZnTe based OPTP measurement scheme. The detailed discussion on OPTP measurements are given in

Chapter 2. Figure 4.7c shows the schematic of optical characterization of hybrid metadvice where the perovskite film is photoexcited using 400 nm optical pump beam to generates photocarrier. The frequency dependent transmission spectra at various pump fluences are shown in Figure 4.9a. The normalized transmission spectra were calculated using $T(\omega) = \left| \frac{E_s(\omega)}{E_r(\omega)} \right|$, where $E_s(\omega)$ and $E_r(\omega)$ are Fourier transformed frequency domain electric field of sample and substrate respectively. In the absence of an optical pump beam, the transmission spectra exhibit strong asymmetric spectral profile (black solid curve, Figure 4.9a) at 0.7 THz. The strong asymmetric line shape in the transmission spectra is the signature of Fano resonance. As explained above, generating the free carrier quenches the amplitude of Fano resonance. Hence, by increasing the optical pump fluence the amplitude of Fano resonance gradually reduces and completely switch off at $250 \mu\text{J}/\text{cm}^2$, as shown in Figure 4.9a. To emulate the experimentally recorded spectra, we performed full-wave 3D frequency domain simulation in CST microwave studio. In the simulation the quartz substrate is treated as lossless material with refractive index 2.1 and Al is treated as lossy metal with predefined permittivity for terahertz frequencies. The floquet periodic boundary conditions are applied in both x and y directions to emulate the collective response of ASRR. The simulated transmission spectra is shown Figure 4.9b that shows close resemblance with experimentally recorded spectra (Figure 4.9a). In simulation the perovskite thin is characterized with variable conductivity. Varying the photoconductivity in simulation is equivalent to increasing the pump fluence in the experiment. Additionally, we provide the simulated electric field distribution at the Fano resonance frequency (0.7 THz) for different photoconductivity (σ) values of perovskite thin film. When $\sigma = 0 \text{ S/m}$, there exists high THz electric field confinement in the capacitive gap of ASRR as shown in Figure 4.9c. Further,

increase the value of σ results in a pronounced suppression of Fano resonance amplitude that manifests as reduction in electric field strength in the capacitive gap, as shown in Figure 4.9c.

Figure 4.9 Photo switching response of the 2D perovskite-based hybrid metadvice. (a) Experimentally measured amplitude transmission spectra recorded at various pump fluence illustrating the switching of Fano resonance. **(b)** Numerically simulated THz transmission emulating the experimental condition of **a**. **(c)** Numerically simulated electric field distribution in hybrid metadvice for different photoconductivity values of 2D perovskite thin film.

To unveil the ultrafast feature of 2D perovskite coated hybrid metadvice, we performed the transmission measurement at different pump-probe delay time (τ_p). Figure 4.10a shows the experimentally recorded transmission spectra at various τ_p where the respective solid colors correspond to the pump-probe delay showed using dots in the inset of Figure 4.10a. Black dot represents the scenario when pump and probe beams are time-matched thus giving rise to maximum change in ΔT . This results in the maximum amplitude quenching of Fano resonance as evident in Figure 4.10 black solid line. Further, the gradual increase in Fano resonance amplitude is evident as free carriers relax back to the equilibrium state, as shown in solid green line in Figure 4.10a. The important point to be noted here that the recovery of Fano occurs within 20 ps time scale. To quantify the modulation depth of Fano resonance, it is calculated as,

$$\text{Modulation } (M) = \frac{|T_{off} - T_{on}|}{T_{off}} \times 100 \%, \text{ where } T_{on} \text{ and } T_{off} \text{ are the amplitude of Fano}$$

resonance with and without optical pump respectively. Figure 4.10b shows the experimentally calculated modulation depth (M) with pump fluence. We observe a systematic increment in M with pump fluence and reach close to unity ($M = 93\%$) at $250\ \mu\text{J}/\text{cm}^2$. In compare to PbI_2 (Chapter 3) coated hybrid metadvice the value of pump fluence is low in 2D perovskite. The inset of Figure 4.10b shows the contour plot of amplitude modulation of Fano resonance at different pump fluence. The color gradient shows the strength of normalized modulation. At Fano resonance frequency (0.7 THz), the maximum modulation is achieved at $250\ \mu\text{J}/\text{cm}^2$.

Figure 4.10 Ultrafast switching of Fano resonance (a) Measured THz transmission spectra recorded at different pump-probe delay instances. It is clear that at peak photoconductivity i.e. black solid line (black dot in inset) the strength of Fano resonance is weak which further strengthen when free carriers are relax to equilibrium i.e. green solid line (green dot in inset). Inset shows the free carrier dynamics where different color dots show the pump-probe delay instances where THz transmission is recorded and shown with same colored solid line. (b) Amplitude modulation (M) of Fano resonance at different optical pump fluences. The contour plot represents the amplitude modulation of Fano resonance at different pump fluence. It is evident that modulation depth for Fano resonance is near unity.

Further to ensure the effect of optical heating on device performance, we measured the terahertz transmission through bare perovskite thin film under the constant illumination of 400 nm optical pump beam. We choose the pump fluence to be $300\ \mu\text{J}/\text{cm}^2$ which is slightly higher than the

pump fluence to achieve near unity modulation. The recorded terahertz transmission spectra are shown in Figure 4.11a. From the Figure 4.11 it is evident that the perovskite film does not degrade under the illumination of optical pump even at 45 min heating. This shows the robustness of our proposed hybrid metadvice.

