

ABSTRACT

Title of dissertation: **ENGINEERING LIGHT-MATTER
INTERACTIONS IN GRAPHENE AND
TRANSITION METAL DICHALCOGENIDES**

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ing**

This thesis describes studies concerning light-matter interactions in graphene and tungsten diselenide in two separate research projects united in theme and application. The research performed for the first project studies the tunability of the nonlinear response in plasmonic graphene disks in the presence of an applied magnetic field. The research performed for the second project studies how electron-beam irradiation affects the excitonic populations in tungsten diselenide, a transition metal dichalcogenide, and whether encapsulation in hexagonal boron nitride is capable of mitigating these effects. For both projects, the properties of the two-dimensional materials were confirmed through Raman spectroscopy and atomic force microscopy, and microelectronic fabrication processes were performed based on electron-beam lithography patterning, with the first project also involving additional processing like plasma etching, metal evaporative deposition, and metal lift-off patterning. For the first project, measurement techniques including transmission spectroscopy, terahertz time-domain spectroscopy, and terahertz pump-probe spectroscopy were used to determine how various factors including radiation wavelength, magnetic field,

material properties, material interactions, and plasmonic resonance structure design affect the light-matter interactions within these engineered graphene disks. For the second project, low-temperature photoluminescence measurements were performed to ascertain the effects of electron-beam irradiation on the excitonic populations in tungsten diselenide with and without a hexagonal boron nitride encapsulation.

ENGINEERING LIGHT-MATTER INTERACTIONS IN GRAPHENE
AND TRANSITION METAL DICHALCOGENIDES

by

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Dedication

This dissertation is dedicated to my wife, Angelica, and daughter, Ella, who have supported me through this journey.

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List of Acronyms

- 2D** two-dimensional. 1
- AFM** atomic force microscopy. 2
- ALD** atomic layer deposition. 7
- APD** avalanche photodiode. 15
- CCD** charge-coupled device. 15
- CVD** chemical vapor deposition. 7
- CW** continuous wave. 59
- e-beam** electron beam. 4
- EEA** exciton-exciton annihilation. 119
- EM** electromagnetic. 1
- FEL** free electron laser. 19
- FET** field-effect transistor. 10
- FWHM** full-width-half-maximum. 132
- hBN** hexagonal boron nitride. 4, 7
- IR** infrared. 1
- LED** light-emitting diode. 11
- LSP** localized surface plasmon. 28
- LSPR** localized surface plasmon resonance. 28
- MBE** molecular beam epitaxy. 7
- MOCVD** metal-organic chemical vapor deposition. 7

NIR near-infrared. 5

PL photoluminescence. 2, 4

PMMA poly(methyl methacrylate). 4

PMT photomultiplier tube. 15

QCE quantum confinement effect. 6

SPP surface plasmon polariton. 26

THz terahertz. 1

THz TDS terahertz time-domain spectroscopy. 2

TMD transition metal dichalcogenide. 1

vdW van der Waals. 6

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Chapter 1: Introduction

In 2004, stable materials that approach the two-dimensional (2D) limit were realized, uncovering unexpected physical properties that deviate from those expected from bulk crystals [1]. These so-called 2D material systems were found to have electronic, optical, and thermal properties that are very different from their bulk counterparts, opening up an entire new way of looking at materials we thought we had already known. The rush to explore and study material systems that can be thinned down to a single atomic layer or molecular layer has led to new knowledge and understanding of materials and the physics that underpins them. Novel properties stemming from quantum confinement and the unprecedented surface-area-to-volume ratio present in 2D materials have opened up new families of materials in application areas once not considered. For example, in graphene, the monolayer allotrope of carbon exhibits much stronger electromagnetic (EM) field confinement compared to bulk noble metal equivalents in the terahertz (THz) and infrared (IR) regimes, potentially allowing for highly efficient THz frequency synthesis [2]. Additionally, in transition metal dichalcogenides (TMDs) such as MoS_2 and WSe_2 , the band gap transitions from an indirect band gap in their bulk form to a direct band gap in their 2D form, allowing them to now efficiently absorb and emit light, thus opening up their use in optical and optoelectronic applications [3–6]. New electronic and optical device concepts and new applications have been proposed and, in some cases, even implemented in the two decades since, but many practical barriers stand in the way of the full adoption of 2D materials. Several challenges exist in the fabrication and processing of 2D materials, so exploration

into how various nanofabrication processes affect the properties of these 2D materials is important to be able to practically make use of them in commercial applications at scale.

This chapter discusses the research objectives and motivation of this body of work, introduces the current landscape of 2D materials, reviews measurement and characterization techniques used in this research, provides an overview of plasmons and plasmonic structures, and finally, details the structure of this dissertation. Although in this Introduction an overview of 2D materials is presented, including a brief overview of the history of 2D materials, 2D material families, and potential applications, a more in-depth description of the synthesis, characteristics, and properties of graphene and monolayer transition metal dichalcogenides (and more specifically, WSe_2) will be provided in Section 2.1 and Section 4.2, respectively. Measurement and characterization methods briefly discussed in this chapter include atomic force microscopy (AFM), Raman spectroscopy, photoluminescence (PL), terahertz time-domain spectroscopy (THz TDS), and THz pump-probe spectroscopy. The fundamentals of plasmonics and light-matter interactions and how they relate to 2D materials are then addressed.

1.1 Research Objectives and Motivation

This dissertation looks to add to the body of knowledge for 2D materials and their applications in two different yet important aspects. In the first section, the research performed addresses the light-matter interactions between plasmonic structures and graphene, and how the plasmonic resonance in the THz frequency range can be changed or tuned in the presence of an external magnetic field. More specifically, for THz applications, the tunability of the nonlinear response in graphene plasmonic disks in a magnetic field for the THz frequency range is explored. This research was motivated to answer how novel physics in two-dimensional material systems and their interactions with external fields could be exploited for electromagnetic spectrum signal detection and tuning. In commercial telecommunications and for signal transmission, the THz frequency band has notoriously few utilization options, leading to a so-called terahertz gap between 0.1 and 10 THz [7, 8]. This part of the EM spectrum typically has limited practical sources and detectors, with many electronics-based options operating at too low a frequency and photonics-based options operating at too high a frequency range [9, 10]. Graphene has great potential as a material that could help fill the void due to its tunable plasmonic properties via electrostatic gating [11, 12] and its extremely high nonlinear optical coefficients in the THz regime that allow highly efficient higher harmonic generation up to the seventh order and the synthesis of signals in the THz frequency range using existing electronic sources and systems [2]. Although the use of external electrostatic fields for tuning the THz radiation absorption using graphene has been explored, less has been studied for external magnetic field effects on the tunability of THz radiation absorption in graphene. Potential applications that an improved understanding would support include magnetically tunable THz filters and magnetic field detectors in the THz range.

The second section of this dissertation will address more practical considerations for us-

ing 2D materials for device fabrication. Specifically, this research compares the effects of electron beam (e-beam) lithography on monolayer WSe₂, a semiconducting TMD, with and without a thin encapsulating layer of hexagonal boron nitride (hBN) using low-temperature PL. This research was motivated by issues observed when plasmonic resonance structures were made in TMDs, where the optical properties of the WSe₂ changed by the fabrication process and the presence of plasmonic structures in ways that were not expected. To determine methods to mitigate this issue, this study was proposed to add to the body of knowledge on how excitonic species within WSe₂ changed due to e-beam irradiation and related processing, while also confirming whether the increasingly common process of encapsulating monolayer TMDs with hBN can mitigate any changes throughout the excitonic spectral range. In previous studies, an incident e-beam has been shown to be capable of displacing atoms via elastic scattering in an exposed WSe₂ monolayer [13–15]. Ionization damage through inelastic scattering has also been discussed in the literature, capable of atomic displacement and defect generation [14–17]. The use of graphene and hBN as protective layers has been reported to mitigate vacancy generation by suppressing atomic displacement through being a barrier, and by reducing or suppressing heat, charge, and electronic excitations associated with an incident electron beam [15, 18–21]. Although a number of studies have been performed on the effects of electron beams on TMDs with and without encapsulation, one that compares the excitonic species populations through low-temperature PL has yet to be performed. Such a study would help provide a more comprehensive view of what happens to the optical properties of TMDs such as WSe₂ under exposure to the e-beam and when exposed to chemicals traditionally used in the e-beam lithography, such as poly(methyl methacrylate) (PMMA) and acetone.

Notably, this second study stems from efforts to research the light-matter interactions between interlayer excitons in TMD heterostructures and electromagnetic fields tuned and concentrated using metal plasmonic resonance structures. Initial research efforts (and one

of the initial proposed research thrusts for this dissertation), involving the study of inter-layer exciton enhancement or tunability in TMD heterostructures with plasmonic resonance structures using photoluminescence, are discussed in the last chapter as future research and next steps. This effort was motivated by understanding how 2D materials could be used at room temperature for near-infrared (NIR) sensing and detection applications.

In summary, the objectives of this dissertation include the following:

1. The exploration of the tunability of the strong thermal nonlinearity in patterned, SiC-sublimated bilayer graphene plasmonic disks in the presence of magnetic fields using THz pump-probe spectroscopy.
2. A comparison study of the effects that electron beam irradiation and the general electron beam lithography process have between hBN-encapsulated and unencapsulated TMD structures using photoluminescence.

1.2 Landscape of Two-Dimensional Materials

The concept of a 2D material was first theoretically considered by Lev Landau in 1937, where it was predicted that 2D crystals (as well as one-dimensional crystals) could not exist above a temperature of absolute zero due to the fact that a perfect crystal structure or the long-range order of the lattice of a material would not be possible due to thermodynamic instability [22]. The theoretical band structure of a 2D layer of carbon was first described by Philip Wallace in 1947 [23], but at this point the Landau-Peierls instability theory was still predominant, and the concept of a free-standing monolayer sheet of carbon would remain a theory. It would take almost 60 years later before Novosolev and Geim at the University of Manchester would experimentally demonstrate and characterize a single-layer free-standing sheet of graphite, which we now call “graphene” [1].

2D materials are defined by their geometric thickness, limited to a single atomic layer or molecular layer, typically in a sheet along the x-y plane held together through covalent or ionic bonds (i.e. strong in-plane bonds), while only weak van der Waals (vdW) forces link these atomically or molecularly-thin layers in the vertical z plane (i.e. weak out-of-plane bonds). These 2D allotropes have characteristically different optical, electrical, and quantum mechanical properties compared to their bulk counterparts. These differences in properties arise from two fundamental effects. The first is the quantum confinement effect (QCE) or spatial confinement of charge carriers in a single plane that dictates the electronic band structure of the material, and for 2D semiconductors, this creates a layer-dependent transition in the band gap. An example of this includes the transition from an indirect band gap in the bulk to a direct band gap as a monolayer for molybdenum disulfide or MoS_2 [3]. The second is the reduced dielectric screening, which enhances the Coulomb interactions between excited carriers (electrons and holes) and leads to an increase in the formation of tightly-bound electron-hole pairs, or excitons. The binding energies of these excitons

are high, allowing them to remain stable even at room temperature. the reduced dielectric screening is responsible for the enhancement of light-matter interactions that can be seen in the strong optical response in 2D semiconductors like monolayer TMDs. Two dimensional allotropes can be found for single elements, such as graphene (carbon), phosphorene (phosphorus), and silicene (silicon), or as covalently-bonded compounds, such as hBN or monolayer TMDs (such as MoS_2 , WS_2 , MoSe_2 and WSe_2).

2D materials are synthesized and produced in a variety of methods, with varying levels of complexity and quality. Common methods for the growth or synthesis of 2D vdW materials can be broadly broken down into exfoliation and vapor deposition. Exfoliation methods that involve the use of a bulk crystal that is then manipulated to extract individual monolayers of the material include mechanical exfoliation, liquid phase exfoliation, chemical etching, and oxidation-reduction processes. Vapor deposition methods, which typically require the precise synthesis of a single atomic or molecular layer of a material, include chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and atomic layer deposition (ALD) techniques. The most common method that has been used since the discovery of 2D materials is mechanical exfoliation of monolayers from a bulk single crystal, colloquially known as the “Scotch tape method” due to the use of the 3M branded tape product used to exfoliate van der Waals materials during the early period of 2D material research after its discovery [1]. In the two decades since its initial use, precise and repeatable methods have been developed for mechanically exfoliating bulk crystals and stacking subsequent monolayers of materials on top of each other with minimal residues [24–26]. This dissertation considers both mechanically exfoliated and epitaxially-grown 2D materials.

1.2.1 Two-Dimensional Material Families

While there are a variety of ways to classify 2D materials, here they will be classified and categorized into families by their chemical composition and bonding configuration. Important families of 2D materials include graphene, hBN, TMDs, transition metal carbides/nitrides (also known as MXenes), and monoelemental buckled materials (also called Xenes). Note that due to structural similarities, hBN and graphene are typically grouped together, with hexagonal boron nitride sometimes referred to as “white graphene”. Graphene is an allotrope of carbon consisting of a monolayer of carbon atoms configured in a hexagonal planar lattice with hybridized sp^2 bonding, as depicted in Fig. 1.1(a). Graphene possesses electrical properties of a semimetal, and has been shown to have extremely high tensile strength. Graphene is also considered the first 2D material to be experimentally demonstrated with a single atomic layer of carbon characterized by Novoselov et al. in 2004 [1]. Hexagonal boron nitride is structurally similar to graphene, with alternating boron and nitrogen atoms in place of carbon atoms in the hexagonal lattice and boron and nitrogen atoms ionically bound as depicted in Fig. 1.1(d). Unlike graphene, which is a gapless semimetal with linear dispersion, 2D boron nitride is an insulator, with a direct band gap energy between 5.9 and 6.1 eV [27, 28], which has made it an ideal substrate for use with other 2D material systems due to the lack of dangling bonds, its atomic smoothness, and its similar lattice constant with other 2D materials like graphene. Semiconducting transition metal dichalcogenides, such as MoS_2 , $MoSe_2$, WS_2 and WSe_2 , are composed of a transition metal atom bonded to a pair of chalcogen atoms in a sandwich structure, with the core composed of the transition metal layer, between layers of chalcogens. These semiconducting sandwich structures can be geometrically configured as hexagonal layered structures with trigonal prismatic coordination [4, 29, 30], as shown in Fig. 1.1(b).

At the monolayer limit, TMDs typically possess a direct band gap and can be semicon-

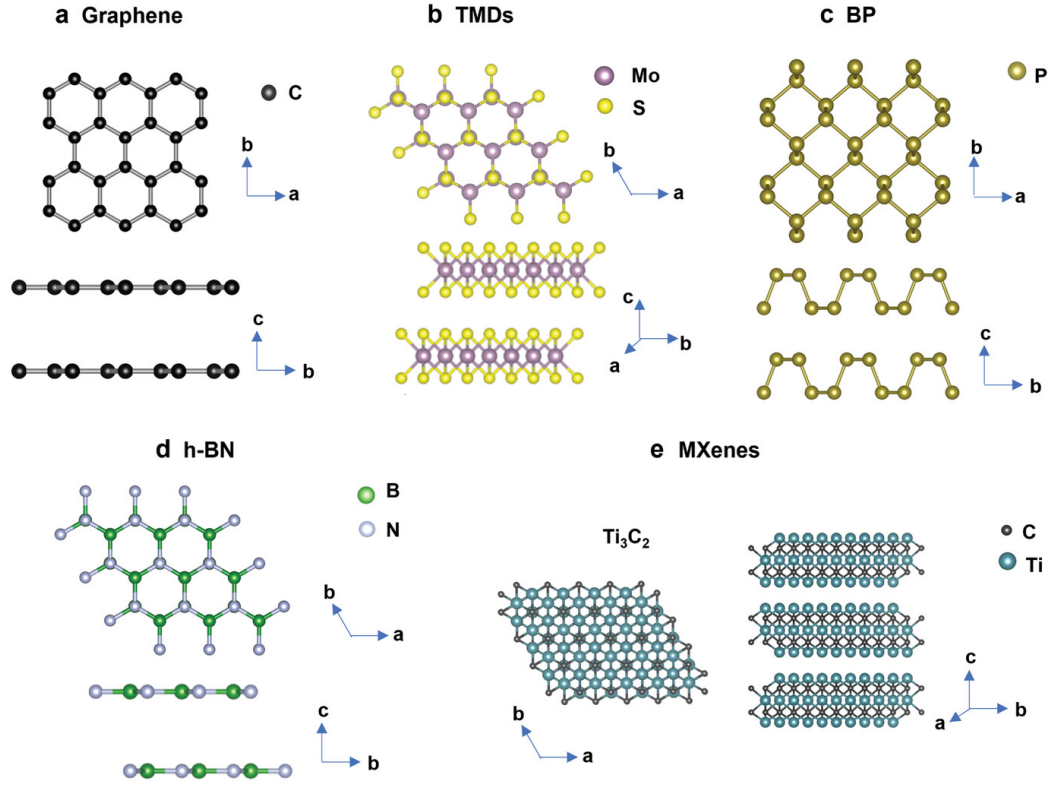


Figure 1.1: Lattice structures of 2D material families including (a) Graphene, (b) Transition Metal Dichalcogenides, (c) Xenes (represented by black phosphorene), (d) Boron Nitride, and (e) MXenes (represented by Ti_3C_2). Reprinted with permission from [31]. Copyright 2023, John Wiley and Sons.

ductors (e.g. MoS_2 or WSe_2), semimetals (e.g. WTe_2 or MoTe_2), or even superconductors (e.g. NbSe_2). This family of 2D materials has been one of the most versatile due to their potential applications in both electronics and optics, which exploit their tunable band gaps, spin-valley physics, and unique excitonic properties. Of the 2D material families listed above, graphene, hBN, and TMDs are van der Waals materials, where individual layers are only weakly held together by van der Waals forces out-of-plane, allowing individual monolayers to be peeled or exfoliated apart through the use of adhesives or liquid solvents. MXenes and Xenes are often metastable in their monolayer forms and must be created through epitaxial growth or precision etching from a bulk material source. MXenes are a large family of 2D materials comprised of transition metal carbides, nitrides, and carboni-

trides. Typically composed of a single type of transition metal arranged in layers that sandwich the carbon or nitrogen layers as depicted in Fig. 1.1(e). Electronically, MXenes are typically metallic with some possessing semiconductor behavior (such as Mo_2C or oxygen-terminated Ti_2C) [32, 33]. Some MXenes notably possess strong plasmonic resonance in the near infrared range, have high transparency in the visible spectrum while remaining electrically conductive, and exhibit high photothermal conversion efficiency [32, 33]. Unlike graphene, which is also a monoelemental 2D material, Xenes do not have an atomically flat, planar structure, but instead have buckled or puckered lattices caused by sp^2/sp^3 hybridization [34–36] as depicted in Fig. 1.1(c). Xenes have diverse electrical and optical properties, with examples in each major category: conductors (borophene, molybdenene), semimetals (silicene, germanene), semiconductors (phosphorene, selenene), and even some potential topological insulators (stanene, bismuthene) [34–36]. Like other 2D materials in the semimetal and semiconductor categories, Xenes tend to have highly tunable properties when exposed to external stimuli. Chemical stability and reactivity vary between Xene families, some such as silicene and phosphorene being very reactive under ambient conditions, while others such as tellurene and antimonene exhibiting higher stability in similar environments [35, 36].

1.2.2 Potential Applications of Two-Dimensional Materials

Two-dimensional materials such as graphene and transition metal dichalcogenides have a wide array of potential applications across several categories including electronics, optoelectronics, sensors, and even energy storage due to their unique properties at the monolayer limit. In the area of electronics, low-power field effect transistors, flexible and wearable electronics, and memristive devices have been proposed using 2D materials such as TMDs such as MoS_2 and WSe_2 [4, 37–40]. Field-effect transistors (FETs) with TMD-

based channels could potentially be scaled beyond the limits of silicon [39, 40]. Graphene-based transistors have been proposed as promising high-frequency transistors that could have cut-off frequencies in excess of 150 GHz [41, 42]. The flexibility and transparency that comes with the thickness of the atomic-scale has opened up the possibilities of using 2D materials for use in wearable electronics and transparent electronics, with 2D insulators (such as hBN), semiconductors (such as TMDs) and conductors (such as graphene and MXenes) allowing full 2D transparent or flexible devices and circuits to be made [4, 32, 39, 41–44]. MXenes show promise in energy storage applications as high-performance electrodes in supercapacitors or batteries due to their high conductivity and their ability to intercalate ions [32, 33]. Optoelectronic and photonic applications such as photodetectors, optical modulators, lasers, light-emitting diodes (LEDs), and photovoltaics have all been proposed or demonstrated using 2D materials, with benefits such as tunability, light weight, and higher performance (high responsivity for photodetectors) offered as justification [4, 38, 44–48]. Two dimensional TMDs have been used to demonstrate lasing as a gain medium at room temperature with low thresholds and as LEDs due to their direct band gap and high electroluminescence efficiency [30, 48–52]. Photovoltaic cells based on 2D TMDs have also been demonstrated with highly efficient solar absorption [3, 38, 48, 50, 53]. As a transparent conductor with robust mechanical properties, graphene has been used in electromagnetic filtering and shielding applications (THz and IR spectral range) [7, 54]. In addition, and pertinent to this work, graphene has been touted as an ideal material for THz detectors and emitters [9, 55–57].

1.3 Measurement and Characterization Methods for Two-Dimensional Materials

This section provides an overview of the measurement techniques that are used in this dissertation. AFM was used to confirm the layer thickness of the 2D materials to ensure that they are truly atomically thin. Raman spectroscopy was used to confirm the number of layers in graphene and WSe₂, as well as to gain additional structural information such as defect densities and mechanical deformation. For the first objective, absorption spectroscopy was used to characterize the resonance frequency of plasmonic structures (i.e. the frequency of radiation that the plasmonic structure most efficiently absorbed). THz pump-probe spectroscopy was then used to characterize the nonlinear absorption in the graphene plasmonic structures in the presence of an external magnetic field. For the second objective, photoluminescence was used to understand the excitonic physics and states present in 2D WSe₂, where the composition and distribution of the excitonic populations can provide information on defects in the material, charge or chemical doping, as well as strain fields in the material.

1.3.1 Atomic Force Microscopy

Atomic force microscopy provides the ability to image and manipulate materials with precision near the atomic scale, enabling height resolutions at the angstrom level. Developed from scanning tunneling microscopy, AFM was invented at IBM by scientists in 1986 [58]. A sharp tip, typically with a diameter of several microns, is used to scan across a material surface while mounted on a cantilever. As the tip approaches the surface, it is drawn to the surface by attractive forces, such as van der Waals and electrostatic forces, but at a point, repulsive forces eventually dominate, forcing the cantilever away from the surface,

allowing for the topological probing of a material surface at atomic resolutions. The deflection of the cantilever is monitored by reflecting a laser beam off of it onto a photodetector array that is position-sensitive. The change in position of the reflected beam is then fed into a feedback electronic circuit to maintain a constant force or height by using piezo-actuators in the cantilever or sample stage to adjust the distance between the cantilever tip and sample. A topographical map is generated from the record of adjustments made during the cantilever's scan across the material surface. This can be seen in a representative schematic of an AFM in Fig. 1.2.

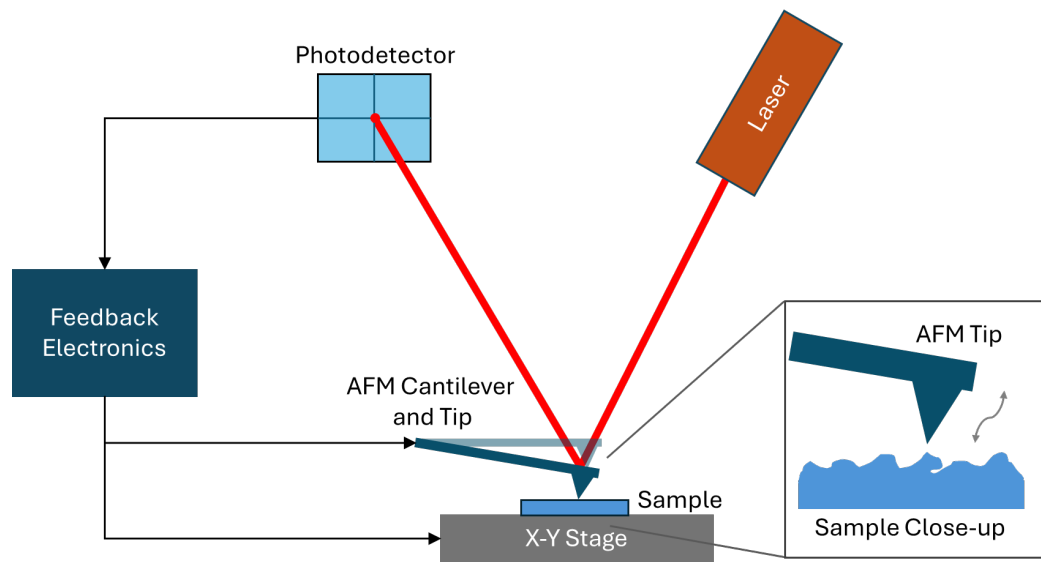


Figure 1.2: Schematic diagram of typical atomic force microscope setup for topography measurements.

Due to the reduced dimensionality of 2D materials such as graphene and transition metal dichalcogenides, determining the thickness and the layer count of a material is critical to determining additional material properties, such as their electrical, optical, mechanical, and thermal properties. Since 2D material thicknesses are typically on the order of angstroms, AFM is critical to physically determining topographic features and confirming

layer counts for these material systems. AFM can be performed under ambient conditions and in various inert environments, allowing rapid quality review and characterization of 2D materials on flat substrates. A topographic measurement of a 2D material like graphene or WSe₂ is typically performed using a tapping mode where the cantilever vibrates at a resonance frequency, which raises and lowers the tip along the surface of the sample, reducing both the shear forces and friction experienced by the sample. This minimizes potential damage to thin, fragile samples from dragging or snagging, that might pull the 2D material off the substrate or tear it.

1.3.2 Raman Spectroscopy

Raman spectroscopy provides a method for optically interrogating a material system to determine the chemical structure, phase, potential defects, and crystallinity of the material by determining the vibrational modes of molecules and crystal lattices. The process involves illuminating a material sample with monochromatic light and detecting the light-matter interactions through the resulting inelastic scattering of photons. Unlike elastic scattering of light (also known as Rayleigh scattering), where the scattered light possesses the same wavelength and energy as the light as the incident light, Raman scattering involves an exchange of energy between incident photons and the material's molecular vibrations or phonons. This interaction produces a Raman shift, where the scattered light's energy and wavelength are altered relative to the incident light (inelastic scattering). Stokes Raman scattering occurs when a photon loses energy to the lattice, resulting in a longer wavelength compared to the incident light, whereas Anti-Stokes Raman scattering occurs when a photon gains energy from the material lattice, resulting in a shorter wavelength. By analyzing these relative frequency shifts, the underlying structural and electronic properties of the material can be fully determined.

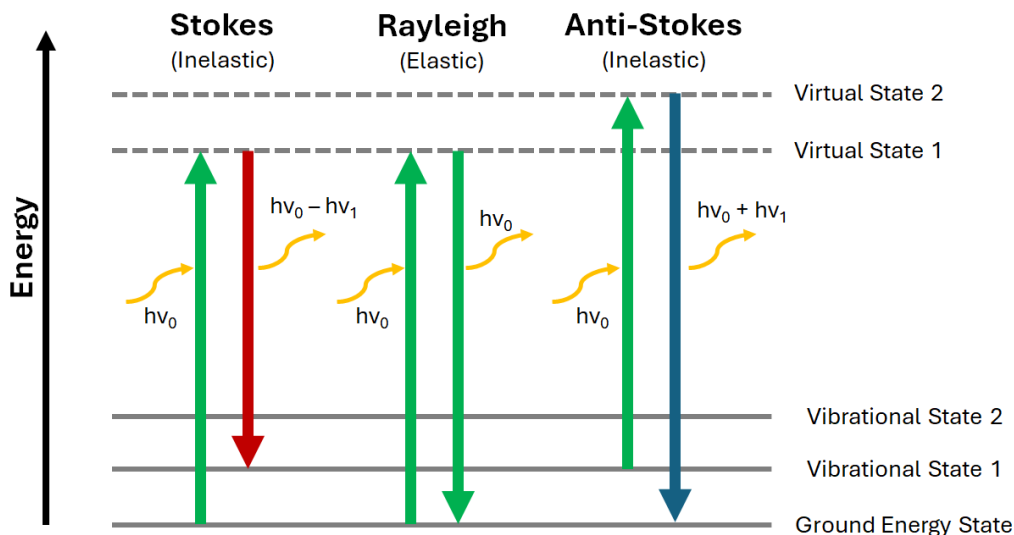


Figure 1.3: Diagram of different forms of scattering including Rayleigh or elastic scattering (center), Stokes scattering (left), and Anti-Stokes scattering (right). Stokes and Anti-Stokes scattering are forms of Raman inelastic scattering. Stokes scattering adds energy to chemical bonds from incident photons while Anti-Stokes scattering takes energy from the chemical bonds in the material to the scattered photons.

A Raman system typically uses a narrow linewidth monochromatic light source, such as a laser, as the incident light that is used to illuminate and probe the bonds in a material. The subsequent scattered light is collected and binned by wavelength using a diffraction grating (periodic structure that diffracts light) within a spectrometer and a photon detector (such as a charge-coupled device (CCD), photomultiplier tube (PMT), or avalanche photodiode (APD) used to detect and count photons). The detected scattered light is analyzed to provide information on the relative shift in energy, providing a unique signature of a material that corresponds to its vibrational modes and chemical structure. The output of a Raman measurement produces a Raman spectrum plot comprised of a Raman intensity (intensity of scattered light that is picked up by the detector) with an arbitrary unit that is plotted with respect to the wavenumber, which represents the energy shift relative to the excitation light source. The Raman shift ($\Delta\tilde{\nu}$) is typically expressed in units of inverse centimeters ($1/cm$ or cm^{-1}) and can be described as:

$$\Delta\tilde{\nu} = \left(\frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}} \right) \quad (1.1)$$

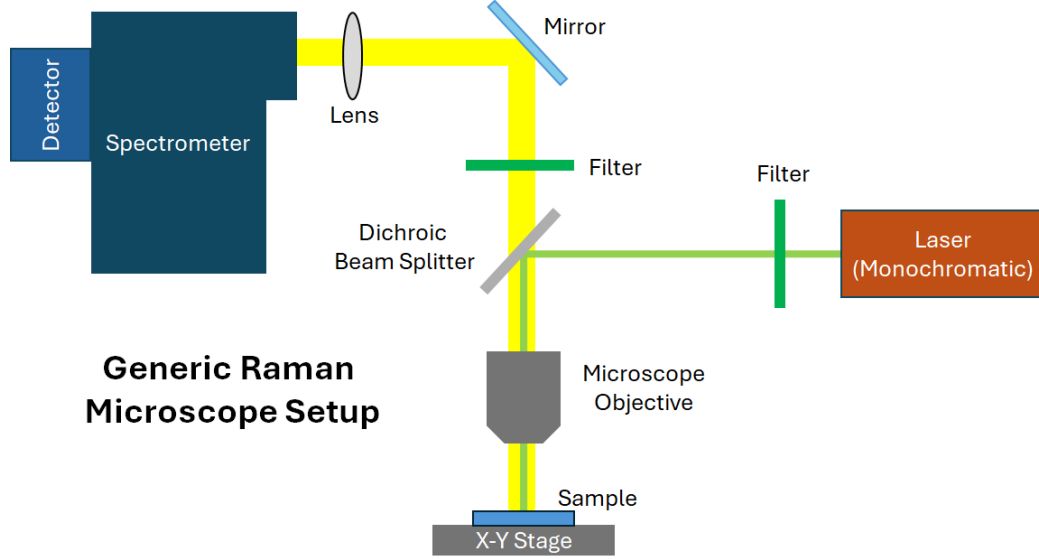


Figure 1.4: Schematic diagram of a generic Raman microscope setup with key components, including laser excitation source, sample stage, objective lens, dichroic beam splitter, focusing lens, spectrometer and detector (commonly a CCD camera).

1.3.3 THz Time-Domain Spectroscopy

THz time-domain spectroscopy is a linear optical characterization technique capable of measuring the electromagnetic response of a material or structure over the terahertz spectral range (typically ranging from 0.1 to 10 THz or between a wavelength range of $30\ \mu\text{m}$ and 3 mm) [59, 60], typically capturing the relative absorption or transmission of THz radiation by a material. This measurement method can also detect responses from plasmonic resonance structures that resonate in the THz frequency range. Material information such as Fermi energy levels, carrier concentration, and electron momentum scattering can be extracted from the output of THz time-domain spectroscopy. Unlike other linear optical spectroscopy techniques that measure the intensity of the photons that pass through a

sample with respect to the photons' energy, wavelength or frequency, THz TDS directly measures the transient electric field of the THz waveform in the time-domain. This transient electric field waveform can be converted into frequency-domain spectral data using a Fast Fourier Transform (FFT), which then can be represented as relative transmission or extinction. Generically, the Fourier transform can be mathematically described as

$$E(\omega) = \int E(t)e^{-i\omega t} dt = \int E(t)e^{-i2\pi f t} dt \quad (1.2)$$

where $E(\omega)$ is the frequency-dependent THz electric field, $E(t)$ is the time-dependent THz electric field, $\omega = 2\pi f$ is the angular frequency, f is the regular frequency and t is time. The FFT is an algorithm used to compute the discrete version of the Fourier transform.

The THz radiation used to interrogate the sample can be generated in a few different ways, with a common method involving the use of an ultrafast laser pulse (with 10-100 femtosecond durations) that is first split into two different beams. One beam, acting as an emitter, is incident on a THz-emitting non-linear crystal or antenna structure to generate THz radiation that is then directed and focused onto the sample. The second beam acts as a detector, which is used as a read-out pulse that is convoluted with the subsequent THz radiation that comes off the sample using a second non-linear crystal or antenna. The detector produces a signal only when the THz emission from the sample and the read-out pulse arrive at the detector at the same time, generating a signal proportional to the instantaneous electric field of the THz pulse from the sample. This can be described by the following proportionality, where the signal from the detector ($S(t)$) [59]:

$$S(t) \propto I_{opt} \otimes E_{THz}(t) \approx \delta(t) \otimes E_{THz}(t) = E_{THz}(t) \quad (1.3)$$

where I_{opt} is the intensity of the optical read-out pulse and $E_{THz}(t)$ is the time-dependent

THz electric field detected from the sample. The read-out pulse is fast compared to the THz emission (femtoseconds vs. picoseconds), which can be approximated as a delta function compared to the transient THz electric field. The convolution of a signal and a delta function result in the original signal such that the signal is essentially the transient THz electric field. A delay line is used to vary the path length of the emitter pulse to control the time it takes to reach the THz emitter with great precision. By changing the arrival time of the emitting THz pulse relative to the read-out pulse, the entire waveform of the THz electric field can be mapped. An example THz TDS setup is shown in Fig. 1.5.

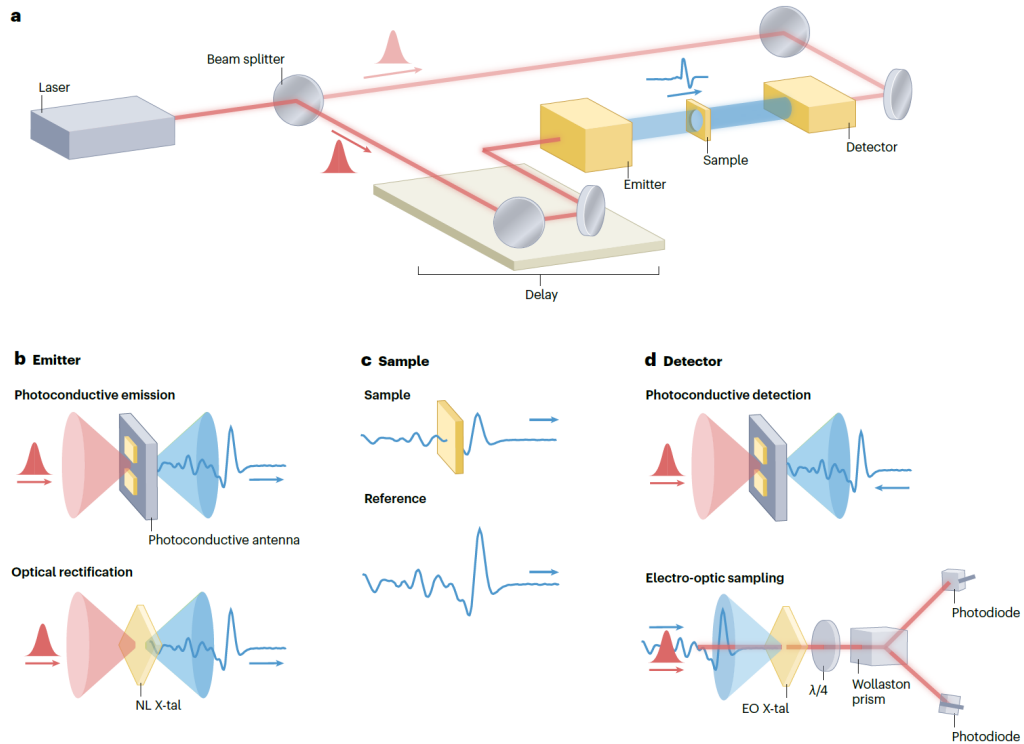


Figure 1.5: Diagram of THz time-domain spectroscopy setup. Major components include a ultrafast pulse laser, beam splitter to generate a emitter beam and detector beam, a delay line, THz emitter, detector, plus beam directing and focusing optics. Reprinted with permission from [60]. Copyright 2023, Springer Nature.

1.3.4 THz Pump-Probe Spectroscopy

THz pump-probe spectroscopy is a nonlinear, time-resolved optical technique that is used to study the ultrafast dynamics of charge carriers. There are multiple methods for the generation and detection of the THz radiation required for this measurement technique, but this description will follow the process used in the experimental work described in future chapters. A THz pulse with a large electric field is used to excite or "pump" a sample or material, and delayed, weaker THz pulses are used to "probe" or read out the transient optical properties of the sample, including the optical conductivity and permittivity of the material. The probe is able to read an instantaneous snapshot of the electric field of the sample. By varying the time between the excitation of the sample via the pump pulse and the read-out of the THz electric field from the sample via the probe pulse, a picture of the time dynamics for the THz electric field such as the decay back to the ground state can be mapped. Because these measurements are resolved at the picosecond time scale, the dynamics of phonons and carriers as well as their transient behaviors can be captured while the sample is in an excited state. The differential transmission or absorption is taken by comparing the electric field from the sample at an equilibrium state (or ground state) with the electric field from the sample in its excited state, and then normalizing it to the equilibrium state electric field. Due to the relatively small change in the electric field between the ground state and the excited state, beam chopping and lock-in amplifiers are used to improve the signal sensitivity and noise rejection of the measurement.

For this example of a THz pump-THz probe spectroscopy setup shown in Fig. 1.6, a free electron laser (FEL) is used as the THz source. A FEL is a special type of laser that uses an accelerated beam of free electrons that move through a magnetic structure called an undulator or wiggler to generate a single "color" of radiation. The magnetic field in the wiggler alternates along its length due to the alternating poles of permanent magnets,

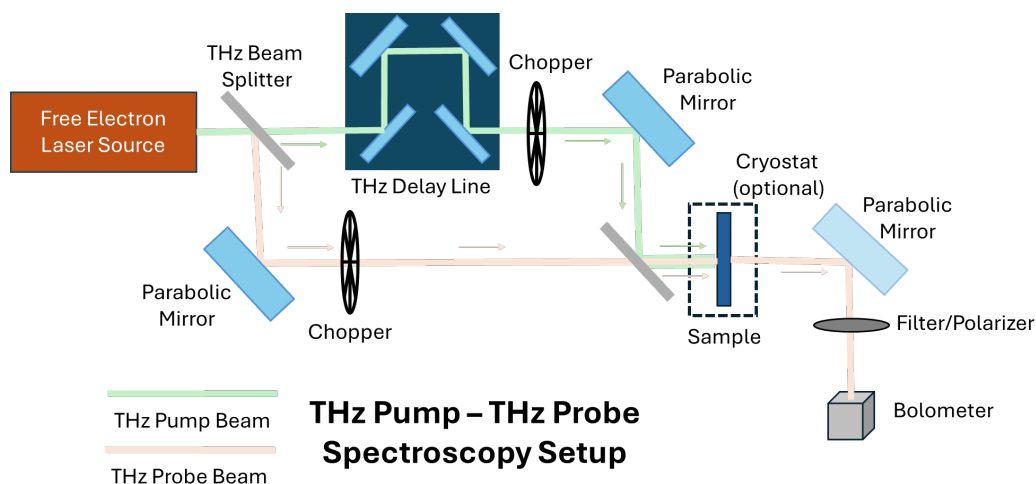


Figure 1.6: Diagram of an example THz pump-probe spectroscopy setup based on a free electron laser source for the THz source. Major components include a THz-generating free electron laser, THz beam splitter to create the pump and probe beams, a THz delay line, choppers and lock-in amplifiers for improved signal sensitivity, an ultrafast pulse laser for the detector gating, and detector setup.

which cause the high-velocity free electrons passing through to oscillate or “wobble” due to the Lorentz force. The free electrons are forced to follow a sinusoidal path laid out by the undulator’s magnetic field, emitting EM radiation associated with the oscillation frequency in the direction of travel. The undulator magnet array period or gap can be adjusted to tune the coherent FEL radiation from the microwave to the THz and even further out to the X-ray spectral regions. A THz beam splitter is used to create a pump and probe beam from the FEL source, with the pump and probe beams moving on separate optical paths. A delay line is used in the pump beam optical path to be able to adjust the timing between the pump and probe beams’ arrival to the sample. The pump and probe beams are then co-propagated and focused at near-normal incidence onto the same spot on the sample with the pump pulse exciting carriers in the sample, and the probe pulse passing through the excited sample at a delay. The transmitted probe pulse is measured by a detector, which in this case is a cooled bolometer. Since the bolometer is a thermal detector, incapable of distinguishing individual pulses from the FEL THz source, the THz pump beam is modulated using an

optical chopper at a frequency on the order of hundreds of Hz, creating a reference signal for a lock-in amplifier. The bolometer converts the incoming THz power into a voltage, and because the pump beam is chopped, the voltage will oscillate at the chopping frequency. The lock-in amplifier only takes into account the component of the bolometer signal that matches the chopping frequency, which represents the transmission change caused by the THz pump pulse.

1.3.5 Photoluminescence

Photoluminescence spectroscopy is a spectroscopic technique that uses a light source to non-destructively interrogate a material to analyze its optical and electronic properties. The incident light interacts with the material, excited by imparting energy into the material system and subsequently causing it to emit light at various wavelengths. The material absorbs the impinging electromagnetic radiation, exciting electrons and transitioning them from lower energy states (i.e., the ground state) to higher energy states. For semiconducting materials, this requires the incident photons to transfer enough energy to the electrons to be excited across the electronic band gap of the material from the valence band into the conduction band. The excited electrons subsequently undergo relaxation and decay processes, where the electron returns to a lower energy state. This process releases the energy in the forms of radiative decay (photon emission) and non-radiative decay, such as vibrational relaxation/thermalization, carrier-carrier scattering (Auger recombination) and defect-assisted/trap-assisted recombination (Shockley-Read-Hall recombination).