Figure 4.11 THz transmission through the perovskite thin film. (a) The perovskite thin film is illuminated with 400 nm pump beam to observe the effect of optical heating. The pump fluence is kept at $300 \mu\text{J}/\text{cm}^2$. It is evident that the effect of optical heating is negligible in THz transmission. (b) Effect of optical pump fluence in the THz transmission through bare z-cut quartz

Further to eliminate any nonlinear effect from substrate (here quartz) in the range of operating pump fluence we performed THz transmission through bare quartz substrate where quartz was kept under 400 nm optical pump. Figure 4.11b shows the recorded THz transmission from bare quartz substrate. It shows that quartz does not include any nonlinear absorption even at $600 \mu\text{J}/\text{cm}^2$, which is much higher than the operating range of pump fluence i.e. $\sim 250 \mu\text{J}/\text{cm}^2$.

4.4 Active flexible metadvice

In the quest of developing ultrafast THz device with low cost and ease of integration, the solution processed semiconductors specially 2D perovskite has shown promising potential. The 2D perovskite has shown low threshold switching ($\sim 250 \mu\text{J}/\text{cm}^2$), high stability and ultrafast control on THz waves. In the previous section we have shown the 2D perovskite-based hybrid metadvice performs really well with rigid substrate (quartz in this case). In the recent years, there has been ever increasing demand for developing flexible metadvice that has huge potential in imaging, wearable device, flexible sensors and portable solar cells. In particular the THz frequency region has attracted considerable attention owing to its unique properties that spans its application domains from non-destructive imaging, material characterization to high-speed wireless communication. To put into a perspective, in current technologies, THz images for security applications are obtained by rotating the detectors through 360° . This makes devices bulky and less portable. Thus, to significantly expand the usable range of THz devices for future disruptive applications, a flexible and portable platform is vital.

In this direction, significant research has been done, such as flexible THz scanner and detectors^[43, 44]. These findings have opened the avenue for the flexible THz photonics. The ease of integration just by spin coating of solution processed 2D perovskite with metasurface allow us to easily translate the ultrafast THz modulation functionalities on flexible platform. For this study, we used polyimide substrate owing to its mechanical flexibility, high thermal stability and low THz absorption. To maintain the simplicity, we fabricated identical ASRR (similar to quartz, previous section) on the flexible polyimide substrate. Figure 4.12a shows the schematic of 2D Perovskite coated hybrid metadvice on flexible substrate where the dimensions of ASRR are

labelled in Figure 4.12b. The optical image of fabricated device along with its bending features are shown in Figure 4.12c. We employed OTP measurement scheme to record the transmission through metadvice. 400 nm optical light is used as pump beam owing to energy higher than the band gap of perovskite thin film. Here again, pumping the perovskite thin film above the bandgap generates the charge carrier which quenches the amplitude of Fano resonance. The advantage of using polyimide substrate is its high thermal stability (stable between -270 to 400°C)^[45], thus the performance of the device does not get affected even at high pump fluence.

Figure 4.12 Active flexible hybrid metadvice. (a) Artistic illustration of optical pumping scheme of THz transmission through flexible hybrid metadvice. (b) Unit cell of THz Fano resonator, where d is the asymmetry = 15 μm , g is the capacitive gap = 3 μm , w is the width of resonator = 6 μm and p is the periodicity = 75 μm (c) Optical image of flexible metadvice fabricated on polyimide substrate.

The THz transmission measurement results are summarized in Figure 4.13. The OPTP measurement reveals the ultrafast carrier dynamics in 2D perovskite thin film. The transient decay dynamics is shown in the inset of Figure 4.13a. The different color dots represent the time instance where the THz transmission measurement has been taken, and the corresponding

transmission spectra are shown with their respective colors in Figure 4.13a. We used a mechanical delay stage to introduce the time delay between pump and probe beam. Red dot represents the time instance when the pump and probe beam are time matched thus the change in THz transmission i.e. ΔT is maximum. At this instance, the density of charge carrier in perovskite thin film are maximum thus manifesting as highly quenched Fano resonance amplitude as shown by solid red line in Figure 4.13. The subsequent relaxation of free carriers results in strengthening the Fano resonance as shown by yellow and green solid colors plots. The complete retrieval of Fano resonance occur within 20 ps. Thus, changing the substrate does not alter the performance of 2D perovskite coated hybrid metadvice in terms of its ultrafast response. Further, we performed pump fluence dependent THz transmission measurement. Increasing the pump fluence increases the number densities of charge carrier, thus Fano resonance amplitude decrease. Figure 4.13b shows the pump fluence dependent THz transmission. We observed complete modulation of Fano resonance at $350 \mu\text{J}/\text{cm}^2$. As compared to quartz substrate, the pump fluence number is slightly higher. It occurs may be due to the difference in morphology of spin coated perovskite thin film on flexible substrate.

Figure 4.13 THz transmission through flexible metadvice (a) THz transmission for different pump-probe delay time. The red solid line represents the maximum Fano resonance modulation owing to maximum photoconductivity. The strength of Fano resonance is retrieved back as farrier carriers are relax to equilibrium (green solid line). Inset shows the free carrier dynamics of pristine 2D perovskite coated on polyimide substrate where dots represent the pump-probe time instances where THz transmission measurements are taken. (b) Optical modulation of Fano resonance. Complete quenching occurs for optical pump of fluence $350 \mu\text{J}/\text{cm}^2$.

Further to show the robustness and flexibility of device performance, we performed the transmission measurement by bending the flexible metadvice. Figure 4.14 shows the experimentally measured THz transmission for bent metasurface. We observe THz modulation for different bent metasurface. The detailed calculation of the curvature of metasurface is given in Appendix A (section A3).

Figure 4.14 Curvature dependent THz transmission measurement (a, b and c) THz transmission measurement from flexible device with radius of curvature (κ) 1.03, 0.84 and 0 cm^{-1} respectively.