Radiative recombination processes result in photonic emission from an electron transitioning from a higher energy state back to a lower energy state, which is also referred to as luminescence. Because excited carriers relax to the band edge before recombining, through processes such as vibrational relaxation and thermalization by the crystal lattice,

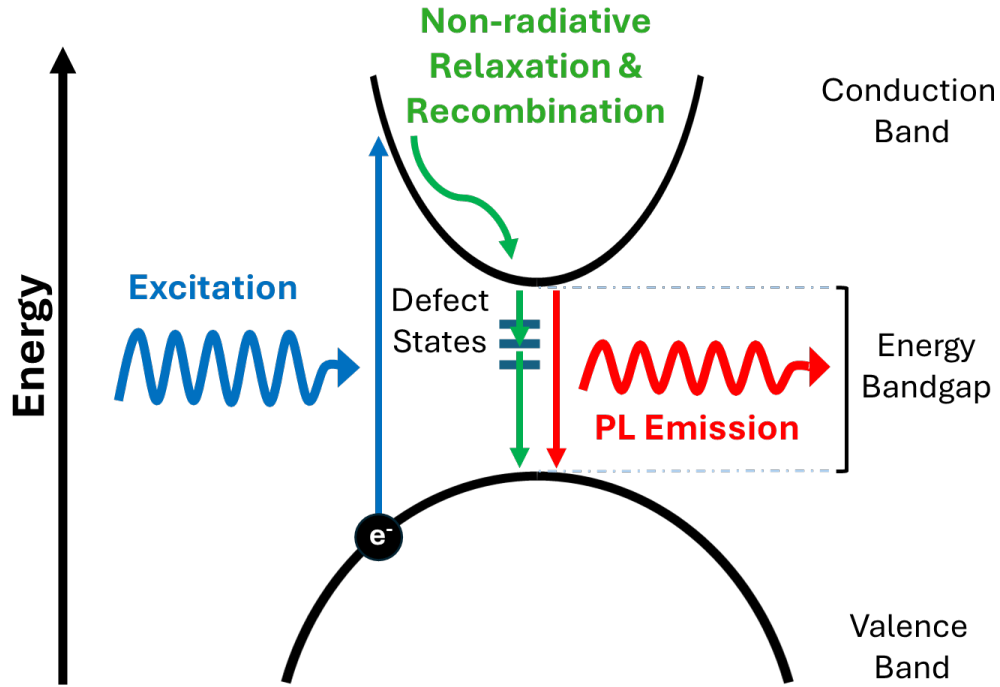


Figure 1.7: Diagram of photoluminescence processes for a direct band gap material including absorption of incident radiation by a valence band electron, excitation of the electron into the conduction band, and subsequent relaxation processes including both non-radiative ones like thermalization, and radiative ones like photon emission.

the emitted photon will typically have a lower energy than the excitation photon and, thus, a longer wavelength compared to the incident EM radiation. For semiconducting materials, the photonic emission provides information on the energy band structure of the material, such as the material's band gap, the density of states, the excitonic states, the material quality and defects, and the excited carrier lifetimes. A diagram of the photoluminescence process for a material with a direct band gap (where the maximum energy level in the valence band and the minimum energy level in the conduction band of a material occur at the same momentum value in k -space) is shown in Fig. 1.7.

In a typical PL spectroscopy setup as shown in Fig. 1.8, a monochromatic light source with a higher energy (i.e. shorter wavelength) than the expected electronic band gap of a sample is used to illuminate the sample and excite electrons from the valence band into the

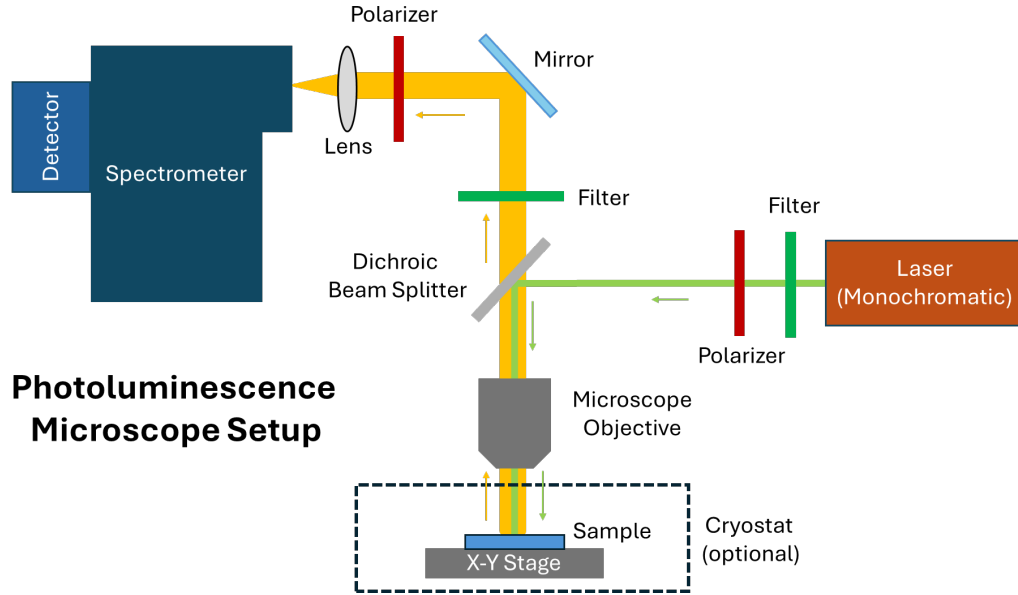


Figure 1.8: Diagram of an example photoluminescence spectroscopy setup, including laser excitation source, sample stage, objective lens, dichroic beam splitter, focusing lens, filters, spectrometer and detector (commonly a CCD camera).

conduction band. Filters can be used to control the power of the laser to vary the excess carrier density, as well as the wavelengths incident on the sample if a broadband source is used. A dichroic mirror and/or beam splitter is used to reflect and direct the incident excitation light source onto the sample while allowing the subsequent lower-energy photon emission coming off of the sample to pass through the same path on its way to a detector. Before reaching the detector, the photoluminescent emission from the sample is first focused into a spectrometer, which uses a diffraction grating to separate and select wavelength ranges to direct toward the detector. The detector, such as a charge-coupled device (CCD) camera, converts photons into electronic signals, with the more photons collected at a particular wavelength or energy leading to a proportionally larger electronic signal. To create a PL intensity plot, these electronic signals are measured with respect to wavelength or energy. For small samples or devices, such as the 2D materials studied in this thesis, an objective lens is used to focus the light onto a smaller area so that the appropriate area

of the sample can be measured and any spatial variations can be resolved. A sample stage with x- and y-axis control allows for the mapping of the photoluminescence with respect to an area. The temperature and environment can be controlled if the sample and stage can be placed in a cryostat.

1.4 Plasmons and Plasmonic Light-Matter Interactions

Plasmons are collective and coherent oscillations of free electrons in a material that are excited by incident radiation, typically in conductive materials such as metals or highly doped semiconductors. These oscillations are considered bosonic quasiparticles and allow for the confinement of electromagnetic fields at dimensions smaller than the wavelength of incident light. Plasmons can be categorized into three main types, depending on where the oscillations of carriers occur and whether they propagate or not, including volume or bulk plasmons, surface plasmon polaritons (SPPs), and localized surface plasmons (LSPs). Example representations of the types of plasmons are shown in Fig. 1.9.

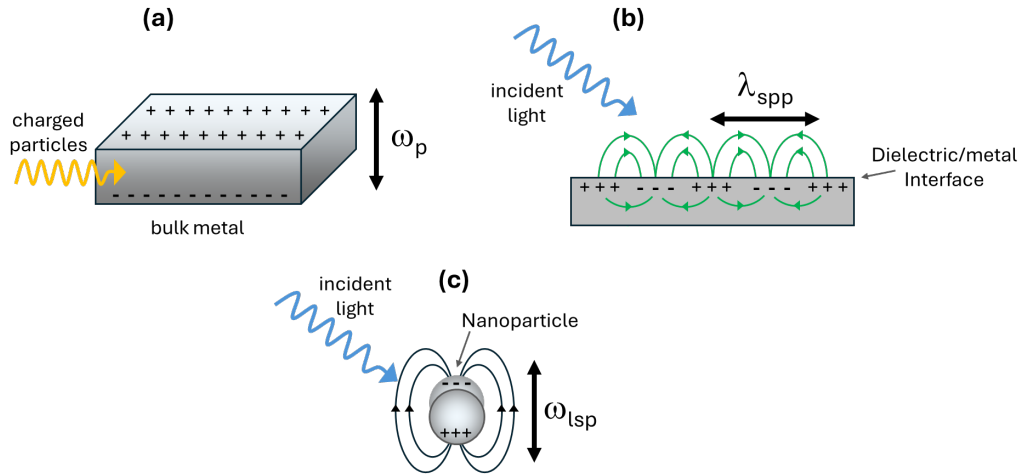


Figure 1.9: Conceptual illustrations of plasmon types including (a) Bulk/Volume Plasmons, (b) Surface Plasmon Polaritons, and (c) Localized Surface Plasmons

1.4.1 Bulk Plasmons

For highly conductive materials such as metals, free carriers in the form of an electron gas exist in the bulk of the material. Free electron oscillations move around fixed positively-charged ionic cores in the lattice of these materials in the form of longitudinal excitations.

When the free electrons collectively displace with respect to the positively-charged lattice due to internal or external stimuli, a restoring force in the form of a depolarization field acts upon the electrons, causing them to oscillate. The natural resonance frequency at which these free electrons oscillate the strongest is called the plasma frequency (ω_p) [61, 62]. This frequency is defined as:

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m^*}} \quad (1.4)$$

where n is the electron density of the material, e is the electron charge, ϵ_0 is the permittivity of the free space, and m^* is the effective mass of the electron. For many metals, this frequency is within the ultraviolet (UV) spectral range [61, 62]. This plasma frequency determines the optical transparency of a conductive material, with wavelengths above the plasma frequency capable of passing through the material, while wavelengths below the plasma frequency are reflected. Bulk plasmons are typically excited through high energy particle impacts, and are typically not excited by transverse light waves since there is limited coupling with the longitudinal excitations in the material [61].

1.4.2 Surface Plasmon Polaritons

Surface plasmon polaritons (SPPs) are collective free electron oscillations that occur at the planar interface between a conductor and an insulator (specifically a dielectric), where coherent oscillations can propagate along the interface as electromagnetic waves, as shown in Fig. 1.9. SPPs are confined to the planar interface between the conductor and the dielectric, in the form of evanescent surface electromagnetic waves, since the intensity of the electric field decays exponentially away from the conductor-dielectric interface [61, 63, 64]. SPPs are excited and generated by the coupling of incident photons at the dielectric-conductor interface with the free carriers present in the conductor. This coupling with light leads to the “polariton” designation but cannot occur directly by light illumi-

nating the interface. The momentum mismatch between the larger momentum of the SPP compared to free photons at the same frequency in the dielectric prevents the SPPs from radiating into the dielectric, but using prism coupling, grating coupling, and defect scattering are methods to increase the photon momentum to match that of the SPP. The natural oscillation frequency of the surface charge density can be described by the surface plasmon frequency (ω_{sp}):

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \epsilon_d}} = \sqrt{\frac{ne^2}{\epsilon_0 m^* (1 + \epsilon_d)}} \quad (1.5)$$

where ω_p is the bulk plasma frequency of the conductor, and ϵ_d is the permittivity of the dielectric, n is the electron density of the material, e is the electron charge, ϵ_0 is the permittivity of free space, and m^* is the electron effective mass [61, 62]. Above the surface plasmon frequency, but below the bulk plasma frequency, SPPs exist with light unable to couple and excite electrons at the surface interface. The surface plasmon frequency, ω_{sp} , also describes the asymptotic limit for light-coupled excitations at the conductor-dielectric interface, and the behavior of the surface plasmon polaritons with different frequency regimes of incident light is defined by the bulk plasma frequency (ω_p), the surface plasmon frequency (ω_{sp}), and the SPP dispersion relation, $k_{sp} = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}$, where k_0 is the wave vector of light in a vacuum, ϵ_m is the dielectric function of the conductor, and ϵ_d is the dielectric function of the dielectric.

At frequencies below ω_{sp} , surface plasmon polaritons can propagate along the interface. When the frequency of the photons matches that of ω_{sp} , an electrostatic standing wave is generated, where the group velocity of the wave goes to zero. When the frequency is greater than ω_{sp} , but less than ω_p , then surface plasmon polaritons do not propagate at the interface as an effective plasmon "band gap". Finally, if the frequency is above ω_p , the photons can pass through the material as it is effectively transparent due to the fact that the electrons in the conductor being unable to screen the higher frequency photons [61].

1.4.3 Localized Surface Plasmons

Localized surface plasmons (LSPs) are non-propagating collective oscillations of free electrons confined to a conductive or metallic structure, such as a nanoparticle, nanodisk, or nanorod, whose dimensions are the same order of magnitude as the plasmon wavelength which are vastly shorter than the vacuum wavelength or the wavelength of incident light. Since the particle is smaller than the wavelength of light, the plasmons cannot propagate away and are forced to oscillate around a fixed positive lattice of the metallic particle's ion cores. Due to the confinement, the collective oscillations create a temporary dipole when the electrons oscillate to one side of the nanoparticle, generating a net negative charge on that side, while the other side has a net positive charge from the exposed positive ion cores. In other words, when driven by the electric field of incident light, electrons are displaced relative to the ion lattice, and the surface of the particle generates surface charges that exert an effective Coulombic restoring force on the electrons. In effect, LSPs behave like a damped-driven harmonic oscillator [61, 62, 65, 66].

Unlike SPPs, LSPs can be directly excited by incident photons because the finite boundary of the metallic nanostructure breaks the translational symmetry, relaxing the momentum conservation rules required for propagating waves [61, 62, 67]. Critically, this excitation requires the plasmonic mode to exhibit a net dipole moment, which enables direct coupling to the oscillating EM wave. The nanostructure acts as an antenna, efficiently absorbing and localizing the electric field of incident light, which it then re-radiates or absorbs through non-radiative processes. The electric field outside of the particle near the oscillating poles can become exponentially stronger than the incident light. This near-field enhancement and massive amplification of the electric field near the surface of the particles are strongest at localized surface plasmon resonance (LSPR). LSPR occurs when the frequency of incident light matches the inherent frequency of collective electron oscillations in the metallic

nanostructure [68, 69]. Since the inherent frequency of collective oscillation in the metallic nanostructure is directly related to the size, shape, material, and dielectric environment of the nanostructure, the LSPR can be tuned by modifying any one or all of these factors [61–64, 66, 68, 70]. In more advanced cases, coupling between nanostructures in arrays or due to close proximity can generate near-field interactions and hybridized field modes that can shift the localized surface plasmon resonance frequency compared to what a single nanostructure might have had [67, 69–71].

Localized surface plasmons are the focus of the light matter interaction studies for the first project discussed in this thesis. In the next chapter, the design and modeling of metallic nanostructures in the form of graphene-based nanodisks will be discussed, and the physics and equations dictating the plasmonic resonance frequency of the designed structure will be described.

1.5 Structure of Dissertation

In the next two chapters, a study reviewing the magnetic field tunability of strong thermal nonlinearity in patterned, SiC-sublimated bilayer graphene disks is described. The modeling, fabrication, and linear and nonlinear characterization of these graphene-based plasmonic structures are described with their results with and without applied magnetic fields. Chapter 2 provides an introduction to this study, along with a description of important graphene properties, graphene's light-matter interactions with THz radiation, the enhancement of these interactions using plasmonic resonance structures, the design and modeling of graphene plasmonic disks, their fabrication, and finally their linear characterization. Chapter 3 describes the efforts with the nonlinear characterization, two-temperature modeling, and the effect of magnetic fields on the nonlinear response of these graphene plasmonic disks in the THz frequency regime. The conclusions of the results of this study are shared in the last section of this chapter.

The following two chapters (Chapters 4 and 5) provide a review of current on-going research studying the effects of defect generation from fabrication processes on monolayer WSe₂, a two-dimensional semiconducting transition metal dichalcogenide, specifically looking at electron beam lithography and its associated processes, and how mitigation methods, such as hexagonal boron nitride encapsulation of these WSe₂ monolayers, could potentially resolve or inhibit some of these defect issues. Chapter 4 provides an explanation of a previous research effort that led to the current electron-beam irradiation study on bare and encapsulated WSe₂, along with a description of the properties, synthesis, characterization and excitonic species associated with these van der Waals semiconductors. Finally, the chapter provides a description of the issues that will be addressed by this fabrication defect study. Chapter 5 provides an introduction to defect generation in transition metal dichalcogenides from electron beam lithography and associated processes, a review of how those

processes affect exciton populations in WSe₂ from previous studies, and an experimental methodology for systematically studying how electron beam irradiation affects excitonic populations in WSe₂ with and without a mitigating encapsulation layer of hexagonal BN (hBN). The results and conclusions are then presented to finalize the chapter.

Chapter 6 provides summaries of the two studies described in this dissertation, followed by follow-up efforts and next steps in the second study, as well as providing some final comments on the body of research presented.

Chapter 2: Graphene and THz Nonlinearity in Graphene Plasmonic Structures

Over the past two decades, there has been a growing interest in developing methods to generate and detect electromagnetic (EM) radiation in the THz frequency range, which is typically defined as 0.3 to 3.0 THz (alternatively defined as the wavelength range between 1 mm and 0.1 mm). Conventional electronic and optical methods for generating and detecting THz radiation have struggled to efficiently cover this part of the EM spectrum, with electronic methods dominating below 300 GHz and optical methods primarily used above 3 THz [9, 72, 73]. A number of methods to bridge this gap are being researched and have been reported, including quantum cascade lasers [9, 74] and photo mixing in semiconductors, which use nonlinear multiplication of lower frequency oscillations in the semiconductor [9, 73]. In both cases, issues with poor conversion efficiency and lack of tunability are problems that need to be addressed.

Developments in the exploitation of graphene plasmons, a 2D material, for the detection and generation of THz radiation have gained a lot of interest, due to evidence of strong coupling of THz EM radiation with graphene plasmons [9, 75–77]. Plasmons, or quantized high-frequency plasma density oscillations in materials with a relatively large free carrier density, can be exploited in graphene to enhance the absorption of EM radiation of a particular frequency based on the carrier concentration, geometry, and structure. This radiation absorption in graphene can be detected optically and even electronically. The transmission

and reflection of incident THz EM waves are affected due to graphene plasmons that are tuned through the carrier density of the graphene and from the geometry of the graphene (typically in periodic structures). Graphene is uniquely suitable for THz applications due to its natural plasmonic resonance in the mid-infrared to THz frequency range [7, 75, 78]. This is a result of the electron carrier density of graphene (n_{graphene}) as it relates to the surface plasmon resonance as described in Eq. (1.5). Graphene patterned into plasmonic structures like ribbons or disks strongly increases the linear and nonlinear optical interaction at resonance through quantum confinement. Graphene plasmons have been reported to be able to compress the wavelength of THz light by a factor of 50-300 compared to its free-space wavelength, which is orders-of-magnitude smaller than the diffraction limit [57, 79].

In this study, the tunability of the strong thermal nonlinearity in patterned, SiC-sublimated bilayer graphene disks in the presence of magnetic fields was explored. Using THz pump-probe spectroscopy we found that the nonlinear response can be dramatically altered in the presence of moderate magnetic fields, leading even to an inversion of the nonlinear response at a field as low as 3 tesla (T). A single layer of bilayer-graphene ribbons can lead to a peak extinction of more than 30% and a pump-induced increase in transmission of about 10% at moderate pump fluence in the $\mu\text{J}/\text{cm}^2$ range. An applied magnetic field was found to induce a circular polarization-dependent splitting in the graphene plasmon resonance, and the strength of that applied magnetic field was observed to dramatically alter the nonlinear response. In magnetic fields, the plasmon hybridizes with the cyclotron resonance, leading to a splitting of the plasmonic absorption into two branches. This splitting can be exploited to tune the optical nonlinear optical response of graphene disks, such that without a magnetic field, a strong pump-induced increase in transmission can be observed, and when applied incident magnetic fields in the range of 3 T the transmission characteristics can change completely, leading to an inverted nonlinearity. A two temperature model

developed by collaborator, Sebastian Matschy (University of Duisburg-Essen), was able to describe the observed behavior in the graphene disks well. Potential applications that the understanding gained from these studies would support include tunable THz filters and detectors.

2.1 Graphene Properties

Since its experimental realization in 2004 by Novoselov and Geim [1], graphene has become one of the most well-studied 2D materials due to its many unique properties. As a two-dimensional allotrope of carbon at one single atomic layer thick, graphene is a van der Waals material that has a honeycomb lattice structure with hybridized sp^2 bonds. Graphene is a Dirac semimetal that possesses a novel band structure where its charge carriers act as massless fermions that follow a linear dispersion relation. This is due to the six Dirac points at its K and K' points in its hexagonal Brillouin zone, where the valence and conduction bands overlap. Unlike many other material systems, and even the bulk counterpart of graphene, electrons in graphene possess a constant Fermi velocity of $v_F \approx 10^6 \text{ m/s}$ [76, 80–83]. These unique characteristics of graphene lead to a number of important mechanical, electronic, and optical properties.

Graphene has unique mechanical properties that have raised interest in its potential for use in high-tensile load applications. Due to its lattice structure, graphene is considered extremely strong, with a reported intrinsic tensile strength of 130 GPa and a Young's modulus of 1.0 TPa for single crystal graphene, making it one of the strongest materials ever tested [84]. Compared to steel, graphene is about 200x stronger (tensile strength) and 5x stiffer (Young's modulus), with a measured breaking strength of 42 Nm^{-1} [84]. The robustness of the 2D material extends to its chemical inertness in many environmental conditions. Additionally, the thermal conductivity of graphene has been reported to be as high as $\sim 5,000 \frac{\text{W}}{\text{m}\cdot\text{K}}$ at room temperature [85]. This is extremely high compared to other traditional thermal conductors at room temperature such as diamond ($2,400 \frac{\text{W}}{\text{m}\cdot\text{K}}$) [86] and copper ($401 \frac{\text{W}}{\text{m}\cdot\text{K}}$) [87].