4.5 References

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Chapter 5

Ultrafast THz photo physics of solvent engineered triple-cation halide perovskite

5.1 Introduction

So far in the previous chapters, we have seen the positive performance of solution-processed halide perovskite for ultrafast terahertz photonic devices. The performance of perovskite integrated terahertz (THz) metadvice is highly depends on the free carrier dynamics of perovskite. Thus, it is imperative to understand the mechanism of free carrier relaxation and the factors that affect it. The theme of this chapter is to address this important question. In this chapter, we investigate the nature of conduction and charge carrier dynamics of mixed organic-inorganic cations [methylammonium (MA), formamidinium (FA) and cesium (Cs)] along with mixed halides [iodine (I) and bromine (Br)] perovskite synthesized in different solvents using optical pump terahertz probe (OPTP) spectroscopy. The reason for selecting mixed cation-anions perovskite is its high ambience stability as compared to single cation-anion. Our studies reveal that carrier mobilities, diffusion length and carrier relaxation dynamics strongly depend on the type of solvent used for the preparation of the perovskite thin film. The mixed cation prepared using dimethylformamide/dimethylsulfoxide (DMSO) solvent shows greater electronic properties like mobility and diffusion length compared to γ -butyrolactone solvent. These findings provide valuable insight to improve the charge carrier transport of perovskite thin film through solvent

engineering that not only is extremely useful for ultrafast THz photonic devices but also benefit in improving the perovskite based solar cell performances.

5.2 Why mixed cation perovskite?

The emergence of hybrid organic-inorganic perovskite (HOIP) has revolutionize the field of solar energy and optoelectronics application such as light emitting devices and lasing owing to its excellent photoconversion efficiency and distinct optical features like high absorption and tunable bandgap. However, one of the major challenges to realize the practical applications using perovskite is its very low ambience instability particularly in the presence of moisture. To mitigate this limitation engineering, the compositions of perovskites offer a positive route. Substituting and mixing the various cations or anions or both offers a broad window for performance optimization. In this regard, mixing the smaller inorganic cation, such as cesium (Cs), has proven to be more effective in stabilizing the phase owing to its smaller size. Recently, mixed organic-inorganic cations (methyammonium, formamidinium and cesium) along with the mixed halides (iodine and bromine) $[\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3]$ have emerged as promising candidate for solar cells with excellent photoconversion efficiency ($\sim 21\%$)^[1] and better ambience stability.

5.3 Optical pump terahertz probe (OPTP) of mixed cation/anion perovskite

To study the carrier dynamics and investigate we employed ZnTe based optical pump terahertz probe spectroscopy where perovskite thin film was photoexcited using 400 nm pump beam and the dynamics of excited carrier were probed using terahertz pulse. In the experiment, the diameter of the optical pump and terahertz probe were kept 6 and 4 mm respectively, to ensure

the uniform excitation of the probe region. Terahertz radiation owing to its low photon energy (1 THz = 4.1 meV) is a perfect candidate to probe the free carrier dynamics in a non-contact way. Additionally, the OPTP spectroscopy gives both the real and imaginary part of the complex optical constants which allows to extract the carrier density, electronic mobility and diffusion lengths.

We prepared the mixed cations (MA/FA/Cs) and anions (I/Br) using two different solutions named as DMF/DMSO and GBL. Both the perovskite thin film spin coated on quartz substrate for OPTP measurement. Photoexciting the perovskite thin film above the bandgap instantaneously generate the free carrier that interacts with terahertz probe pulse, thereby reducing the transmission. Thus, monitoring the change in terahertz transmission ($\Delta T/T$) unravels the free carrier relaxation dynamics. We employed 400 nm as an optical pump beam owing to energy ($E \sim 3.1$ eV) higher than the bandgap ($E_g \sim 1.58$ eV)^[2] of perovskite thin film. To unravel the carrier dynamics, we measured the change in transient photoconductivity of the perovskite thin film as terahertz photoconductivity is directly proportional to the product of charge carrier and carrier mobilities. Here, we assume that the carrier mobilities do not change with pump-probe delay thus decay in terahertz transient reflects the temporal evolution of charge carrier densities. To illustrate it more clearly, we write the mathematical expression of terahertz photoconductivity using thin film approximation^[3] as:

$$\Delta\sigma(t_p) = \frac{\epsilon_0 c}{d} (n_{air} + n_{sub}) \frac{-\Delta T(t_p)}{T_{No\ pump}} \quad (5.1)$$

where, ΔT is the change in terahertz transmission, c is the velocity of light, $T_{No\ pump}$ is the terahertz transmission when the optical pump is absent, ϵ_0 is the vacuum permittivity, n_{air} , n_{sub}

are the refractive index of air and substrate (in our case quartz) respectively and d is the thickness of perovskite thin film. Also, $n = \Delta\sigma(t_p)\mu$, thus monitoring the change in photoconductivity allow to capture the carrier dynamics.

Figure 5.1 THz transient dynamics (a, b) THz transient dynamics recorded using time-resolved THz spectroscopy for perovskite thin film prepared using DMF/DMSO and GBL solvent respectively.

Figure 5.1 shows the change in terahertz transient dynamics recorded at various pump fluence for the perovskite film prepared using DMF/DMSO and GBL solution, respectively. To understand the carrier relaxation mechanism, we performed rate equation fitting, as shown in Figure 5.1 in solid lines. The detailed procedure for fitting the THz transient are given in Appendix A (section A4). Mathematically, the rate equation is given by^[4]:

$$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n \quad (5.2)$$

where “ n ” is the carrier density, k_1 , k_2 and k_3 are the monomolecular, bimolecular and Auger recombination rate constants, respectively. The extracted time constants are shown in Table 1.

Solvent	k_1 (s ⁻¹)	k_2 (cm ³ s ⁻¹)	k_3 (cm ⁶ s ⁻¹)
GBL	$(1.5 \pm 0.3) \times 10^8$	$(6.2 \pm 1.2) \times 10^{-10}$	2.4×10^{-27}
DMF/DMSO	$(1.0 \pm 0.84) \times 10^8$	$(2.6 \pm 1.8) \times 10^{-10}$	4×10^{-28}

The identical values of monomolecular and bimolecular constants ensure identical diffusion length at low carrier concentration as shown in Figure 5.2. At higher charge carrier concentrations, Auger recombination processes reduce the diffusion length. Thus, perovskite thin film prepared using GBL solvent shows lower diffusion length at high carrier concentration owing to its high value of k_3 .