In addition to its extremely high thermal conductivity, graphene has exceptional electronic transport directly as a result of its sp^2 hybridization, which facilitates delocalized π

electrons across a conjugated system of overlapping p orbitals. This enables unprecedented carrier mobilities, with reports as high as $1,000,000 \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$ when suspended and cooled to cryogenic temperatures [88]. On substrates such as hexagonal boron nitride, mobilities still remain superior to traditional semiconductors, reaching $\sim 140,000 \text{ cm}^2/\text{V}\cdot\text{s}$ at 7.2 K [89] and $\sim 100,000 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature [90]. These values exceed the mobilities typically reported for silicon by over two orders of magnitude. Furthermore, quasi-free-standing bilayer epitaxial graphene (QFS BLG) on (0001) SiC exhibits mobilities of $4,400 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature with an extremely narrow Drude response [12, 55]. Due to its linear dispersion relation, graphene exhibits a strong ambipolar electric field effect, where electrostatic gating allows for the continuous tuning of the carrier type and density up to $\sim 10^{13} \text{ cm}^{-2}$ [1, 80, 88, 91]. This combination of high mobility, ambipolar operation, and low Ohmic loss makes graphene a good candidate for high-frequency device applications [2, 8, 9, 42, 92–94].

Optically, graphene exhibits a flat broadband absorption of $\sim 2.3\%$ per monolayer in the visible spectrum, which is a value determined solely by the fine-structure constant and rather than specific material parameters [95, 96]. Although largely transparent in the visible range, graphene exhibits uncharacteristically strong light-matter interactions at the infrared (IR) and terahertz (THz) frequencies [7, 8, 10, 45, 46, 75, 77, 97–99]. In the THz regime, graphene's conductivity follows Drude-like behavior governed by intraband absorption, enabling the efficient production of hot carriers. These carriers can be exploited for strong nonlinear responses and harmonic generation [12, 77]. Consequently, the combination of high electronic mobility with these novel optical properties makes graphene highly suitable for the detection of IR and THz and optoelectronic modulation [9, 46].

2.2 THz Plasmonics and Light-Matter Interactions in Graphene

Of particular importance for THz applications, and as alluded to in the previous sections, graphene has unique plasmonic properties due to its electronic band structure, where charge carriers behave as massless Dirac fermions. The collective oscillations of charge carriers in graphene are distinctly different from the plasmonic response of noble metals and even conventional two-dimensional electron gases (2DEGs) in semiconductors. Since graphene is a Dirac semimetal, its carrier density is several orders of magnitude lower than that of traditional noble metals, with doped graphene possessing carrier densities between $5 \times 10^{12} \text{ cm}^{-2}$ and 10^{14} cm^{-2} , and with noble metals like Au or Ag possessing carrier densities on the order of $5 - 6 \times 10^{22} \text{ cm}^{-3}$ [72]. Due to the difference in dimensionality and the difference in dispersion relations, this results in a plasmonic response that is typically active in the THz and far-IR regimes, rather than the visible and near-IR regimes associated with metals [7, 75]. Furthermore, confined graphene plasmons in graphene nanoscale structures exhibit substantially stronger sub-wavelength confinement in this frequency range, capable of confining electromagnetic fields at a scale that is order of magnitudes smaller than the diffraction limit, while reducing dissipative losses compared to noble metal-based plasmonic structures [46, 99]. The plasma frequency in these systems is dictated by both the geometry of the graphene structure and the carrier density of the material. This is a primary advantage for graphene over noble metals, as the carrier density can be dynamically tuned through multiple methods, including electrostatic gating and chemical surface doping.

The ability to adjust the effective doping and carrier density of graphene by electrostatic gating allows for dynamic modification of the plasmon frequency [54, 56]. This capability enables the detection of narrow THz frequency bands over a wide spectral range by simply adjusting the applied gate voltage. To further enhance light-matter interactions, graphene can be modified with periodic structures to dramatically enhance radiation absorption at the

plasmon frequency through localized field enhancement in the immediate vicinity of the structures [11, 100]. Additionally, graphene's small effective cyclotron frequency, which is comparable to its plasmon frequency, allows for the use of external magnetic fields to tune the resonance frequency, which is a focus in this dissertation. This leads to the generation of magnetoplasmons, which can significantly enhance the magneto-optical response of the material [101, 102]. For this study, graphene plasmonic disks were chosen as the LSP structure has a response that is independent of polarization (including right- and left-handed circularly polarized radiation) and their plasmon confinement in all directions in the graphene plane. Since nanodisks confine the plasmons in all directions, they significantly boost light-matter interactions at higher photon energies, possess polarization independence, and support rotational or chiral modes [54].

Graphene plasmonic resonance structures also significantly amplify the inherent nonlinear response of the material at THz frequencies [12]. This strong nonlinearity is not primarily derived from nonlinear susceptibility or band structure effects, but instead is dominated by fast thermal effects in highly doped graphene [103, 104]. As the charge carriers are heated by absorbed THz radiation, the Fermi edge is smeared, and because the density of states in graphene increases linearly with energy, the chemical potential must decrease to maintain a constant number of electrons. This reduction in chemical potential leads to a characteristic transient red shift of the plasmon frequency, which can be seen using THz pump-probe spectroscopy, resulting in pump-induced increases in transmission, often on the order of 10% at moderate fluences [77, 105]. Although thermal nonlinearities are typically slow in most material systems, carrier cooling in graphene is sufficiently fast to allow for extremely efficient harmonic generation in the THz range [2].

2.3 Optical Conductivity of Graphene

While the plasmonic resonance describes the collective response of the charge carriers to an external radiation field, the dynamic tunability and enhanced light-matter interactions of graphene plasmonics are fundamentally rooted in the material's complex surface conductivity. Graphene's interaction with incident EM radiation and more specifically, THz radiation is directly related to the optical conductivity of graphene ($\sigma(\omega)$), which can be described by three components including intraband processes, interband processes, and Kerr-type nonlinear processes:

$$\sigma(\omega) = \sigma_D(\omega) + \sigma_{inter}(\omega) + \sigma_{NL}(\omega) \quad (2.1)$$

where $\sigma_{intra}(\omega) = \sigma_D(\omega)$ represents the optical conductivity of intraband processes, described by the Drude model, $\sigma_{inter}(\omega)$ represents the optical conductivity of interband transition processes, and $\sigma_{NL}(\omega)$ represents the contribution of Kerr-type nonlinear effects [45, 72, 73, 81, 106, 107].

The intraband transitions involve the absorption of photon energy by electrons in the material and then moving to high energy states within the same energy band. For doped graphene, this would typically be a conduction band transition. This process is dominant at lower frequencies like the IR and THz ranges [7, 108], and is well-described by the Drude model, which is why it is sometimes called the Drude contribution. The dominance of the intraband transitions in this frequency range is due to the suppression of interband transitions via Pauli blocking in doped graphene as the Fermi level shifts away from the Dirac point. This contribution to optical conductivity is highly tunable through the change in chemical potential, μ_c , which is equal to the Fermi level in graphene at $T = 0$ K. Since the charge carriers in graphene behave as a massless Dirac fermion and have a linear energy

dispersion, the intraband response differs from classical metals, scaling with the square root of the carrier density rather than linearly as is the case with noble metals [81, 106]. The intraband or Drude contribution to the optical conductivity of graphene can be expressed as [106]:

$$\sigma_{Drude}(\omega) = \frac{e^2 E_F}{\pi \hbar} \frac{1}{\hbar \gamma - \hbar \omega} = \frac{D}{\pi(\gamma - i\omega)} \quad (2.2)$$

where e is the electron charge, E_F is the local Fermi level with respect to the Dirac point, $\hbar$ is the reduced Planck's constant, γ is the relaxation or scattering rate, ω is the angular frequency of incident radiation on graphene, and D is the Drude weight of graphene.

For graphene, the Drude weight is defined differently compared to those of classical metals and semiconductors with parabolic energy dispersions. For these conventional materials, the Drude weight is defined as $D = \frac{\pi n e^2}{m^*}$, where n is the charge carrier density, e is the electron charge and m^* is the effective mass of the electron [81, 108]. Graphene's two-dimensional nature and linear energy dispersion significantly change the Drude weight equation. For the low-temperature regime where the thermal excitation energy is much lower than the Fermi level of graphene ($k_B T \ll E_F$), the Drude weight can be expressed as [77, 81, 108]:

$$D = \frac{e^2 v_F}{\hbar} \sqrt{\pi |n|} = \frac{e^2 E_F}{\hbar^2} \quad (2.3)$$

where e is the electron charge, v_F is the Fermi velocity of graphene ($v_F \approx 10^6$ m/s [76, 80–83]), $\hbar$ is the reduced Planck's constant, n is the carrier density, E_F is the local Fermi level with respect to the Dirac point, γ is the relaxation or scattering rate and ω is the angular frequency of incident radiation. The Fermi velocity can be written in terms of the Fermi energy for graphene as:

$$v_F = \frac{E_F}{\hbar\sqrt{\pi|n|}} \quad (2.4)$$

In cases where the graphene being used is undoped and $E_F \approx 0$ or in high-temperature scenarios where $k_B T \geq E_F$, a temperature-dependent Drude weight can be used [77, 108]:

$$D(T) = \frac{2e^2}{\hbar^2} k_B T \ln \left[2 \cosh \left(\frac{\mu(T)}{k_B T} \right) \right] \quad (2.5)$$

where $\mu(T)$ is the temperature-dependent chemical potential of graphene, k_B is the Boltzmann constant, and T is the carrier temperature. However, it should be noted that for doped graphene that is typically used ($E_F \approx 0.25 - 0.5 \text{ eV}$) and at room temperature or lower ($k_B T \approx 0.0259 \text{ eV}$ at $T = 300 \text{ K}$), Eq. (2.3) is a relatively good and valid approximation.

The momentum scattering rate can also be temperature-dependent in the same scenario where $k_B T \geq E_F$, as it factors in a number of scattering mechanisms, which may include contributions from plasmon damping from impurity scattering, acoustic and optical phonon scattering, and electron-electron interactions [72, 81]. The temperature-dependent scattering rate ($\gamma(T)$), can be expressed as [77, 109]:

$$\Gamma(T) = \frac{\Gamma_0 E_F}{\mu(T)} + \frac{k_B T E_F V_D^2}{4\hbar^3 v_F^2 \rho_S^2} \quad (2.6)$$

where Γ_0 is an impurity scattering constant, V_D is the acoustic deformation potential, and ρ_S is the 2D mass density for graphene. The first term describes the scattering due to long-range Coulomb impurities, while the second term describes the scattering from acoustic phonons. Many of the parameters such as the impurity scattering constant, the acoustic deformation potential, and the Fermi velocity were acquired experimentally.

The interband transitions involve the absorption of photon energy by electrons in the material and then jump energy states from the valence band to the conduction band. How-

ever, since Dirac fermions must follow the Pauli exclusion principle, electrons can only make this transition if the destination state in the conduction band is available (empty). For doped graphene with chemical potential $\mu_c \neq 0$, the lower states in the conduction band are filled, preventing interband transitions from occurring. In the case of doped graphene, Pauli blocking occurs for these transitions unless the incident photon energy is $\hbar\omega = 2|\mu_c|$. At $T = 0$ K, $E_F = \mu_c$, and is also a good approximation at low temperatures. This process is dominant at higher frequencies in the visible and near-IR range [7], making doped graphene fairly transparent in this range due to Pauli blocking. The interband contribution to graphene's optical conductivity can be expressed as [106]:

$$\sigma_{inter}(\omega) = \frac{e^2}{4\hbar} \left(1 + \frac{1}{\pi} \arctan\left(\frac{\hbar\omega - 2E_F}{\hbar\gamma}\right) - \frac{1}{\pi} \arctan\left(\frac{\hbar\omega + 2E_F}{\hbar\gamma}\right) \right) - i \frac{e^2}{8\pi\hbar} \ln \left(\frac{(2E_F + \hbar\omega)^2 + (\hbar\gamma)^2}{(2E_F - \hbar\omega)^2 + (\hbar\gamma)^2} \right) \quad (2.7)$$

where e is the electron charge, E_F is the local Fermi level with respect to the Dirac point, $\hbar$ is the reduced Planck's constant, γ is the relaxation rate (where $\Gamma = \hbar\gamma$ is the scattering rate) and ω is the angular frequency of incident radiation on graphene.

Kerr-type nonlinear processes typically only occur when very strong electromagnetic fields are incident on the graphene. Unlike interband and intraband/Drude processes that describe the linear optical response, in this regime the optical conductivity is no longer just a function of incident radiation frequency, but also becomes a function of radiation intensity, resulting in a large third-order nonlinear optical susceptibility ($\chi^{(3)}$). Typically, for the optical Kerr effect, the refractive index, and in consequence the optical conductivity, changes proportionally to the intensity of incident radiation. These processes typically occur in the visible and near-IR frequency range, and third-order susceptibility can be several

orders of magnitude higher in graphene and in graphene plasmonic resonance structures compared to typical bulk dielectrics [79, 103]. The Kerr-type nonlinear contribution to graphene's optical conductivity can be expressed as [107]:

$$\sigma_{NL}(\omega) = -i \frac{3e^2}{32\pi\hbar} \frac{(ev_F)^2 \hbar^2}{E_F^4 \omega^3} (1 + i\alpha_T) \quad (2.8)$$

where e is the electron charge, E_F is the local Fermi level with respect to the Dirac point, $\hbar$ is the reduced Planck's constant, γ is the relaxation rate (where $\Gamma = \hbar\gamma$ is the scattering rate), ω is the angular frequency of incident radiation on the graphene and α_T is the coefficient to account for two-photon absorption in graphene.

Adding the contributions of all these terms from Eq. (2.2), Eq. (2.7), and Eq. (2.8) nets the total graphene sheet conductivity $\sigma(\omega)$. Expanding each of the contributions nets the following equation, noting that the Drude weight, D , and the scattering rate, Γ , are used in the intraband component, as described above.

$$\begin{aligned} \sigma_{Gr}(\omega) = & \frac{D}{\pi} \frac{1}{\gamma - i\omega} + \frac{e^2}{4\hbar} \left(1 + \frac{1}{\pi} \arctan \left(\frac{\hbar\omega - 2E_F}{\hbar\gamma} \right) - \frac{1}{\pi} \arctan \left(\frac{\hbar\omega + 2E_F}{\hbar\gamma} \right) \right) \\ & - i \frac{e^2}{8\pi\hbar} \ln \left(\frac{(2E_F + \hbar\omega)^2 + (\hbar\gamma)^2}{(2E_F - \hbar\omega)^2 + (\hbar\gamma)^2} \right) - i \frac{3e^2}{32\pi\hbar} \frac{(ev_F)^2 \hbar^2}{E_F^4 \omega^3} (1 + i\alpha_T) \end{aligned} \quad (2.9)$$

where D is the Drude weight, ω is the frequency of the THz radiation, γ is the momentum scattering rate, e is the charge of an free carrier (electron), $\hbar$ is the reduced Planck's constant, E_F is the local Fermi level with respect to the Dirac point, $\hbar\omega$ is the photon energy of radiation at frequency ω , v_F is the Fermi velocity of graphene, and α_T is a coefficient to account for two-photon absorption in graphene.

For heavily doped graphene with carrier densities at $n > 5 \times 10^{12} \text{ cm}^{-2}$ with a Fermi

energy level above 250 meV and with incident radiation in the THz range with photon energies of $0.4 \text{ meV} < \hbar\omega < 40 \text{ meV}$ (covering ~ 0.1 THz to 10 THz), Eq. (2.9) can be greatly simplified. Typically, the interband contribution ($\sigma_{inter}(\omega)$) can be deemed negligible when interband optical transitions are forbidden due to Pauli blocking [7, 9, 10, 46, 106]. This requires that the photon energy of the incident radiation be at least half of the graphene Fermi level where $\hbar\omega < |E_F|$ [7, 82, 104], and that the thermal energy be substantially smaller than the Fermi energy level of graphene where $k_B T \ll |E_F|$ [94, 96]. The contribution from Kerr-type nonlinear processes can typically be deemed small enough to be ignored if it is assumed that the incident electric fields from the radiation are weak enough that (1) the induced current relates linearly to the electric field [107], (2) the incident radiation does not elevate the temperature of the electron gas enough that the $k_B T \ll |E_F|$ assumption is no longer true, and (3) multiphoton absorption processes are not triggered [2]. In summary, when an electromagnetic wave with a frequency below 10 THz and sufficiently weak intensity is incident on highly doped graphene at low temperatures, then the graphene optical conductivity will be dominated by free-carrier intraband transitions that can be accurately described by the Drude model, where:

$$\sigma_{Gr}(\omega) \approx \sigma_{Drude}(\omega) = \frac{e^2 E_F}{\pi \hbar} \frac{1}{\hbar\gamma - \hbar\omega} = \frac{D}{\pi(\gamma - i\omega)} \quad (2.10)$$

where e is the electron charge, E_F is the local Fermi level with respect to the Dirac point, $\hbar$ is the reduced Planck's constant, γ is the relaxation or scattering rate, ω is the angular frequency of incident radiation on the graphene, and D is the Drude weight of graphene.

From this starting point, the optical conductivity can be further modified to take into account the response of graphene to an external magnetic field by converting the optical conductivity into an in-plane tensor. In the absence of a magnetic field, the in-plane optical response of graphene is isotropic, where the optical conductivity tensor is propor-

tional to the identity matrix, inferring that the conductivity is independent of polarization ($\sigma_{xx}(\omega) = \sigma_{yy}(\omega)$ and $\sigma_{xy}(\omega) = \sigma_{yx}(\omega) = 0$) [8, 106]. When a static magnetic field (B) is applied along or perpendicular to the graphene plane, the Lorentz force induces both longitudinal and transverse electronic currents, which changes $\sigma_{xy}(\omega) = -\sigma_{yx}(\omega)$ to a finite contribution to the optical conductivity. Based on the assumptions made for Eq. (2.10), the magneto-optical transport in graphene can be incorporated using the semiclassical Boltzmann transport equation formalism that incorporates a magnetic field-dependent cyclotron frequency (ω_c) to the Drude-based optical conductivity outlined in Eq. (2.10) [82, 106]. The optical conductivity tensor of graphene becomes:

$$\hat{\sigma}(\omega, B) = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \quad (2.11)$$

Noting that $\sigma_{xx} = \sigma_{yy}$ and $\sigma_{xy} = -\sigma_{yx}$, this leads to magnetic field-dependent optical conductivity tensor equations:

$$\sigma_{xx}(\omega) = \frac{e^2 |E_F|}{\hbar^2} \frac{(\gamma - i\omega)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.12)$$

$$\sigma_{xy}(\omega) = \frac{e^2 |E_F|}{\hbar^2} \frac{\omega_c(B)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.13)$$

where e is the electron charge, E_F is the local Fermi level with respect to the Dirac point, $\hbar$ is the reduced Planck's constant, γ is the relaxation or scattering rate, ω is the angular frequency of incident radiation on the graphene, and $\omega_c(B)$ is the magnetic field-dependent cyclotron frequency. The cyclotron frequency characterizes the rotational frequency of the charge carriers when influenced by an applied magnetic field with perpendicular incidence to the graphene plane. As with Drude weight, and other components of the optical conductivity, graphene's cyclotron frequency differs from the classical definition for conventional

metals and semiconductors due to its linear energy dispersion and massless Dirac fermion behavior. Using the same semiclassical Boltzmann transport formalism, the cyclotron frequency for monolayer graphene can be expressed as:

$$\omega_{c-1L} = \frac{eBv_F^2}{|E_F|} \quad (2.14)$$

where e is the electron charge, B is the external magnetic field normal to the graphene plane, v_F is the Fermi velocity of graphene, and E_F is the local Fermi level with respect to the Dirac point.

For AB-stacked bilayer graphene, the coupling between the two stacked layers fundamentally alters the band structure, altering the linear energy dispersion expected of monolayer graphene to a more conventional parabolic energy dispersion at low energies, which means the behavior of charge carriers in bilayer graphene are no longer massless Dirac fermions [41, 110]. The more conventional definition of the cyclotron frequency can be used where:

$$\omega_c = \frac{eB}{m_c^*} = \frac{E_c}{\hbar} \quad (2.15)$$

where the cyclotron frequency can be expressed with e being the electron charge, B being the external magnetic field normal to the bilayer graphene plane, and m_c^* being the cyclotron mass, or the transition energy, E_c , of the highest occupied and the lowest unoccupied Landau level, with $\hbar$ being the reduced Planck's constant. For AB stacked bilayer graphene, the Landau level energy equation is given as [111, 112]:

$$E_n = \frac{1}{\sqrt{2}} \left| \gamma_1^2 + (2n+1)\Delta_B^2 - \sqrt{\gamma_1^4 + 4(2n+1)\gamma_1^2\Delta_B^2 + \Delta_B^4} \right|^{\frac{1}{2}} \quad (2.16)$$

with $\Delta_B = \sqrt{2\hbar|B|}v_f$, the elementary charge, e , the externally applied magnetic field with

a normal incidence to the graphene, B , the Fermi velocity of graphene, $v_F \approx 10^6 \text{ m/s}$, the Landau level filling factor, n , and the interlayer hopping term, γ_1 used to calculate the filling factor for the Landau levels. For the interlayer hopping term, a value of $\gamma_1 = 0.3 \text{ eV}$ was used due to the good fit with the simulation results. Additionally, this value also had excellent agreement with measurements performed by other groups [41, 110, 113]. The filling factor, n , is dependent on the Fermi energy and the external magnetic field, and was used to calculate the cyclotron energy using the equation:

$$E_c = E_{n+1} - E_n \quad (2.17)$$

Compared to monolayer graphene, where the cyclotron frequency is calculated using Eq. (2.14), the cyclotron frequency for bilayer graphene is slightly increased. Additionally, because of the parabolic-like energy dispersion, the cyclotron mass has been treated as nearly constant, with an estimated effective mass of $m \approx 0.036m_e$, where m_e is the free electron mass, in certain regimes [57].