To calculate the diffusion length, L_D , we need to extract the initial mobility. The initial mobility is extracted using Equation 1, from the photoconductivity expression. The initial mobility depends on the peak photoconductivity $\mu = \Delta\sigma(t_{peak}) / q\eta N_0$ where, q is the elementary charge, N_0 is the initial charge carrier density, and η is the quantum yield of excitation which is equal to the ratio of the induced charge-carrier density and the absorbed photon density. The initial carrier density is estimated using:

$$N_0 = \frac{\alpha(\lambda)\lambda f(1 - 10^{-OD})}{hc} \quad (5.3)$$

where α is the absorption coefficient at the excitation wavelength ($\lambda = 400$ nm, for our case), f is the incident pump fluence, and $(1 - 10^{-OD})$ is the fraction of pump light absorbed by the

sample, where OD is the optical density given by $OD = 0.434 \alpha l$, where l is the thickness of perovskite thin film.

Since the value of η lies between 0 and 1 ($0 \leq \eta \leq 1$), we extract the lower limit of charge-carrier mobility using $\eta = 1$. The extracted mobilities at various pump fluences are shown in Figure 5.2. The figure shows that the carrier mobilities for the perovskite thin film prepared using DMF/DMSO (shown as solid red line) is high as compared to the thin film prepared using GBL solvent (shown as solid black line). Also, by increasing the pump fluences, the mobilities decrease from 300 to 80 $\text{cm}^2 (\text{V s})^{-1}$ for the DMF/DMSO prepared film, while it decreases from 90 to 15 $\text{cm}^2 (\text{V s})^{-1}$ for the GBL solvent. Both types of thin films exhibit the identical decreasing trend with increasing pump fluence. We attribute this to increase in electron scattering rate. At high pump fluences, the rise in free carrier densities leads to Auger recombination which mainly involves many-body effects thus increases the scattering rate of free carriers. The mathematical relation between mobility and scattering rate is following: $\mu = e/\Gamma m$, where e , Γ , and m are the elementary charge, scattering rate and mass of free carrier respectively. From the mathematical relation, it is clear that increasing scattering rates reduces the carrier mobilities which is also evident in the experimentally extracted mobilities shown in Figure 5.2. The solid red line represents the variation of carrier mobility as a function of pump fluence for the perovskite film prepared using DMF/DMSO solvent, while the solid black line depicts the mobilities for GBL prepared solvents. Figure 5.2 clearly shows that the film prepared using DMF/DMSO solvent shows higher mobility compared to GBL solvent. This reflects the fact that the morphology of film affects the electronic mobility.

Figure 5.2 Extracted mobility for GBL and DMF/DMSO solvent prepared thin film.

After extracting the mobility, we evaluated the diffusion length, LD, using the extracted rate constants shown in Table 1 and initial carrier mobility using the formula^[5]:

$$L_D = \sqrt{\frac{D}{R_{total}}} \quad (5.4)$$

where, D is the diffusion constant given by $D = \mu k_b T e^{-1}$, here k_b , T, and e are the Boltzmann constant, temperature and elementary charge, respectively. R_{total} is the total recombination rate which depends on rate constants and carrier density

$$R_{total} = k_1 + nk_2 + n^2k_3 \quad (5.5)$$

Figure 5.3 depicts the extracted diffusion length as a function of charge carrier densities. The red and black solid lines represent the diffusion length for perovskite film prepared using DMF/DMSO and GBL solvent, respectively. It clearly exhibits the significant differences in the diffusion length at higher carrier densities that arises due to high Auger recombination rate in the GBL solvent prepared perovskite thin film.

Figure 5.3 Diffusion length calculated by THz spectroscopy reveals that the perovskite film fabricated using DMF/DMSO solvent has high diffusion length.

The extracted mobilities and the diffusion length for the perovskite film prepared using DMF/DMSO and GBL solutions exhibit significant differences. These differences can be attributed to the difference in the film quality due to perovskite-solvent interaction. Figure 5.4 shows the morphology of the spin-coated perovskite thin films prepared using both the solvents. Clearly, the morphology appears to be strongly dependent on the choice of the solvent. The SEM images of the perovskite thin film prepared using DMF/DMSO (Figure 5.4a), and GBL (Figure 5.4b) solvents reveal that the film quality does depend on solvent. The DMF/DMSO solvent prepared films have compact and bigger grain sizes, while GBL based solvent results in a granular texture film. The slow crystallization in GBL solvent gives more defect dominated films, that in turn restricts the mobility and the diffusion length.

Figure 5.2 SEM image of mixed cation/anion perovskite thin film synthesized using (a) DMF/DMSO and (b) GBL

In conclusion, the OPTP study on perovskite thin film prepared using different solvent provide important insights on free carrier dynamics. These informations are critical and useful as it allows to smartly select solvent to prepare the perovskite thin-film based on the application. To put into a perspective, for ultrafast terahertz photonic devices, the free carrier relaxation needs to happen at picoseconds time scales, and the presence of defects assist faster relaxation. As another example, GBL solvent slow the crystallization rate thus it will be more useful in carbon-based perovskite cells where the slower crystallization rate help in better infiltration of perovskite solution through the carbon layer in the ZrO₂ scaffold^[6, 7]. Thus, engineering the solvent in the preparation of perovskite thin film is of great importance for efficiently utilizing the properties of perovskite in various applications.

5.4 References

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Chapter 6

Conclusion and Future direction

With the advent of metamaterials (MMs), there has been rapid growth in terahertz (THz) research activities. Over the year, MMs have offered exciting features and application in the field of photonics. Their structural simplicity and ease to tune on-demand optical properties are the major driving force that provided unprecedented control on electromagnetic waves (specifically here THz waves).

The objective of this thesis was to develop ultrafast THz photonic devices based on solution processed semiconductors (perovskite). A systematic study on the optical characterization of perovskite thin films were presented to unravel the charge carrier dynamics. Followed by this, the integration of MM with perovskite thin film on rigid as well as flexible substrate were presented to demonstrate the ultrafast modulation of THz electric field. The works presented in the thesis show a new prospect to develop a cost effective and efficient ultrafast THz device. This will lay a platform for the new generation of MM based photonic devices in the THz region and bridge the existing gap which is known as “THz-gap”.

Here we present the chapter wise conclusion: In chapter 1, we presented the general introduction of THz waves, metamaterial and optical properties of the solution processed perovskite family. A comparative study between conventional and halide perovskite semiconductor is presented to showcase the potential of perovskite for new generation of ultrafast THz photonic devices.

In the first section of chapter 2, we discussed about the basics of numerical tools that have been utilized to simulate the optical properties of MMs. Followed by this, a detailed section dedicated

to THz time domain spectroscopy (THz-TDS) is presented. It included both the photoconductive antenna and nonlinear crystal (ZnTe) based THz TDS systems and their underlying working mechanism. The experimental layout of Optical pump and terahertz probe (OPTP) is shown which is the heart of this thesis. And the chapter is concluded with the fabrication details of MMs.

Chapter 3,4 and 5 outline the different works of solution-processed perovskite-based hybrid MM hybrid system. In chapter 3, we unravel the ultrafast free carrier dynamics in PbI₂ thin film using time-resolved THz spectroscopy. The integration of thin film of PbI₂ with MM structures enables near unity switching of Fano resonance at 150 ps time scale. Further, the interaction of strongly confined THz electric field with PbI₂ exhibit the change in carrier dynamics. This finding is important as it provides a viable route to develop next-generation active metadvice with multifunctionalities.

Chapter 4 includes the optical characterization of 2D perovskite where using for the first-time using time resolved THz spectroscopy, we showed the dynamics of excitons. The results reveal that the quantum well structure present in 2D perovskite act as an additional channel for the photoexcited free carrier to relax back at ultrafast time scale which is fastest in the solution processed perovskite semiconductor family. As an application outlook, we integrated the MM with 2D perovskite in rigid as well flexible platform and experimentally demonstrated near unity switching of Fano resonance at 20 ps time scales.

The chapter 5, discusses about the optical properties of perovskites prepared using a different solvent. This study suggests that the optical properties of perovskites highly depends on the type of solvent which being used during the fabrication process. These findings are important as it

provides an insight to smartly fabricate the perovskite based on the required optoelectronic properties.

6.1 Future works

6.1.1 Active tuning of photon-phonon coupling

Strong light-matter interaction is the key enabler for numerous potential applications in various branches of science such as chemistry, photonics, biosensing, nonlinear physics and many more. Metamaterial offers a simple and tunable platform to confine on-demand terahertz (THz) electric field inside a cavity. Thus, MMs can be an ideal platform to study the coupling of THz electric field and matter resonance interactions. There are many materials whose lattice vibrations lie in THz spectral region, thus integration of such materials with MM opens up new avenue to study the light-matter interactions which are vital from fundamental as well as a technological point of view.

In this prospect, interaction of THz electric field with halide perovskite is important as it offers a potential way to tune the optoelectronic properties of perovskite. In general, the interaction between light and matters are quantified based on the interaction strength and can be categorized as strong and weak coupling. Both interactions regime is important and offers unique phenomena, as an example, the weak coupling interaction of emitter with cavity alters the spontaneous emission rate of emitter which is given by Purcell factors. Similarly, the strong coupling regime is important to probe many fundamental phenomena and overcome the losses in the coupled system. In this regard, the investigation of perovskite with a strongly confined THz

electric field facilitated by MMs is important. To start, we plan to couple the perovskite phonon mode with MM resonance. The preliminary experimental results show that perovskite has phonon modes which lie in the THz spectral region. Figure 6.1 shows the measured complex conductivity of perovskite which suggest a phonon mode neat 1 THz associated with the bending and stretching of the Pb-X (halide) bonds^[1, 2]. Appearance of phonon modes in conductivity spectra follows Lorentz behavior, where the real and imaginary parts are fitted simultaneously using the standard Lorentz Oscillator model described in Eqn. 1

$$\sigma(\omega) = -i\varepsilon_0\omega(\varepsilon_\infty - 1) + \left(\frac{\varepsilon_0\omega_p^2 \omega}{i(\omega_0^2 - \omega^2) + \omega\Gamma_1} \right) \quad (6.1)$$

where ω_p , ω_0 and Γ_1 are plasma frequency, phonon resonance frequencies and the scattering rate for the oscillator, respectively. The fitting parameters are show in Table 1 which confirms the phonon resonance frequency at 1 THz.

Perovskite	f_0 (THz)	ω_p(THz)	Γ_1 (THz)	ε_∞
	0.99	10.07	2.53	1

To investigate the coupling, we plan to integrate LC resonator with perovskite. The coupling of strongly confined THz electric field in the capacitive gap of the LC resonator with phonon resonance may lead to a strongly coupled system. That manifests as splitting in the transmission spectra of perovskite integrated MM hybrid system. Further, the active tuning of coupling strength via optical pumping is also an important aspect that we will investigate in this study.

Figure 6.1 Terahertz conductivity of perovskite thin film. The peak at 1 THz corresponds to the phonon mode associated with bending and stretching of lead (Pb) and halide (X) bond. The black solid line is experimentally calculated, and red dash line is the Lorentz fit using Eqn. 6.1.