2.4 Modeling of Graphene Disks

The optical conductivity and its response to external magnetic fields serve as the basis for determining the localized plasmonic response of the graphene disks that were fabricated in this study. Using these tensor-based conductivity models as a numerical solver and, more specifically, as a general-purpose electromagnetic simulator based on the finite integration technique (FIT), we have discretized the integral form of Maxwell's equations rather than the differential form. The graphene disks were designed and fabricated based on calculations and modeling performed using Dassault Systemes CST Studio Suite, to ascertain the best disk diameters (d) based on the material properties of the graphene and the target plasmon resonance frequency to maximize the absorption at the excitation frequency available for circular polarization, limited by the availability of the quarter wave plates, which in this case is on the order of 3.5 THz. The electromagnetic field simulation software was used to simulate the transmission spectra of the graphene disks to understand and estimate the linear response. The simulations also helped determine the periodicity of the graphene disk array (Λ) to balance the optimization of the fill factor in order to maximize the interaction with the EM field, but minimize detrimental EM coupling effects between neighboring disks. The graphene disks need to be spaced far enough to reduce the resonance frequency red-shift that close coupling causes, as well as linewidth broadening of the transmission and extinction, but need to be close enough together to enable the coupling-enhanced plasmonic nonlinearity caused by the high localized field intensity. The magnetic field-dependent dielectric function tensor based on the Drude-dominant optical conductivity was calculated to model the magnetic field dependence of the graphene conductivity on a field normal to the graphene disk array and, by extension, the magnetic field dependence of the resonant frequency of the graphene disk plasmon [106]. From previous studies, the magnetic field dependence was incorporated through the addition of a cyclotron frequency incorporated

into the Drude conductivity equations as described in Section 2.3 [41, 110, 113]. The cyclotron frequency has a square dependence on the applied magnetic field and provides a relatively small but noticeable contribution to the Drude conductivity of graphene. When incorporated into the electromagnetic field simulation, the plasmon resonance frequency magnetic field dependence is predicted to split between the right- and left-circular plasmon resonances comparable to the plasmon linewidth.

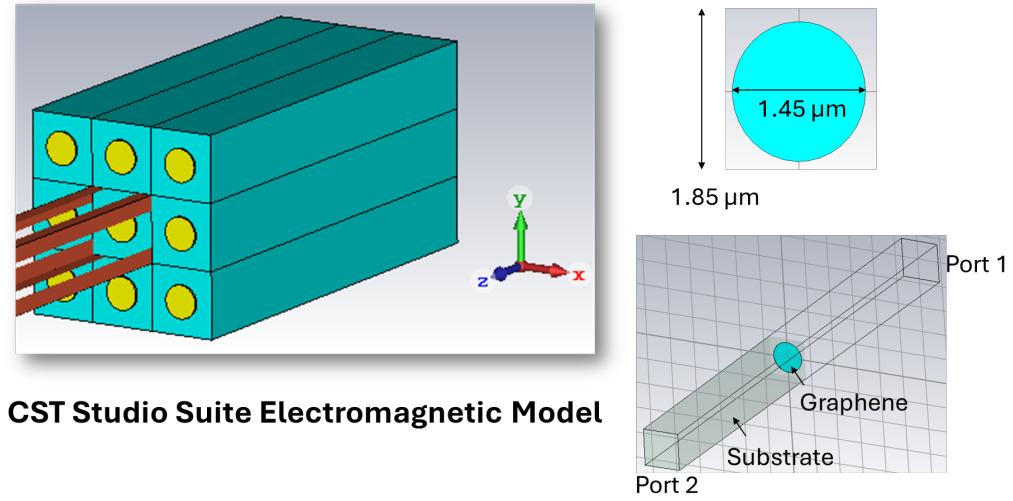


Figure 2.1: CST Studio Suite example visualization of the simulated structure with associated parameters.

The dielectric function tensor of the graphene disks was modeled by prescribing a magnetic field-dependent optical conductivity tensor based on the Drude conductivity equations as described in Section 2.3:

$$\sigma_{xx}(\omega) = \frac{e^2 |E_F|}{\hbar^2} \frac{(\gamma - i\omega)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.18)$$

$$\sigma_{xy}(\omega) = \frac{e^2 |E_F|}{\hbar^2} \frac{\omega_c(B)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.19)$$

where the conductivity components are described by the Fermi energy of graphene, E_F ,

carrier charge, q , vacuum permittivity, ϵ_0 , Planck's constant, h , and the carrier scattering rate of graphene, γ . The magnetic field dependence was incorporated through the addition of the cyclotron frequency, ω_c .

The dielectric function tensor of the graphene response based on the Drude conductivity equations shown in Eq. (2.12) and Eq. (2.13), were calculated with the conversion factor:

$$\epsilon(\omega) = \frac{i}{\omega\epsilon_0 t} \sigma(\omega) \quad (2.20)$$

where ω is the angular frequency of incident radiation, ϵ_0 is the vacuum permittivity, t is the thickness of the material, and $\sigma(\omega)$ is the optical conductivity. Inserting Eq. (2.12) and Eq. (2.13) into Eq. (2.20) gives the relative dielectric tensors, respectively:

$$\epsilon_{xx}(\omega) = \frac{i}{\omega\epsilon_0} \sigma_{xx}(\omega) = \frac{ie^2|E_F|}{\omega\epsilon_0\hbar^2} \frac{(\gamma - i\omega)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.21)$$

$$\epsilon_{xy}(\omega) = \frac{i}{\omega\epsilon_0} \sigma_{xy}(\omega) = \frac{ie^2|E_F|}{\omega\epsilon_0\hbar^2} \frac{\omega_c(B)}{(\gamma - i\omega)^2 + (\omega_c(B))^2} \quad (2.22)$$

where E_F is the Fermi energy of graphene, e is the carrier charge, ϵ_0 is the permittivity of free space, $\hbar$ is the reduced Planck's constant, γ is the carrier scattering rate of graphene, t is the graphene thickness, and $\omega_c(B)$ is the magnetic field-dependent cyclotron frequency as described in Eq. (2.15).

To properly model the graphene material, we acquired estimated carrier densities and material thicknesses from collaborators from the U.S. Naval Research Laboratory who synthesized the quasi-freestanding bilayer epitaxial graphene (QFS BLG) that was used in this study. With that information, a dielectric function tensor was provided to the EM solver to optically and electrically model the graphene in the simulation tools. Dassault Systemes CST Studio Suite simulated the graphene plasmonic disks and generated the linear

Table 2.1: Material and Carrier Parameters used for Graphene Disk EM Modeling

Parameter	Units	Value
Carrier Density (n)	cm^{-2}	9.78×10^{12}
Chemical Potential (μ_c)	eV	-0.350
Material Thickness (t)	nm	0.335
Relaxation Time ($\tau = 1/\gamma$)	ps	0.116
Substrate permittivity (relative) (ϵ_{SiC})	none	12.25
Substrate Thickness (t_{sub})	μm	300

response via transmission spectra while varying the incident magnetic field with linearly polarized radiation and with right- and left-hand circularly polarized radiation (RCP and LCP, respectively). At the plasmon resonance of the graphene disk, the transmission at a resonant frequency is minimized due to the enhanced radiation absorption and electric field confinement at that frequency; thus, a substantial drop in transmission relative to the substrate transmission is observed at the plasmon resonance frequency. A list of graphene and substrate parameters used for the numerical calculations is listed in Table 2.1.

A target plasmon resonance of 3.5 THz was selected to match the available frequency range where quarter wave plates were available for generating circular polarized radiation at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) free electron laser facility (free electron laser at the electron linear accelerator with high brilliance and low emittance, or FELBE) where THz pump-probe measurements were going to be taken. A disk diameter of $d = 1.45 \mu\text{m}$ and a graphene disk array periodicity of $\Lambda = 1.85 \mu\text{m}$ were found to be optimal values for the fabrication of a graphene plasmonic disk array that would have a plasmonic resonance frequency of approximately 3.5 THz based on the properties of the QFS BLG being provided. This was confirmed by simulating both an individual graphene disk as well as small arrays with the specified diameter and periodicity in an external magnetic field normal to the graphene plane of $B = 0 \text{ T}$. The simulated normalized transmission using incident left-circularly polarized radiation provides the expected frequency shift of

the peak extinction due to the change in the external magnetic field due to its influence on the cyclotron frequency. Fig. 2.2 provides the simulated linear response for applied magnetic fields of 0 T, 3 T, and -3 T, using left-circularly polarized radiation.

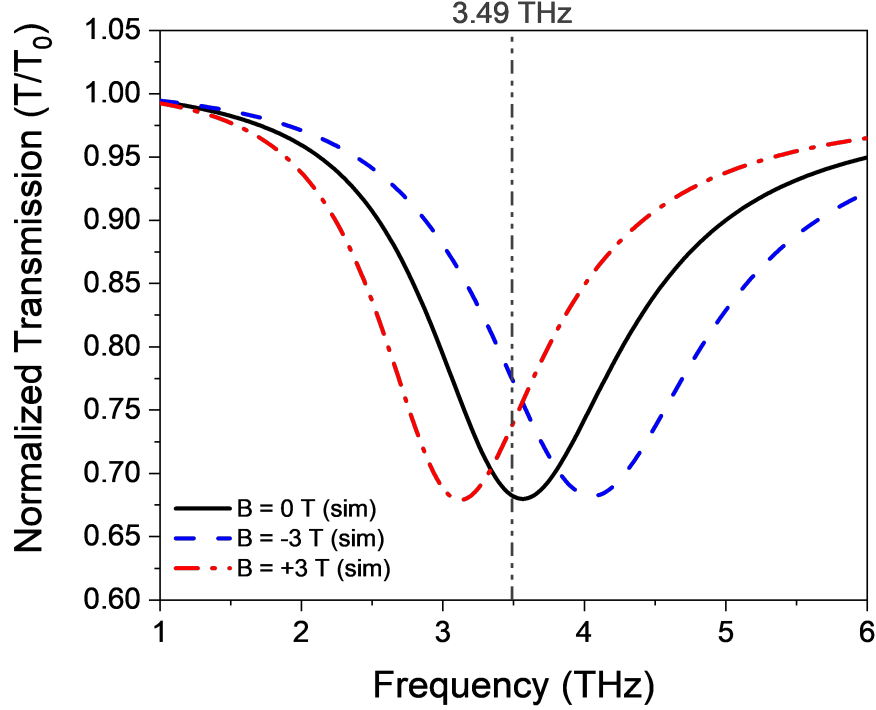


Figure 2.2: Normalized calculated transmission spectra with applied magnetic fields of 0 T, +3 T, and -3 T using left-circularly polarized (LCP) radiation. The 3.49 THz line provides a reference to the measured maximum absorption.

When a static magnetic field is applied normal to graphene plasmonic disks or other plasmonic structures, the zero-magnetic field LSP resonance (ω_0) hybridizes with the magnetic cyclotron resonance (ω_c), and this hybridization causes the original single plasmonic peak to split into two distinct frequency branches with an upper branch frequency mode (ω_+) and a lower branch frequency mode (ω_-) [76, 101]. Because these two branch frequency modes correspond to opposite directions of rotational electron motion, they can be selectively excited by using either left-circularly polarized (LCP) or right-circularly polar-

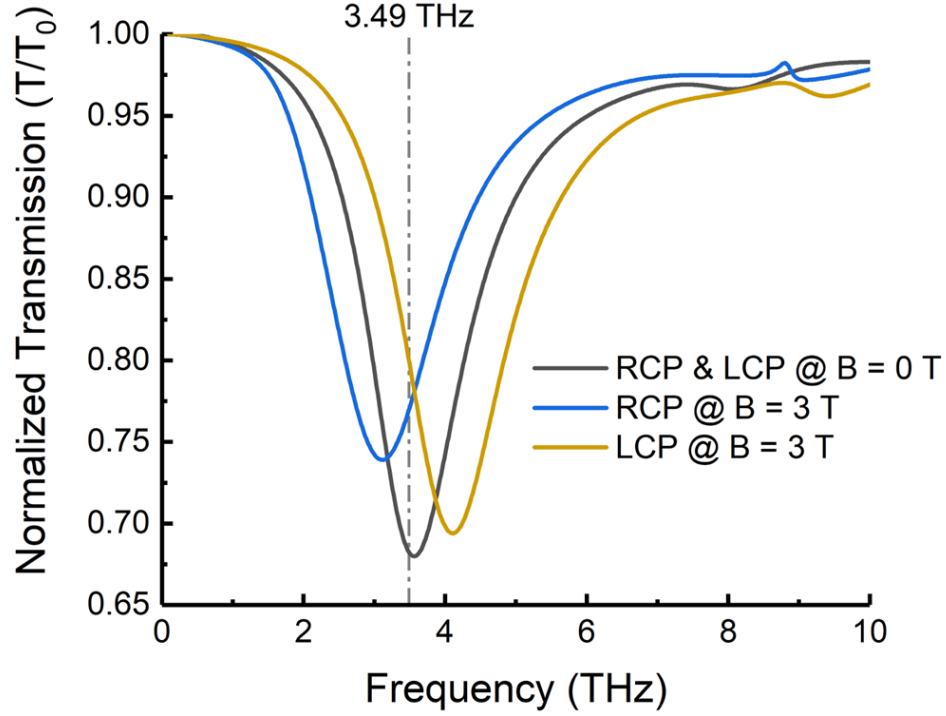


Figure 2.3: Normalized calculated transmission spectra with applied magnetic fields of 0 T and +3 T comparing the plasmon resonance shift or frequency shift in peak extinction between left-circularly polarized (LCP) and right-circularly polarized (RCP) radiation.

ized (RCP) radiation, which has been described in the literature as [76, 101]:

$$\omega_{\pm} = \sqrt{\omega_0^2 + (\omega_c/2)^2} \pm \frac{|\omega_c|}{2} \quad (2.23)$$

where ω_0 is the plasmon resonance frequency at $B = 0$, and ω_c is the cyclotron frequency. This is evident when the calculated transmission spectra of graphene plasmonic disks are compared using LCP and RCP radiation with and without an applied magnetic field. Fig. 2.3 provides the simulated linear response for applied magnetic fields of 0 T and 3 T, comparing the frequency shift and the magnitude of the peak extinction depending on the circular polarization of the incident radiation (LCP vs. RCP).

From the numerical calculations, it was also observed that when strong external mag-

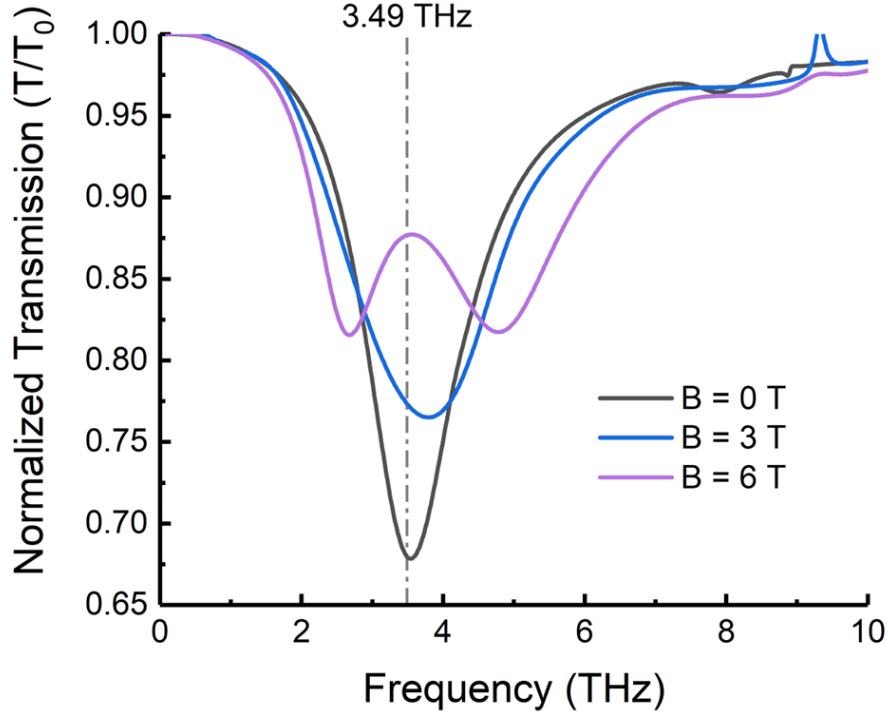


Figure 2.4: Normalized calculated transmission spectra with applied magnetic fields of 0 T, +3 T, and +6 T comparing behavior of the linear response when using linearly polarized radiation as the B-field strength is increased. The 3.49 THz reference line specifies the frequency of the measured plasmon resonance.

netic fields are applied to the graphene plasmonic disk, even for incident linearly polarized radiation, a peak split in the transmission spectrum is observed due to the upper and lower branch frequency modes shifting in opposite directions. This has been postulated to be due to the different frequency dependence of the two branches, with the upper branch behavior being primarily due to interior or bulk magnetoplasmons in the interior of the graphene disk, while the lower branch behavior is driven by edge magnetoplasmons that are pushed to the boundaries of the graphene disks, forming rotating dipole currents along the edge of the disk [76, 101]. The frequency of the upper branch mode increases as the magnetic field increases in strength, while the frequency of the lower branch mode decreases as the magnetic field strength increases. This branch splitting due to an increase in external magnetic

field strength can be seen in the calculated normalized transmission spectral comparison in Fig. 2.4, where the linear response with respect to an increase in magnetic field strength using linearly polarized radiation is simulated.

2.5 Graphene Disk Synthesis and Characterization

With the graphene disk design determined and its linear optical response simulated, quasi-freestanding bilayer epitaxial graphene (QFS BLG) was used to fabricate graphene disk arrays using conventional electron-beam lithography processes. The quality of the graphene material was characterized before fabrication, and then the linear optical response was also confirmed before the nonlinear response of these graphene disks was experimentally studied. This section provides details regarding the synthesis, patterning, and characterization of graphene-based plasmonic structures on a silicon carbide (SiC) substrate.

2.5.1 Graphene Synthesis

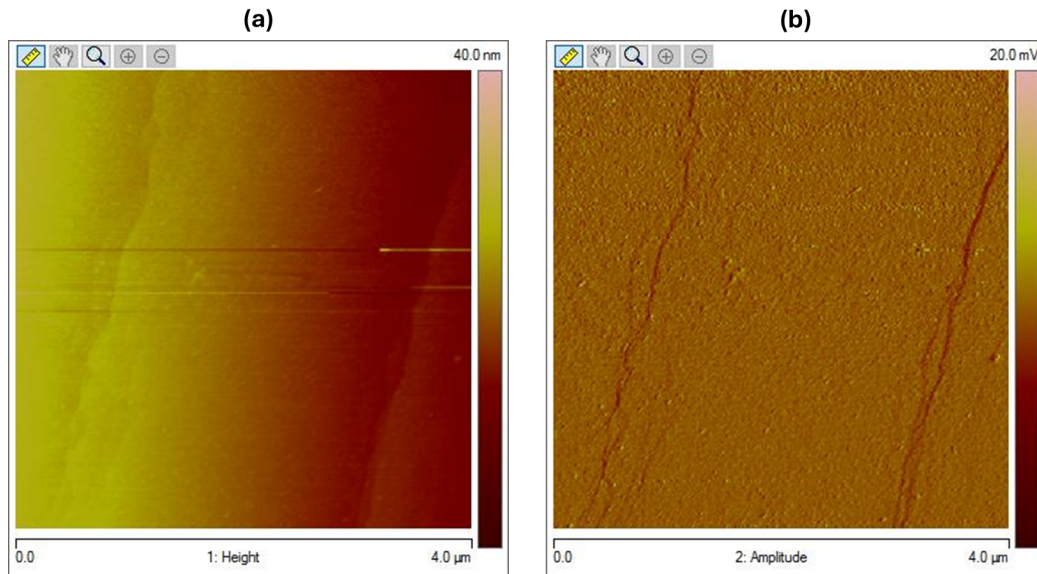


Figure 2.5: Atomic force micrograph of quasi-freestanding bilayer epitaxial graphene provided by U.S. Naval Research Laboratory collaborators. Only the SiC terraces are visible, with an RMS surface roughness of less than 1 nm. (a) An AFM height map and (b) an AFM amplitude map are provided to show the low surface roughness of the material.

The graphene used in this study was grown on SiC using the SiC sublimation process on the Si-face of the wafer. A semi-insulating 6H-SiC wafer with a Si-terminated (0001) is

first etched in a high-purity hydrogen gas environment at temperatures in excess of 1,500 °C to remove polishing damage [55, 93]. The SiC then undergoes a graphitization process by being heated to temperatures of 1,580 °C in an inert argon environment, sublimating Si from the wafer and leaving behind bonded graphene layers [55]. A hydrogen passivation technique was used at a temperature of 1,050 °C in a carrier gas mixture of hydrogen and argon to create a quasi-freestanding bilayer graphene film, reducing the effects associated with substrate coupling [55, 93, 114]. The graphene was provided by collaborators at the U.S. Naval Research Laboratory. The AFM measurements shown in Fig. 2.5 of unpatterned graphene on SiC substrates provided by the U.S. Naval Research Laboratory determined that the RMS surface roughness of the SiC substrate was less than 1 nm, with only the SiC substrate terraces being visible features.