6.1.2 Color tunable ultrafast photonic device

So far, the active metamaterial has seen a diverse range of active materials integrated with MM. Based on the choice of dynamic material, their functionalities vary. The natural progression in the development of active metamaterial is to introduce multifunctionality without changing the passive structure. One of the great obstacles to develop multifunctional metadvice is that the free carrier dynamics of the integrated active materials is difficult to alter after their post process. Thus, smart integration of various active materials with different properties such as bandgap and carrier dynamics may open a potential route. In this regard, halide perovskite offers a promising route owing to its tunable bandgap feature.

Figure 6.2 Schematic for realizing color tunable response (a) Terahertz asymmetric Fano resonator with two layer of active materials with different bandgap and carrier dynamics. (b) Cross section view of the resonator illustrating the silicon (Si) and perovskite (Prv) in the capacitive gap. The large penetration depth of 800 nm in perovskite thin film allow to photoexcite Si thus enabling only the Si photoexcitation by 800 nm. Perovskite thin film cannot be photoexcited by 800 nm owing to large bandgap (> 1.6 eV). While 400 nm pump due to low penetration depth only photoexcite perovskite thus enabling color dependent response of active metadvice.

Here, we plan to integrate perovskite with silicon to achieve pump wavelength dependent ultrafast feature of hybrid metadvice. The schematic of MM is shown in Figure 6.2. The idea is to deposit a stack of 2D/3D perovskite and silicon (Si) in the MM gap. The bandgap of 2D/3D perovskite are higher than 800 nm pump energy^[3] while other hand Si has bandgap 1.1 eV that can be photoexcited by 800 nm pump energy. The charge carrier dynamics in 2D perovskite and Si are completely different where the free carriers relax with few picoseconds in 2D perovskite owing to quantum confinement, on the other hand free carrier relaxation in Si can be varied from microseconds (μ s) to nano seconds (ns). The absorption coefficient of perovskite^[4] suggests the penetration depth for 800 nm optical light vary in the range of 300-400 nm while for 400 nm optical pump beam it is below 100 nm. Thus, the smart integration of perovskite (thickness below 100 nm) and Si can enable wavelength dependent active metadvice that response differently by changing the pump wavelength.

Figure 6.3 (a) Absorption coefficient of methyl ammonium lead iodide perovskite to calculate the wavelength dependent penetration depth^[4]. (b) Penetration depth of perovskite for 800 and 400 nm are 400 nm and 50 nm calculated using $l = 1/\alpha$, where α is the absorption coefficient of perovskite shown in a.

6.2 References

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Appendix A

A1. Circuit model for active Fano resonance:

The reduction in Fano resonance amplitude by increasing the photoconductivity of the active material in the capacitive gap follow exponential decay as a function of photoconductivity, shown in Figure A1a. To elucidate the observed exponential behaviour, we modelled the active metamaterial (MM) with the simple electrical-circuit model. The schematic of Fano resonator with active material in the capacitive gap is shown in Figure A1b.

Figure A1: Electric circuit model for active Fano resonator (a) Amplitude of Fano resonance as a function of the conductivity of active material present in the resonator gap. Dot-dashed line represents the simulated result, where we call the amplitude of Fano resonance as figure-of-merit (FoM), while the solid line represents the curve generated using circuit formula Eq.1. (b) Schematic of an analogues electric circuit for active Fano resonator. Here as example, silicon (Si) is shown as active material thus it is called, Si-TASR (Si-terahertz asymmetric split ring resonator).

This system is identical to the capacitor circuit where the two gaps act as capacitors and the active material placed in the gaps acts as a resistor. The photodoping of active material changes the conductivity that in turn change the resistance. Thus, the photodoped active material is

modelled as a variable resistor. The equivalent circuit model is shown in Figure A1b. The exponential decay of Fano resonance amplitude as a function of photoconductivity can be understood by charge-discharge effect in the capacitor circuit. In the absence of an optical pump, the incidence terahertz (THz) induces a circulating surface current and strong electric field confinement in the gap as can be seen in Figure A1c. This induces a net capacitance in the system. In the presence of the optical pump, the conductivity of active material that is present in gap increases which gradually shorts the gap by increasing the photoconductivity. It results in a reduction of electric field in the gap exponentially analogous to discharging of charge in RC circuit. The relation between electric potential stored in Fano resonator gap and conductivity can be given by:

$$V_c = V_0 e^{-R\sigma} \quad (1)$$

here, V_c is the stored electric potential, V_0 is applied voltage, R is a constant which depends on inversely proportional to the permittivity of active material present in gaps, and σ is the conductivity of active material. Equation 1 is derived using the concept of discharging of the RC circuit. The discharge in RC circuit is written by:

$$V_c = V_0 e^{-\frac{t}{\tau}} \quad (2)$$

where τ is the RC time constant equal to $\tau = RC$. Expressing the R in terms of conductivity σ and using the expression of the parallel plate capacitor, the equation 2 can be rewritten as:

$$V_c = V_0 e^{-\frac{t_0 A_1 g}{l \epsilon_r A_2} \sigma} = V_0 e^{-R\sigma} \quad (3)$$

where, l and A_1 are the length and cross-section of Fano resonator arm, g and A_2 are the capacitive gap separation and area respectively, ϵ_r is the permittivity of the active material placed in the gap and R is a constant that inversely depends on ϵ_r .

Thus, using equation 3 we can say that by increasing the conductivity of active material in the capacitive gap the confined THz electric field decay exponentially which in turn reduces the strength of Fano resonance that also follow exponential decay trend. Figure A2 shows the simulated transmission spectra for 2D perovskite integrated Fano resonator where, it is clear that for the case of Fano resonance there exists strong electric field in the gap (Figure A2c) while for the absence of Fano resonance the electric field decays out.

Figure A2: Fano resonance modulation in hybrid metadvice: (a) Optical pumping of hybrid metadvice. (b) Cross-section view of 2D perovskite coated hybrid metadvice (which is shown in Figure A2a) (c) Fano resonance modulation upon photoexcitation. Black solid curve represents the excited Fano resonance in perovskite coated hybrid metadvice (Figure A1a) when there is no pump, in this case we observe the confinement of terahertz electric field in the gap of metamaterial resonance. On the other hand, red solid line represents the case when Fano

resonance is modulated due to optical pumping which results in the quenching of confined terahertz electric field in the gap of metamaterial resonator.

A2. Derivation of photoconductivity:

To derive the photoconductivity formula for thin film, we start with the transmission function when perovskite thin film is present on substrate. The analytical expression of transmission function is given by:

$$\frac{T(\omega)}{\Phi(\omega)} = \frac{2n(n_{sub} + 1)\exp[-i\alpha]}{(1 + n)(n + n_{sub})\exp[-in\alpha] + (n - 1)(n_{sub} - n)\exp[in\alpha]} \quad (4)$$

where n is the complex refractive index of sample (in our case perovskites film), n_{sub} is the terahertz refractive index of quartz substrate, d is the film thickness, c is the speed of light, ΔL is the difference in thickness of sample and reference substrates which is 0 in our case, α is $\frac{\omega d}{c}$ and the phase term Φ is equal to $\exp\left[\frac{-i\omega\Delta L(n_{sub}-1)}{c}\right]$.

For thin film, $in\alpha < 1$, thus the exponential $\exp[in\alpha] \sim 1 + in\alpha - n^2\alpha^2/2$. After expanding Eq.4. we get

$$\frac{\Phi(\omega)}{T(\omega)} \approx \frac{1}{(1 - i\alpha)(1 + n_{sub})} \times \left[\left(1 - \frac{n^2\alpha^2}{2}\right)(1 + n_{sub}) - i\alpha n^2 - i\alpha n \right] \quad (5)$$

Now using the complex conductivity expression $\sigma = i\omega\epsilon_0(1 - n^2)$, we express σ in terms of known quantity which is equal to:

$$\sigma = \frac{-\varepsilon_0 c}{d} \frac{(1 - \alpha)(1 + n_{sub}) \left(1 - \frac{\Phi}{T}\right)}{(1 - i\alpha/2)(1 + n_{sub})} + \frac{\frac{-\varepsilon_0 \omega \alpha}{2} (1 + n_{sub})}{(1 - i\alpha/2)(1 + n_{sub})} \quad (6)$$

Now $\Delta\sigma = \sigma_{pump} - \sigma_{No\ pump}$ thus, using Eq.6 we get the expression of $\Delta\sigma$ as:

$$\Delta\sigma = \frac{\varepsilon_0 c}{d} (1 + n_{sub}) \frac{-\Delta T}{T} \quad (7)$$

where $\Delta T = T_{pump} - T_{No\ pump}$ change in THz transmission with and without optical pump.

A3. Radius of curvature calculation for the flexible metasurface used in chapter 4:

Figure A3: Schematic of radius of curvature

$$\sin(\alpha/2) = d/2R$$

$$\sin(l/2R) = d/2R$$

Now expanding “sin(x)” we get:

$$\frac{l}{2R} - \left(\frac{l}{2R}\right)^3 \frac{1}{6} = d/2R$$

$$R = \sqrt{\frac{l^3}{24(l-d)}}$$

$$\kappa = 1/R$$

A4. Fitting procedure for THz transient in Figure 5.1:

According to rate equation the carrier recombination dynamics is governed by rate equation as which is given by following:

$$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n \quad (8)$$

where, n , is the charge carrier density, k_1 , k_2 and k_3 are the monomolecular, bimolecular and Auger recombination rate constants, respectively. However, in the experiment we record the change in terahertz transmission due to optical pumping i.e. we record $(\Delta T/T)(t)$, where ΔT is photoinduced change in THz transmission and T is THz transmission where the optical pump is absent. The charge carrier number density depends on change in THz transmission by following relation:

$$n(t) = \Phi C \frac{\Delta T}{T}(t) \quad (9)$$

where, Φ is photon-to-free carrier conversion, C is a proportionality constant that depends on number of absorbed photons n_0 given by:

$$n_0 = \frac{\alpha(\lambda)\lambda f(1 - 10^{-OD})}{hc} \quad (10)$$

where α is the absorption coefficient at the excitation wavelength ($\lambda = 400$ nm, for our case), f is the incident pump fluence, and $(1 - 10^{-OD})$ is the fraction of pump light absorbed by the sample, where OD is the optical density given by $OD = 0.434 \alpha l$, where l is the thickness of perovskite thin film.

Thus, substituting the expression of “ n ” in Eq.8. results in following:

$$\frac{dx}{dt} = -C^2\Phi^2k_3x^3 - C\Phi k_2x^2 - k_1n \quad (11)$$

where $x = \frac{\Delta T}{T}$. Hence, we fit the Figure 5.1 (in main text, chapter 5) with Eq.11. that gives the values of Φ^2k_3 , Φk_2 and k_1 . Since the value of Φ is unknown, and its value lies between $0 < \Phi < 1$, thus we calculate the upper limit of rate constants.

A5. Carrier dynamics explanation:

The relaxation of photoexcited charge carrier follows various paths to relax back to the equilibrium state. Figure A4 shows the schematic diagram that illustrates the recombination mechanism for the photoexcited free carrier to relax back in semiconductor. Typically, the free carrier follows trap-mediated, bimolecular recombination or many-body assisted Auger recombination.

Figure A4: Various pathways for charge carrier relaxation (a) This is trap-assisted recombination where, the photoexcited free carrier relax to ground states by interacting the defects states. (b) It represents the bi-molecular recombination where the electron-hole pairs recombine and generates photons. It depends on the number density of both the electron and photons. (c) This is many-body assisted Auger recombination, where the electron interacts with third party such as electron or phonon to relax to the equilibrium. The image is taken from ^[1].