2.5.2 Graphene Plasmonic Disk Patterning and Characterization

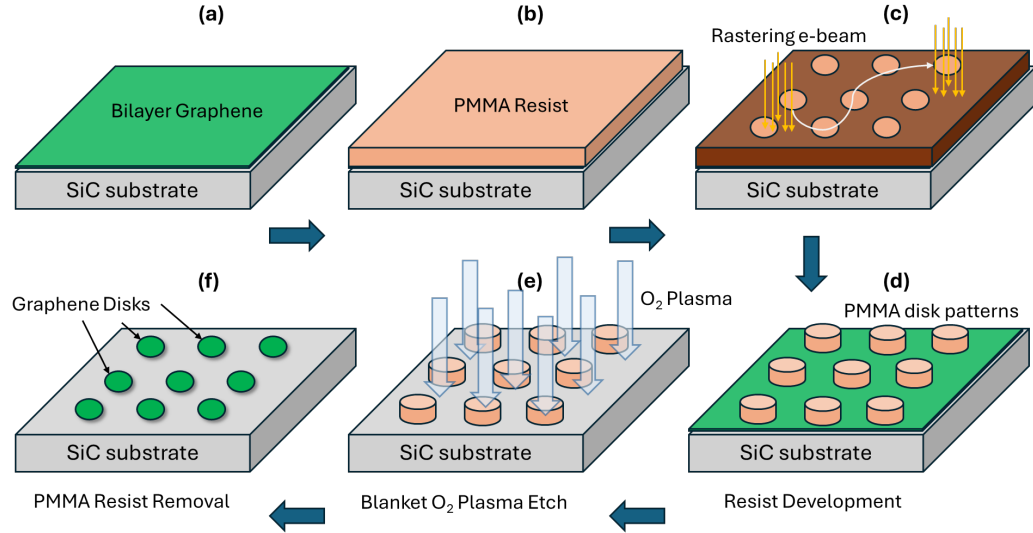


Figure 2.6: Process flow for fabrication of graphene disk array, (a) starting with cleaned graphene on SiC, (b) spinning on e-beam resist, (c) patterning the resist with e-beam lithography, (d) developing the resist, (e) etching the graphene, and (f) removing the resist mask to leave behind patterned graphene disks on an insulated SiC substrate.

The graphene was patterned into a 2 mm x 2 mm square array of disks with diameters of 1.48 μm and with a periodicity of 1.85 μm using electron beam lithography. The fabrication process flow is outlined in Fig. 2.6. A 8 mm x 8 mm SiC substrate with quasi-freestanding epitaxial bilayer graphene was cleaned using an acetone rinse followed by an isopropyl alcohol rinse. The substrate and graphene were dried using nitrogen gas and were heated to 110 °C on a hot plate to remove any moisture from the sample. A polymethyl methacrylate (PMMA) resist, specifically, PMMA 950 A4 from Kayaku/MicroChem spun on at 4,000 RPM to a thickness of approximately 300 nm. A 100 kV high-tension Vistec/Raith EBPG electron beam lithography system with a 400 μm aperture was used to pattern the positive PMMA resist. After development and inspection, the PMMA resist was used as a masking layer for the oxygen plasma etch to remove the exposed graphene, thereby forming isolated disks of bilayer graphene. A PVA TePla Ion Wave plasma asher using an oxygen plasma-

based recipe with a relatively low power setting (100 W) performed the graphene etch. After etching, the resist was removed using acetone heated to 80 °C for several minutes. The etched graphene disk array on SiC was finally cleaned using an isopropyl alcohol immersion bath followed by a drying process using nitrogen gas.

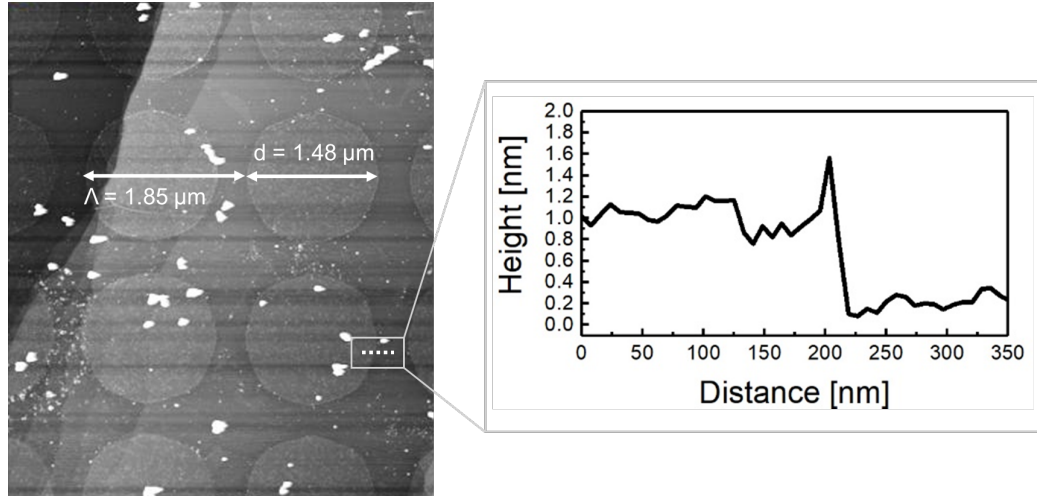


Figure 2.7: Atomic force micrograph of the fabricated graphene disk array on SiC. The dotted line indicates where a height profile is taken, showing that the measured graphene thickness was on the order of 0.6 - 0.7 nm. Lateral measurements show that the graphene disk diameter and periodicity are 1.48 μm and 1.85 μm respectively.

Atomic force microscopy (AFM) was used to confirm the size, shape, and thickness of the graphene disks. The dimensions of the disk were within 5% of the diameter of the target 1.48 μm and the periodicity was within similar tolerances. As shown in Fig. 2.7, the measured thickness of the graphene was on the order of 0.6 to 0.7 nm, which is close to the expected thickness for a bilayer graphene film.

Raman spectroscopy measurements were taken using a WiTec alphaR 300 confocal Raman microscope. A 532 nm continuous wave (CW) laser was used as the incident light source, while a spectrometer with a 1800 g/mm grating and a cooled doped Si charge-coupled device (CCD) detector was used to confirm the existence and quality of the graphene. In Fig. 2.8, the G peak is located at the expected location of $\sim 1580\text{ cm}^{-1}$, and the 2D peak

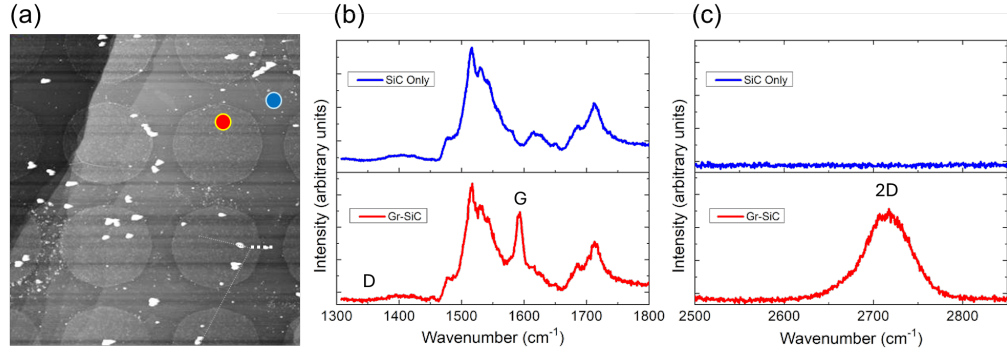


Figure 2.8: (a) Atomic force microscopy image of fabricated bilayer graphene disk array on SiC indicating where Raman measurements were taken. (b) Raman spectroscopy was used to confirm the existence of bilayer graphene, characterized by the presence of a G peak at $\sim 1580 \text{ cm}^{-1}$ and (c) a 2D peak at $\sim 2700 \text{ cm}^{-1}$ that has a slight shoulder at $\sim 2680 \text{ cm}^{-1}$ as described in Ferrari, et. al [115]

appears to possess a broader, upward-shifted shape and a slight shoulder between $\sim 2650 \text{ cm}^{-1}$ and $\sim 2750 \text{ cm}^{-1}$ that are characteristic of bilayer graphene [115, 116]. Reference measurements were taken on the bare SiC substrate to confirm the graphene Raman signatures and to determine peaks related specifically to the SiC substrate.

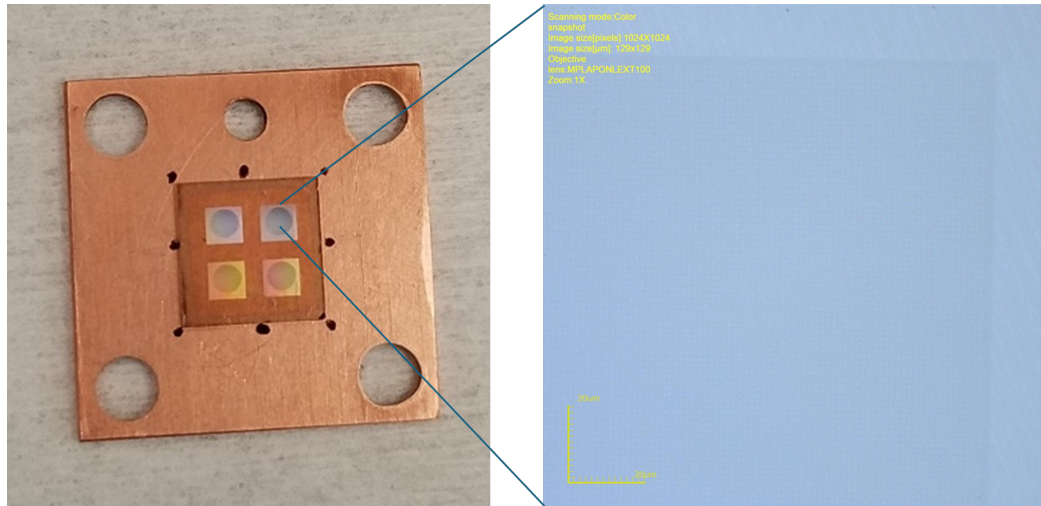


Figure 2.9: Image of the patterned graphene arrays on SiC mounted to a copper sample holder for use in measurement setups.

After some initial characterization, the patterned graphene sample was mounted onto a

copper-based sample holder for use in various measurement setups and cryostats as shown in Fig. 2.9.

2.5.3 Linear Optical Response of Graphene Plasmonic Disks

Prior to nonlinear measurements, Fourier transform infrared (FTIR) transmission spectroscopy and conventional THz time-domain spectroscopy (THz TDS) were used to measure the plasmon resonance of the disks in the absence of a magnetic field. A bare 2 mm x 2 mm SiC substrate served as a reference to the measurement. The measurements were performed at room temperature ($\sim 23^\circ\text{C}$) in a nitrogen-purged environment to suppress water absorption. The measured transmission as a function of the frequency (from THz TDS) is plotted in Fig. 2.10 where the measured transmission has been normalized to that of the SiC substrate transmission reference measurement. The measurement setup used is similar in configuration to what is depicted in Fig. 1.5. When the frequency is resonant with the plasmon frequency at approximately 3.5 THz, a peak extinction of $\sim 30\%$ is observed. This matches well with the calculations via the electromagnetic field simulation software package by Dassault Systemes, CST Studio Suite. The simulated transmission spectra is plotted with the measured normalized transmission spectra in Fig. 2.11 with the uncertainty of the measured transmission in gray. The graphene disks were modeled by prescribing a magnetic field-dependent dielectric function tensor matrix based on the Drude conductivity as described in Section 2.3 and Section 2.5 [106].

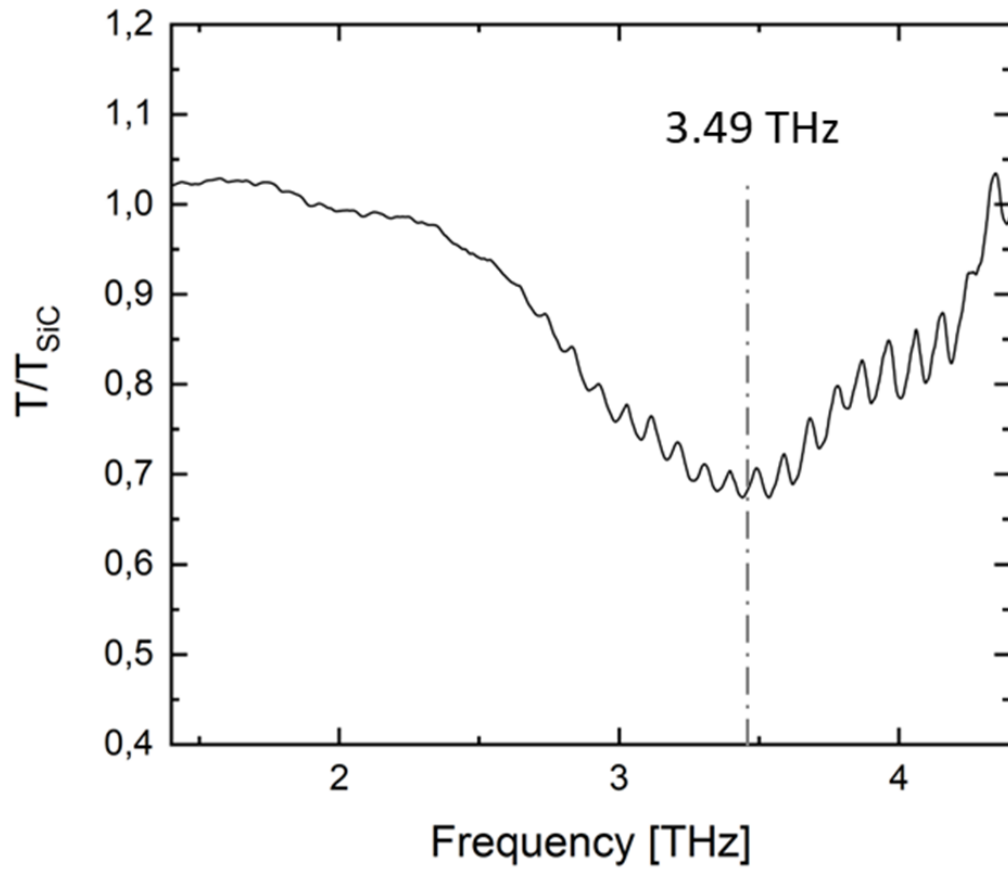


Figure 2.10: Measured linear transmission of the graphene disk array on SiC with a disk diameter of $1.45 \mu m$ and a periodicity of $1.85 \mu m$. The measured peak absorption occurs at the plasmon resonance frequency of 3.49 THz for these particular graphene disks.

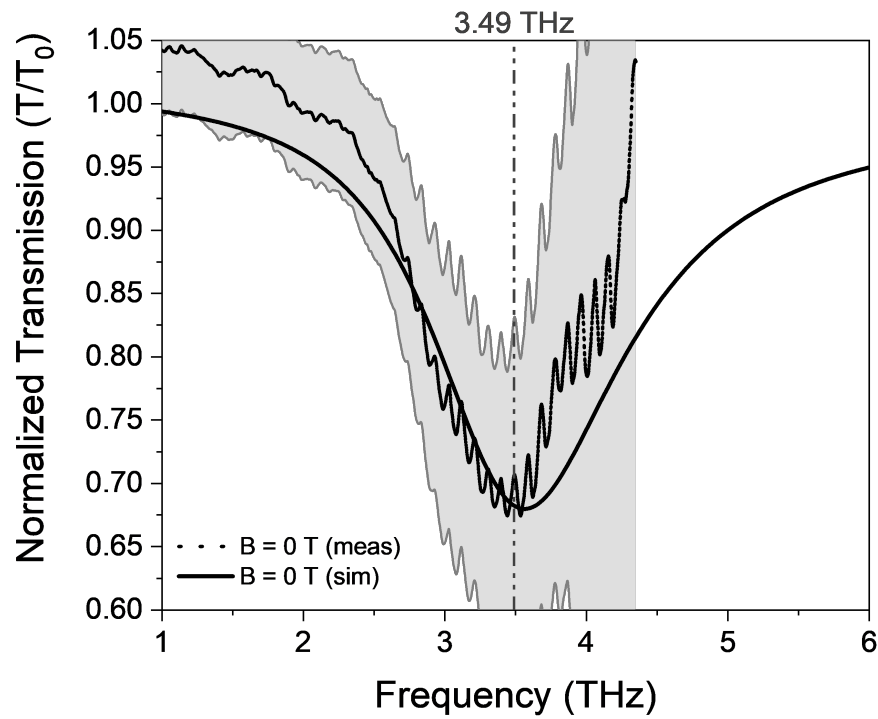


Figure 2.11: Measured linear transmission (THz TDS) normalized to the SiC substrate reference for a graphene disk array with diameters of $1.45 \mu\text{m}$ and a periodicity of $1.85 \mu\text{m}$ compared against the numerically calculated normalized transmission with the same graphene disk array parameters. The confidence interval is highlighted in gray.

Chapter 3: Magnetic Tuning of THz Nonlinearity in Graphene Plasmonic Structures

3.1 Magnetic Field-Dependence of Nonlinear Light-Matter Interactions in Graphene Disks

The linear response of magnetoplasmons in graphene-based plasmonic resonance structures (including nanoribbons and nanodisks) have been explored since the 2010's. Experimental demonstrations of the effects of plasmon frequency branch mode splitting due to bulk plasmons on the interior of the structures responding opposite to the edge plasmons at the confinement borders of the structures have been reported [76, 101]. Additionally, the linear optical response in graphene plasmonic structures have been actively tuned through electrostatic gating and changing the field strength of an applied magnetic field, allowing for a level of tunability not achievable with conventional metal plasmonic structures [56, 101, 102].

The nonlinear response of magnetoplasmons in graphene-based plasmonic resonance structures, like graphene disks, is an area of research where additional understanding of the tunability of the nonlinear response based on changing the field strength of an applied magnetic field would be beneficial to the body of knowledge in this field. The nonlinear optical response of the graphene disks that were designed and modeled in the previous chapter was studied with respect to the presence of a uniform applied magnetic field. THz pump-probe

spectroscopy was used to understand how the change in transmission with respect to time using a single color radiation line, both on and off the plasmonic resonance of the graphene disks, could be tuned based on adjusting the magnetic field strength normal to the graphene disk array. THz pump-probe measurements were performed at the Helmholtz-Zentrum Dresden-Rossendorf facility in Dresden, Germany by collaborators at the University of Duisburg-Essen for this study. A two-temperature numerical model was used to describe the expected change in transmission with respect to the applied magnetic field for direct comparison with the experimental results from the THz pump-probe spectroscopy.

3.2 Experimental Setup for Magnetic Field-dependent Nonlinear Pump-probe Measurements

To characterize the nonlinear absorption of the magnetoplasmons, collaborators from the University of Duisburg-Essen helped me perform pump-probe measurements at the free-electron laser (FEL) facility, FELBE, at the Helmholtz-Zentrum Dresden-Rossendorf. The free electron laser at the electron linear accelerator with high brilliance and low emittance (FELBE) provides an ultrashort THz pulse with a duration in the picosecond range and a repetition rate of 13 MHz. The photon frequency is tunable in a wide range, spanning from 1.2 THz to about 60 THz. This allows for measurements above and below the plasmonic resonance of the graphene nanodisks. Three sets of measurements were taken to observe the nonlinear response of the magnetoplasmons in the fabricated graphene disk arrays. The first set of measurements were performed at a photon frequency of 3.5 THz, which comes close to the measured plasmon frequency of the graphene disks, where the measured extinction via THz time-domain spectroscopy was maximized. These measurements were performed with linearly polarized radiation, as the FEL at the HZDR facilities naturally provides the linear polarization. The 3.5 THz beam pulses had a duration of 16 ps. The purpose of this first set of measurements was to understand the nonlinear response of the magnetoplasmons in a magnetic field when both the upper and lower magnetoplasmon frequency branch modes are excited. The second set of measurements were also performed at a photon frequency of 3.5 THz, but quarter-wave plates, made of quartz, were introduced into the beam path to convert the linearly polarized radiation to circularly polarized radiation. The circularly polarized beam pulses had a duration of 20 ps. Because the upper and lower magnetoplasmon frequency branch modes are excited by opposite directions of rotational electron motion, the circularly polarized radiation selectively excites only one

of the branches depending on the direction of the circular polarization [76]. The third set of measurements were performed significantly above resonance at 4.3 THz with linearly polarized radiation and a 6.4-ps pulse duration. This measurement was performed to determine and demonstrate how the magnetic field can be used to tune the resonance frequency of the magnetoplasmons in the graphene disks.

A pellicle beam sampler was exploited to split off about 2% of the radiation to serve as the probe and was guided through a mechanical delay stage to set the time delay between the pump and probe pulses. A parabolic mirror was used to focus the parallel pump and probe beams under a small angle to the sample that was kept in a magneto-optical cryostat at a temperature of 60 K in a helium atmosphere. Magnetic fields of up to ± 7 T were applied perpendicular to the sample surface, or normal to the bilayer graphene disks. The probe radiation was collected after passing through the magneto-optical cryostat with a second parabolic mirror and guided to a bolometer while the pump radiation was blocked. The pump-induced change in transmission was then recorded as a function of the time delay between the pump and probe beam.