Trap-assisted recombination relies on the individual carrier (electron or hole), where the electrons get captured by the trap states (created by the presence of defect) and release its energy in the form of heat or vibration. The bi-molecular recombination involves both the electron and holes thus depends on quadratically on number density (i.e. n^2). In this process, the photon gets emitted during the relaxation thus enhancing the bi-molecular recombination is important for LED application. Finally, Auger recombination is a process that involves many body particles. Here, electron-hole recombination accompanied by energy or momentum transfer to a third participant that could be either electrons, holes or phonons.

To find out the contribution of each pathway, calculating the transient photoconductivity for various pump fluence is essential. If the time constant is constant is increasing with increasing the pump fluence it reflects that the recombination is dominated by trap assisted as due to

increase in pump fluence, the volume of trap states decreases which in turn increases the time constant. While on the other hand if the time constant decreases with an increase in pump fluence it means the relaxation is dominated by Auger recombination, as it depends on charge carrier density. In the case when time constant is constant with pump fluence then the recombination is assisted by phonon-mediated due to hot phonon bottleneck ^[2].

A6. THz modulation using bare perovskite thin film:

Integration of perovskite thin film with metamaterial (MM) resonator enables the resonance modulation. The sensitivity of resonance, particularly the Fano resonance towards external perturbation offers near unity modulation at low pump fluence as shown in chapter 3 and 4. However, the presence of active material only in the resonator gap effects the Fano resonance amplitude upon photoexcitation without modulating the other frequencies of THz. While, in our case we are spin coating the perovskite thin film on MM structures, thus the presence of perovskite thin film beside the resonator gap will induce background modulation of THz amplitude at other frequencies too in the presence of optical pump. To quantify this, we performed a control measurement where we spin coated the perovskite thin film on the quartz substrate and photoexcited the carrier using 400 nm (above the bandgap). Figure A5 shows the broadband modulation of THz waves for different optical pump fluences. From figure it is clear that under the illumination of optical pump broadband modulation occur. However, the modulation depth is very low. We can observe 20 % of modulation depth in the frequency ranging from 0.1-1 THz at pump fluence 350 $\mu\text{J}/\text{cm}^2$.

Figure A5: Broadband modulation of THz using optical pumping of bare perovskite thin film.

A7. Effect of background modulation in THz Fano resonator:

In case of spin coating the perovskite thin film on MM resonator the remnant perovskite thin film apart from resonator gap induces the background modulation of THz waves. However, there exists contrasting difference between THz amplitude modulation at Fano resonance frequency and other frequency where Fano resonance is not present. This is due to the highly sensitive nature of Fano resonance towards external perturbation. Thus, Fano resonance switch off at very low pump fluence which is low enough to induce contrasting difference in THz amplitude modulation at other frequencies other than Fano resonance frequency. For example, in Figure A5, we noticed that under the presence of an optical pump with pump fluence $350 \mu\text{J}/\text{cm}^2$, there is very low amplitude modulation. However, the presence of perovskite thin film on the top of

MM resonator reduces the initial resonance strength of Fano resonance owing to base conductivity of perovskite thin film as can be seen in Figure A6a. Black solid line Fano resonance without the perovskite thin film after coating the perovskite there is reduction in the amplitude of Fano resonance due to base conductivity of perovskite as shown as red solid line in Figure A6a. Figure A6a shows the experimentally recorded Fano resonance modulation of in spin coated perovskite MM structure. The presence of perovskite thin-film also induces red shift in resonance due to change in capacitance. Also, from the experimental spectra, we can observe that there is very low amplitude modulation at frequencies other than Fano frequency. To further prove this, we performed the numerical simulation, and the simulated spectra is shown in Figure A6b. In simulation we put the perovskite only in the gap to show that the amplitude is only modulated at Fano frequency.

Figure A6: Effect of eminent perovskite on Fano modulation (a) Experimentally recorded transmission spectra for spin-coated perovskite on MM resonator (b) Simulated transmission spectra for perovskite coated MM resonator system.

A7: AFM images of perovskite thin film

Figure A7: AFM images (a, b, c) AFM images of 2D, mixed 2D-3D and 3D perovskite respectively.

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Appendix 1

Journal publications:

1. **Abhishek Kumar**, Ankur Solanki, Manukumara Manjappa, Sankaran Ramesh, Yogesh Kumar Srivastava, Piyush Agarwal, Tze Chien Sum and R. Singh, "Excitons in 2D perovskites for ultrafast terahertz photonic devices," *Science Advances*, vol. 6, no. 8, p. eaax8821, 2020, doi: 10.1126/sciadv. aax8821.
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3. **Abhishek Kumar**, Yogesh Kumar Srivastava, Manukumara Manjappa, and Ranjan Singh, "Color-Sensitive Ultrafast Optical Modulation and Switching of Terahertz Plasmonic Devices," *Advanced Optical Materials*, vol. 6, no. 15, p. 1800030, 2018, doi: 10.1002/adom.201800030.
4. Prakash Pitchappa, **Abhishek Kumar**, Haidong Liang, Saurav Prakash, Nan Wang, Andrew A Bettiol, Thirumalai Venkatesan, Chengkuo Lee, Ranjan Singh, "Frequency-Agile Temporal Terahertz Metamaterials," *Advanced Optical Materials*, doi: 10.1002/adom.202000101.
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10. Manukumara Manjappa, Yogesh Kumar Srivastava, Ankur Solanki, **Abhishek Kumar**, Tze Chien Sum, and Ranjan Singh, "Hybrid Lead Halide Perovskites for Ultrasensitive Photoactive Switching in Terahertz Metamaterial Devices," *Advanced Materials*, vol. 29, no. 32, p. 1605881, 2017, doi: 10.1002/adma.201605881.