3.3 Simulated Magnetic Field Dependence of THz Transmission for Graphene Disks

In order to understand and anticipate the nonlinear response from magnetoplasmons with these graphene disk arrays, numerical modeling of the pump-probe experiment was performed with much of the simulation work being performed by Sebastian Matschy at the University of Duisburg-Essen. This modeling effort was done concurrently with the experimental measurements described in Section 3.2 to be able to directly compare the experimental results with the numerical model calculating the change in transmission with respect to both the magnetic field and the change in time. The model is based on the two-temperature model that was already exploited to investigate the nonlinear absorption of graphene plasmonic ribbons in the absence of a magnetic field [12, 77]. The absorption as a function of the frequency was calculated via:

$$\frac{\Delta T(\omega)}{T_0} = \left| 1 + \frac{dZ_0}{\pi(1+n_{\text{SiC}})} \frac{D(T)}{\left(\Gamma(T) - i\frac{\omega^2 - \omega_p^2(T)}{\omega}\right)} \right|^{-2} \quad (3.1)$$

where d represents the fraction of the surface covered by graphene, Z_0 is the free space impedance, and n_{SiC} is the refractive index of the SiC substrate. The Drude weight D , scattering rate Γ , and plasmon frequency ω_p depend on the temperature of the carrier distribution as described in [95]. To account for the magnetic field, the plasmon frequency in Eq. (2.12) was substituted with Eq. (2.23) [76, 101]. To derive the temperature evolution of the free carriers during the pump-probe cycles, the differential equation [117–119]:

$$\alpha T \frac{dT}{dt} + \beta(T^3 - T_L^3) = A(\omega, T)I(t) \quad (3.2)$$

with α as the specific heat of the electron gas, β as the supercollision cooling coefficient, T as the temperature, T_L as the lattice temperature, t as time, I as the laser intensity, and A as the absorption coefficient, was used. The laser intensity $I(t)$ describes the temporal evolution of the pump pulse, which is assumed to be Gaussian; the pulse duration was derived from the measured FEL spectra. Additional parameters used in this model include the Fermi energy, $E_F = 320\text{meV}$, the plasmon resonance frequency, $\omega_p = 2\pi(3.55\text{ THz})$, and a constant scattering rate of $\Gamma = 2\pi(0.8\text{ THz})$. For the supercollision cooling coefficient (β), a value of $1\text{ Wm}^{-2}\text{K}^{-3}$ was chosen to fit the relaxation time in the model to the experimental data. The value is also in good agreement with values reported in previous works as well [118, 119].

It should be noted that no fitting parameter is included to match the signal strength to the measurements. Additionally, the two-temperature model does not account for variations of the scattering rate between the upper and lower branch frequency modes, which might be present due to the differences in the electron motion between the two branches. As described in Section 2.4, the higher frequency mode corresponds to the circular electron motion within the interior or bulk of the graphene disks, while the lower frequency mode is associated with the graphene disk edge boundaries' skipping orbits. This distinction between the two branches becomes larger at higher magnetic field strength.

3.4 Magnetic Field Tunability of Graphene THz Transmission Characteristics

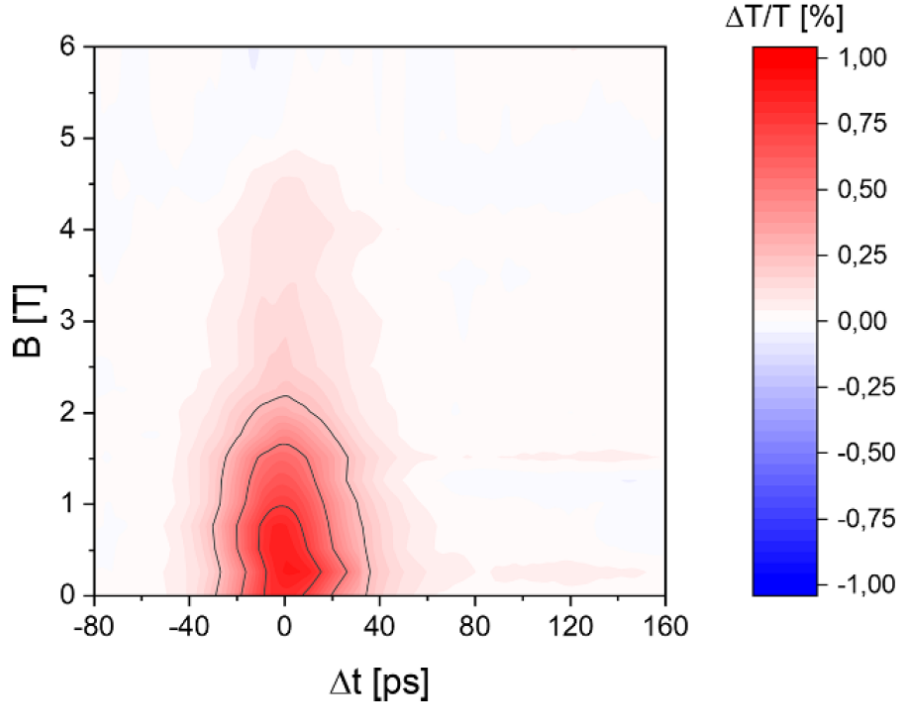


Figure 3.1: Experimental three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift based on THz pump-probe spectroscopy using an applied magnetic field. The pump and probe laser pulses consisted of linearly polarized radiation at 3.5 THz, had a full-width-half-maximum (FWHM) of 16 ps, and a fluence of 42 nJ/cm^2

A set of pump-probe measurements taken with linearly polarized radiation and magnetic fields of up to 6 T is shown in Fig. 3.1. The relative change in transmission is color coded as a function of the time delay between the pump pulse with a fluence of 42 nJ/cm^2 , and the probe pulse. The time delay is shown on the x-axis and the magnetic field on the y-axis. Without magnetic field, a pump-induced increase in transmission of about 0.8% was observed, which is consistent with measurements on graphene ribbons made from the same material [12]. Within about 40 picoseconds, the signal relaxes back to equilibrium,

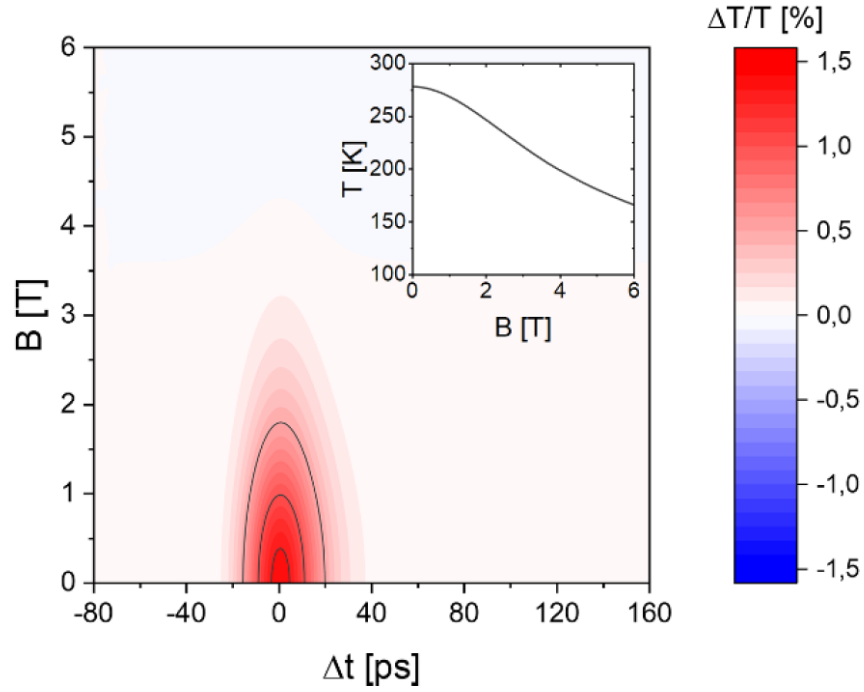


Figure 3.2: Numerically simulated three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift with parameters matched to the experimental measurement. Model assumes the 3.5 THz pump and probe pulses are linearly polarized.

emphasizing the fast cooling of the hot carriers. The increase in transmission is attributed to the redshift of the plasmon frequency as the hot carrier distribution results in a decreased chemical potential. For fields above 1 T, the pump-probe signal is strongly quenched, until above 5 T where no signal is observed.

As can be seen in Fig. 3.2, the results of the model match well with the experimental data. Interestingly, the model shows significant heating of the carrier distribution even at high magnetic fields, where no pump-probe signals are visible (cf. inset in Fig. 3.2). This is caused by the red shift of the plasmon frequency upon carrier heating, which results in a pump-induced increase (decrease) in transmission when the photon frequency is above (below) the plasmon frequency. As the magnetic field is applied and the plasmon frequency splits into the upper and lower branches, the linearly polarized radiation still interacts with

both branches. While the lower branch leads to an increase in transmission, the upper branch causes the transmission to decrease, leading to a zero net change of the differential transmission above 5 T.

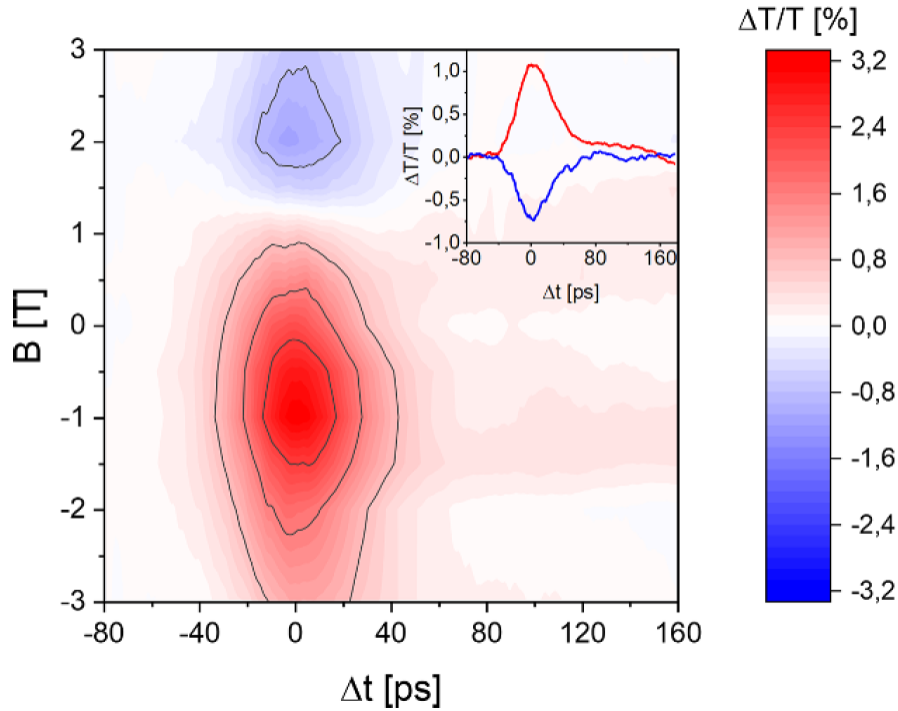


Figure 3.3: Experimental three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift based on THz pump-probe spectroscopy using an applied magnetic field. The pump and probe laser pulses consisted of circularly polarized radiation at 3.5 THz, had a full-width-half-maximum (FWHM) of 20 ps, and a fluence of 42 nJ/cm^{-2}

To further investigate the role of the upper and the lower branch, we performed pump-probe measurements with circularly polarized radiation. In this case, only one of the two branches is interacting with the pump and probe radiation. For measurements taken using linearly polarized radiation, the orientation of the magnetic field does not play a role, but for measurements using circularly polarized radiation, the sign of the magnetic field determines which of the two branches interacts with the radiation. The results of this experiment, in which the magnetic field was tuned in the range between -3 T to 3 T are shown in

Fig. 3.3. A positive change in transmission is observed at -3 T, indicating that the plasmon frequency is below the photon frequency. As the magnetic field is tuned towards zero, the amplitude of the pump-probe signal increases, until resonance is reached at about -0.8 T and the maximum increase in differential transmission is observed. For increasing positive magnetic fields, the signal is quickly quenched to zero and eventually changes sign above 1.5 T. The negative sign of the signals can again be understood by the thermal redshift of the plasmon frequency caused by the hot carriers. As was the case of linearly polarized radiation, the calculations match the experimental findings for circularly polarized radiation as well, as shown in Fig. 3.4.

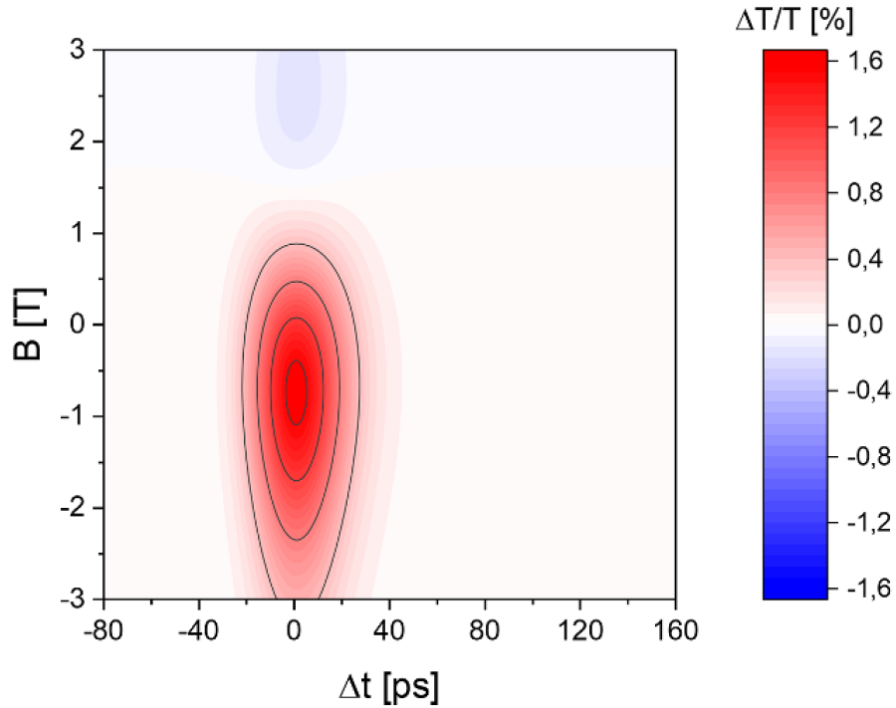


Figure 3.4: Numerically simulated three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift with parameters matched to the experimental measurement. Model assumes the 3.5 THz pump and probe pulses are circularly polarized.

To investigate the detuning of the magnetoplasmons and use of the magnetic field to adjust the plasmon frequency response of the graphene disks, the FEL was significantly

detuned with respect to the plasmon frequency. At a wavelength of $69\text{ }\mu\text{m}$ or equivalent frequency of 4.34 THz , no pump-probe signal was observed without a magnetic field present. Because the measurement was performed with linearly polarized radiation, only one orientation of the magnetic field was measured due to the isotropic plasmonic resonance of the graphene disks. For elevated fields of more than 2 T , a clear positive pump-probe signal is observable, the peak change in transmission is around 4.5 T , and at 7 T , only a slight change in transmission is measurable, as shown in Fig. 3.5. This evolution of the peak change in transmission with respect to the magnetic field is expected as the magnetoplasmon is tuned into resonance with the photon frequency at around 4 T . For magnetic fields below that value, the magnetoplasmon frequency is below the photon frequency, leading to positive, but small pump-induced, changes in transmission. Above 5 T , the magnetoplasmon frequency is above the photon frequency and a sharp drop in signal is expected, eventually leading to a change in sign at the maximum magnetic field strength available of 7 T , as shown in the calculation in Fig. 3.6.

Compared to the measurements shown in Fig. 3.1 and Fig. 3.3, the signal is much shorter, mainly due to the shorter pulse duration of the FEL, which is around 6 ps opposed to 20 ps in the earlier measurements. This shorter pulse duration has also been taken into account in the model, with the results shown in Fig. 3.6. Unlike previous studies on unpatterned graphene that reported an increase in relaxation time in strong magnetic fields [120, 121], only a slight dependence on the magnetic field was observed. Without a magnetic field, a relaxation time of 21 ps was observed at resonance, which increased to 27 ps at 4.5 T . This might be related to the bilayer nature of the sample or defects that enable scattering with out-of-plane phonons.

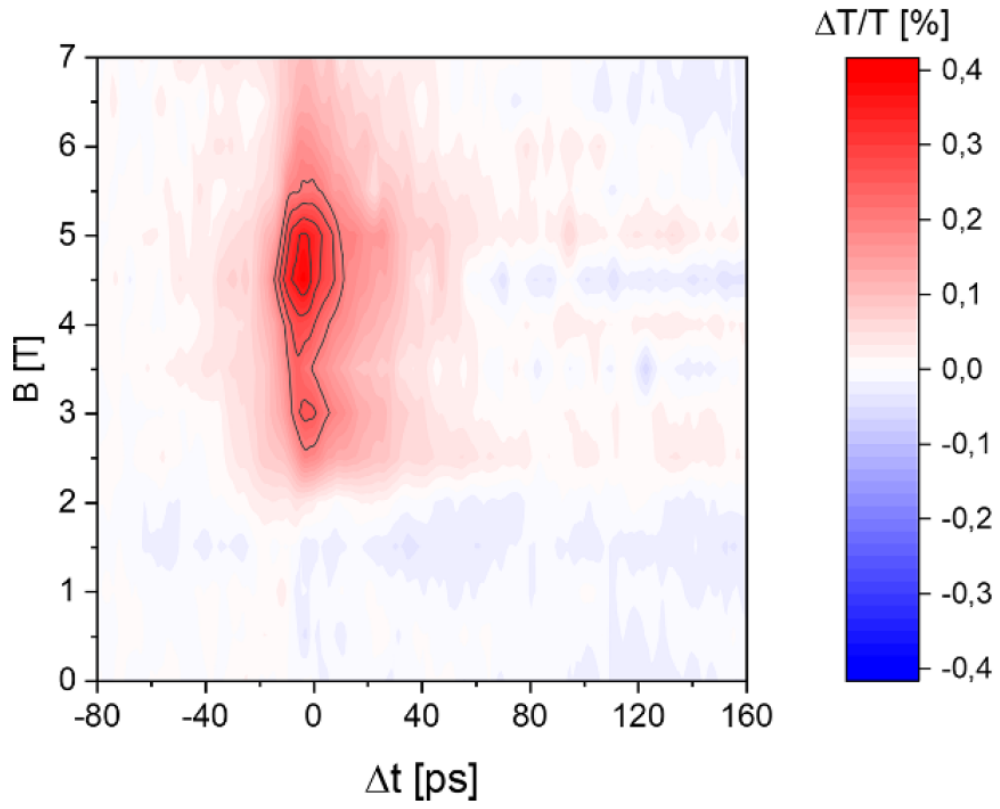


Figure 3.5: Experimental three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift based on THz pump-probe spectroscopy using an applied magnetic field. The pump and probe laser pulses consisted of linearly polarized radiation at 4.34 THz, had a full-width-half-maximum (FWHM) of 6.4 ps, and a fluence of 370 nJ/cm^{-2}

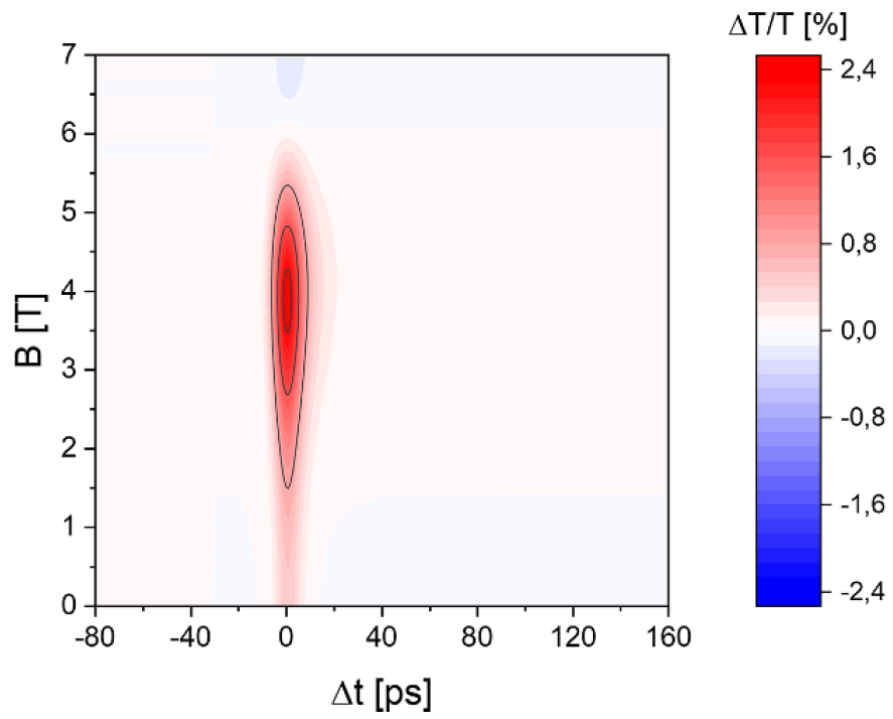


Figure 3.6: Numerically simulated three-dimensional plot of change in transmission through graphene disk array due to a temperature-induced redshift with parameters matched to the experimental measurement. Model assumes the 4.34 THz pump and probe pulses are linearly polarized.

3.5 Conclusions

In conclusion, we investigated the influence of a magnetic field on the optical nonlinearity observed in plasmons in graphene disk arrays fabricated from quasi-freestanding bilayer epitaxial graphene on SiC. It was experimentally shown that the nonlinear optical response is governed by the heating of charge carriers that lead to a red-shift of the plasmon frequency. When pumped with strong THz radiation resonant with the plasmon frequency of the graphene disks, the absorbed radiation raises the electron temperature in the graphene, lowering the chemical potential (and the associated Fermi energy) and causes the plasmon resonance to weaken, broaden, and shift to a lower frequency. This change in the plasmon resonance frequency reduces the absorption and generates a strong transient increase in transmission. This can be numerically modeled with relatively good agreement using a Drude-based two-temperature model. When an external magnetic field is present, a cyclotron resonance is introduced that hybridizes with the plasmon resonance in the graphene disks, which are capable of spatially confining and localizing fields. This allows for the plasmon frequency and the plasmonic resonance of the graphene disks to be magnetically tuned, including its nonlinear response, leading to the observation that the change in transmission due to a strong transient pulse of radiation can be tuned based on the magnetic field and the circular polarization of the incident radiation. In short, depending on the relative photon frequency with respect to the plasmon frequency, the nonlinear behavior can be tuned across a wide range frequency range, i.e. the super-linear transmission at resonance can be inverted to be sublinear with moderate magnetic fields in the 3 T range. In contrast to earlier experiments on multilayer epitaxial graphene, only a minor change in relaxation time was observed.

Chapter 4: Electron Beam Effects on Exciton Emission in Transition Metal Dichalcogenides

In addition to graphene, other two-dimensional (2D) materials show unique and potentially useful light-matter interactions that can be tuned or enhanced using plasmonic structures. Transition metal dichalcogenides (TMDs) have shown promise as low-dimensional van der Waals semiconducting materials for novel electronic devices, such as field effect transistors [122–124], light emitting diodes [125], photodetectors [126], and solar cells [127, 128]. The integration of metallic nanostructures on TMD-based heterostructures and stacks to exploit the use of localized surface plasmons for the modification of the local electric field has been a recent topic of study. Early experiments demonstrated that enhanced light emission was possible from monolayer MoS₂ using plasmonic nanodisk arrays [129], and from these initial studies several important results were confirmed. It was found that metallic plasmonic resonance structures were capable of both enhancing light-matter interactions as well as inducing photoluminescence (PL) quenching through light absorption or electron transfer from the TMD surface to the metallic structure. When a dielectric spacer layer was introduced between the plasmonic structures and the TMD, the charge transfer was suppressed, and the PL enhancement of two orders-of-magnitude was observed [52]. These plasmon-exciton interactions (also called plexcitons or plasmon exciton polaritons) and the potential for them to be tunable through the use of electrostatic gating have made this combination of plasmonic resonance structure and TMD device a promising candi-

date for applications such as ultrafast optical circuitry and electro-plasmonic modulators [30, 130]. To fabricate nanoscale metal plasmonic resonance structures for generating localized surface plasmons on TMDs, electron beam lithography is a common method for patterning structures at the nanometer scale. After the fabrication of Au-based plasmonic disks on monolayer WSe₂ films, the optical response was found to have shifted significantly from its optical response before fabrication, and it was suspected that the cause of the change was defect generation or the introduction of surface charging from the electron-beam lithography process. Trying to understand and mitigate fabrication-based defects and charging for surface-sensitive materials such as monolayer TMDs became the new focus of this second study.

The next two chapters provide an introduction to this project and an explanation for why this study occurred, an overview of TMDs, the effects of the electron beam lithography process on TMDs, the possible effects of defect generation on exciton populations in TMDs, a description of the experimental methodology, and a comparison of results between hBN-encapsulated and unencapsulated WSe₂ to understand how effective some reported mitigation methods are to protect the WSe₂ from common fabrication processes. In summary, the effects of electron beam irradiation based on typical electron beam lithography (EBL) processes and parameters are reviewed from the change in optical properties of WSe₂ monolayer films, specifically looking at the change in exciton populations at low temperatures ($T = 4\text{--}5\text{ K}$). Bare, unencapsulated monolayer films of WSe₂ and monolayer films of hBN-encapsulated WSe₂ were treated with the same EBL process, with their optical response compared to understand how excitonic populations are affected with and without a widely accepted damage mitigation technique of hBN encapsulation [44, 51, 131–137].

4.1 Origin of Study - Plasmonics, Light-Matter Interactions in Transition Metal Dichalcogenides, and Fabrication Issues

With exciton studies in TMDs having been a popular area of research in the past decade, with implications in the optoelectronics field, methods to enhance emission rates using resonant cavities and structures have been studied by a number of research groups on a variety of monolayer TMDs [138–147]. Strong light-matter coupling has been reported between excitons from TMD monolayers and various plasmonic resonance structures, leading to the study of hybrid polaritons called “plexcitons”. Experimental measurements including angle-resolved reflectance spectroscopy, photoluminescence, dark-field scattering spectroscopy, emission/reflectance spectroscopy, absorption/extinction spectroscopy, and pump-probe spectroscopy have all been used to understand the exciton interactions with plasmonic resonance or antenna structures. There does exist a gap in the study of how plasmonic structures can be designed or engineered to interact with interlayer excitons in TMD heterostructures, and this was to be a major topic of study for this thesis work.

4.1.1 Proposed Plasmon-Exciton Studies on TMD Heterostructures

The initial proposed study was to address the plasmonic tuning or enhancement of interlayer excitons in TMD heterostructures using metallic plasmonic resonance structures for near-infrared (NIR) sensing applications. The tunability optical response was to be studied through the use of engineered plasmonic resonance structures, designed for optimal frequency resonance at the PL excitation wavelength, the intralayer exciton emission wavelengths of the constituent TMD monolayers, and the interlayer exciton emission wavelength. As a continuation of studying light-matter interactions involving 2D materials and plasmonic resonance structures, this research effort reviewed the light-matter interactions

and potential signal tunability or enhancement of interlayer excitons in transition metal dichalcogenide (TMD) heterostructures using patterned, plasmonic disks based on noble metals in the infrared spectral regime. The excitonic properties of the TMD monolayers and their associated heterostructures were explored and characterized before and after the implementation of fabricated plasmonic resonance structures to alter the optical response. Using photoluminescence and Raman spectroscopy, we hoped to determine the effects of engineered plasmonic resonance structures on the excitonic species generation in TMD heterostructures and monolayers.

4.1.2 Fabrication of Plasmonic Resonance Structures on hBN-encapsulated WSe₂

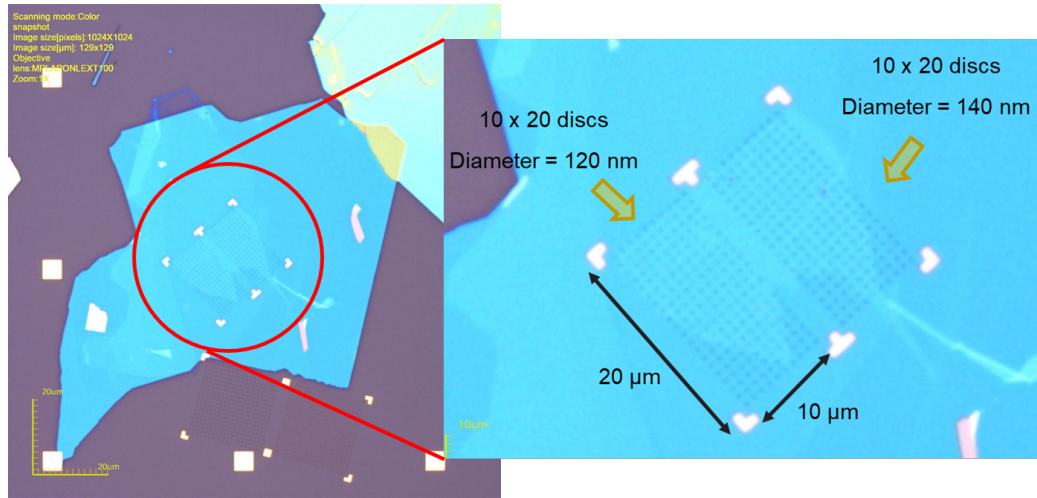


Figure 4.1: Fabricated plasmonic structures on hBN-encapsulated WSe₂.

The plasmonic structures were modeled and fabricated to optimally absorb and concentrate fields at the excitation wavelength and near the neutral exciton resonances and emission wavelengths. Initial designs for the Au plasmonic disks were numerically modeled using the finite-difference time-domain (FDTD) method via the software EM solver pack-

age, Ansys Lumerical. Plasmon disk arrays based on Au with diameters of 120 nm and 140 nm and a thickness of 50 nm were fabricated on hBN-encapsulated WSe₂ monolayers to test the optical response before committing WSe₂ / MoSe₂ heterostructures. Electron beam lithography was performed to pattern the Au disk arrays on top of the hBN-encapsulated WSe₂ using the same procedure described in Section 5.3. Past reports indicated that hBN encapsulation of TMD monolayers preserved the optical and electronic properties of the TMD by increasing the threshold energy required for chalcogen displacement in the TMD lattice and preventing other process-related defects and trapping [19, 30, 51, 148]. Gold metal and a 1 nm thick Ti adhesion layer were deposited using a CHA electron-beam evaporator with a deposition rate of 4 angstroms/s, for a total thickness of 50 nm. A lift-off process using acetone immersion at room temperature was performed to remove the PMMA resist and unnecessary Au. A micrograph of the fabricated Au plasmonic disks on a hBN-encapsulated WSe₂ monolayer is provided in Fig. 4.1. The process flow described is outlined in Fig. 4.2.

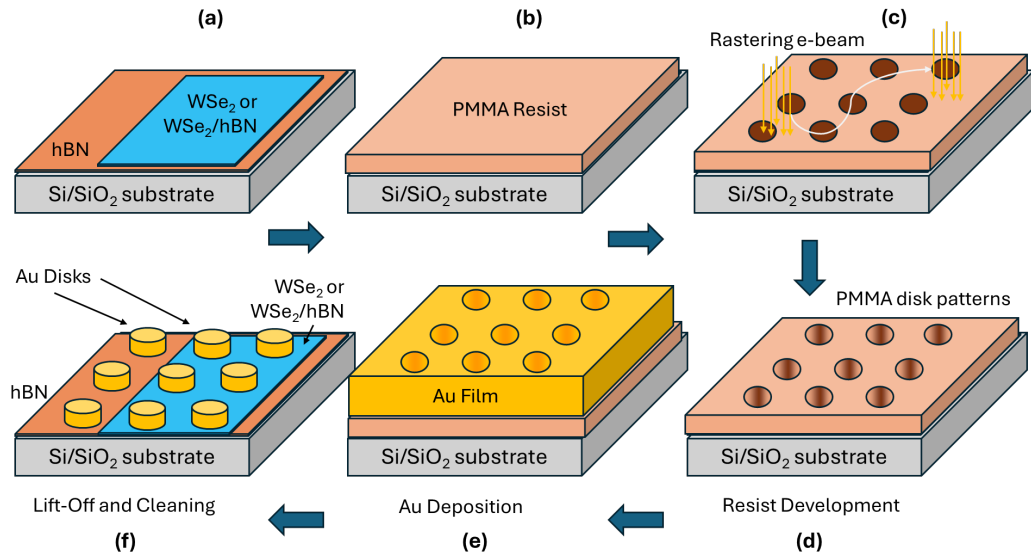


Figure 4.2: Diagram of plasmonic structure fabrication on TMD heterostructures, where (a) a WSe_2 monolayer film or hBN -encapsulated monolayer is prepared, (b) coated in a PMMA resist and soft-baked, (c) patterned using e-beam lithography, (d) developed in an MIBK-based immersion, (e) blanket-deposited with Au, and then (f) lifted off using an acetone immersion process, leaving behind patterned Au plasmonic disks.

4.1.3 Characterization of hBN-encapsulated WSe₂ with and without Au Plasmonic Disks

A collaborator at the Army Research Laboratory, Christopher Kuhs, provided dark-field scattering spectroscopy on Au disks with both the 120 nm and 140 nm diameters, to verify the localized surface plasmon resonance (LSPR) and absorption peak of the plasmonic structures on the hBN-encapsulated WSe₂. The results of the measurements are shown in Fig. 4.3, where it can be assessed that the estimated plasmonic resonances for the 120- and 140 nm diameter Au disks were approximately 702 nm and 727 nm, respectively. The achieved plasmon resonant wavelength coincides with the optical band gap of the WSe₂ layer, which was our objective when choosing the dimensions of the gold nanoparticles [4, 43, 149–155]. The full-width half-maximum (FWHM) of the scattering peaks were very broad, on the order of 100 nm, indicating that the polycrystalline nature of the Au film and the relatively large size of the disk (typically described as < 50 nm in diameter) generate a large non-radiative damping effect on the plasmonic response [61, 65]. Additionally, the presence of the Ti adhesion layer could potentially compromise the plasmonic properties to some extent, weakening the resonance intensity and potentially broadening the FWHM [69].

PL measurements were performed before and after the patterning and deposition of Au plasmonic disks on the hBN-encapsulated WSe₂ monolayer sample. A WiTec alpha300 R confocal microscope was used to perform measurements with the sample mounted in a Janis cryostat cooled to 78 K under vacuum (1×10^{-6} hPa). A continuous wave (CW), 532 nm laser was used with incident power ranging in the 100 μ W and 500 μ W. The light was focused approximately to a spot size of 1 μ m using a Zeiss 63x objective (NA = 0.75). A WiTec UHTS VIS spectrometer and CCD camera equipped with a 600 g/mm grating as used for the PL measurements. Comparing the PL spectra with and without

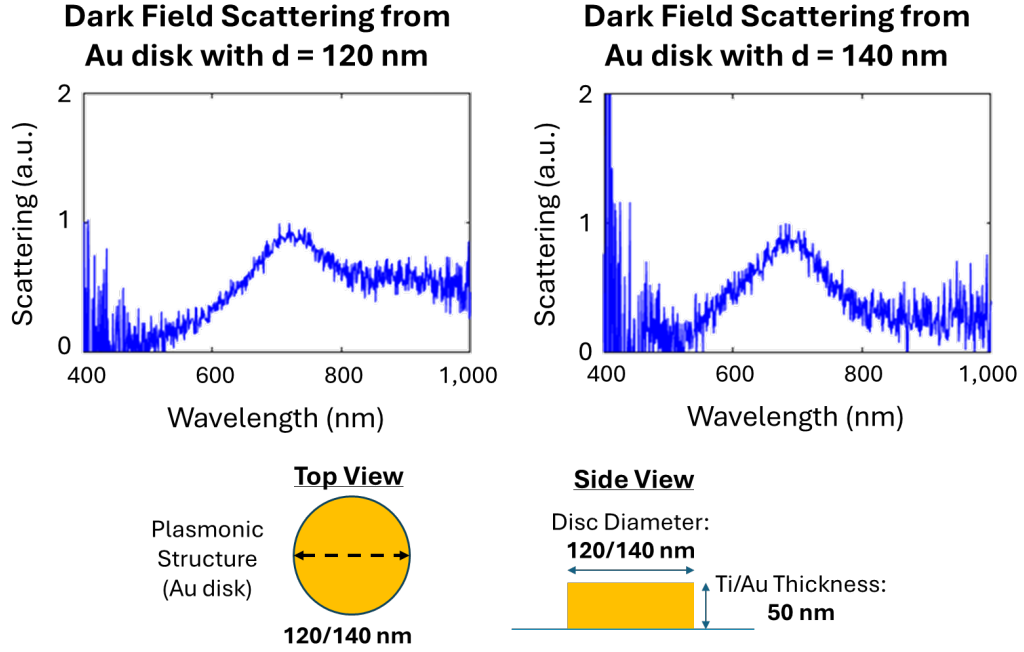


Figure 4.3: Dark-field scattering spectroscopic measurements on Au-based plasmonic disks with diameters of 120 nm and 140 nm, and with a thickness of 50 nm. The estimated plasmonic resonance of the 120 nm diameter Au disks was approximately 702 nm and the estimated plasmonic resonance of the 140 nm diameter Au disks was approximately 727 nm. In both cases, the scattering peaks were very broad.

the Au plasmonic disks present, there is an obvious shift in the main PL peak associated with the optical band gap of the monolayer WSe₂, starting at 725.6 nm prior to the Au plasmonic disks and shifting to about 740.1 nm (a 14.5 nm shift), and a broadening of the main PL peak. The PL spectrum after the plasmon disks were added also had what appeared to be inhomogeneous broadening that is typically associated with sample degradation or structural modification to the WSe₂ due to excitons bound to chalcogen vacancies [156, 157]. Because the WSe₂ was encapsulated by hBN, the observed broadening of the photoluminescence peak was not expected. With questions pertaining to the ability to fabricate plasmonic resonance structures on top of TMD heterostructures without drastically changing the optical response of the material, we decided to change the direction of study, with a new focus on understanding how the optical response with regards to exciton popu-

lations changes due to lithography processing, and to what extent does hBN encapsulation of WSe₂ reduce the changes in the excitonic response compared to unencapsulated WSe₂ samples.

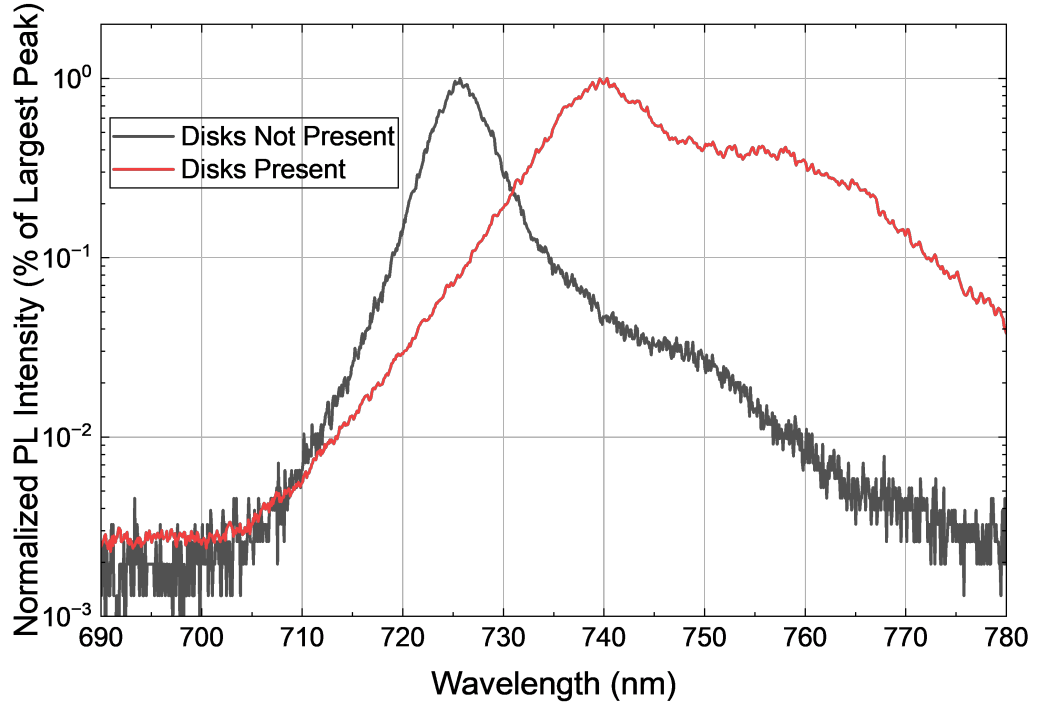


Figure 4.4: PL spectra of hBN-encapsulated WSe₂ before and after the addition of 140 nm diameter Au disks, with excitation source focus on a 1 μm spot size. The PL peak associated with the neutral bright exciton before the addition of 140 nm diameter Au disks was centered at ≈ 725.6 nm, shifting to ≈ 740.1 nm after the addition of the plasmonic disk structures. In addition to a peak broadening post-plasmonic disk addition, an inhomogeneous broadening of the PL spectrum between 750-780 nm is indicative of defect generation or material degradation.

In addition to the issues with plasmonic resonance structure fabrication, a number of complicating factors led to the change in efforts, including the complexity and the variability of stacking multiple monolayer films with hBN spacer or encapsulation layers as well as graphene-based gating for stacked TMD heterostructures with a large enough area to support fabricated plasmonic resonance structures. An exhaustive exploration of the lithographic penalties on 2D TMD heterostructures would require a large number of encapsu-

lated 2D bilayer heterostructures, each with sufficiently large area, and identical properties. This would be a research feat on its own, and not something that any group can reasonably provide, even ones as capable as our collaborators. In an attempt to minimize the materials needed to continue the research efforts, we continued using strictly monolayer WSe₂.

4.2 Properties of Two-Dimensional WSe₂

Transition metal dichalcogenides, such as *MoS*₂, *MoSe*₂, *WS*₂, and *WSe*₂, are emerging semiconductors that possess unique optical and electronic properties when thinned down to a single molecular layer (typically a trilayer composed of a transition metal layer of atoms sandwiched between two chalcogen layers). When approaching the two-dimensional limit of these materials, exploitable properties can appear for a number of applications, including large excitonic binding energies ranging from 0.4 eV to 0.9 eV, high mobilities for charge-neutral species, discrete direct band gaps ranging from 0.75 eV to 2 eV, and the ability to engineer heterostructures with van der Waal coupling interactions [158–160]. Additionally, due to the reduced Coulomb screening in these materials, TMDs can possess large transition dipole moments that allow the existence of excitons and a strong light-matter coupling up to room temperature [138–141, 161]. These properties, along with the fact that TMD optoelectronic properties can be tuned or modulated using electrical, optical, and thermal external stimuli, provide the potential for the development of novel visible and infrared detectors with room-temperature operation. Electrically, WSe₂ has some interesting use-cases due to its unique charge transport behavior, even compared to other TMDs such as MoS₂. When used as field effect transistors, WSe₂ natively exhibits ambipolar behavior due to its relatively high hole mobility compared to its electron mobility. Hole mobilities between 90-500 cm²V⁻¹s⁻¹ have been reported [6, 43, 49, 137], and electron mobilities between 7-30 cm²V⁻¹s⁻¹ have been demonstrated [43, 49]. From a thermal and vibrational standpoint, WSe₂ has been reported to have high in-plane thermal conductivity with a reported value of 246 Wm⁻¹K⁻¹ for the A_1^g phonon mode and 185 Wm⁻¹K⁻¹ for the E_{2g}^1 mode [162]. In this research effort, monolayer WSe₂ was used due to the availability from collaborators, and due to its interesting properties compared to other well-studied TMDs, such as MoS₂.

The electronic band structure of WSe₂ drastically changes at the monolayer limit. Like other TMDs, WSe₂ transitions from an indirect band gap in its bulk form to a direct band gap in its monolayer, 2D form, where the direct band gap is located at the K and K' points of the Brillouin zone. Monolayer WSe₂ has an optical band gap with reported values of 1.63-1.66 eV or 747-761 nm at room temperature ($T = 293\text{-}299\text{ K}$), which is also the emission energy of the neutral bright exciton [4, 43, 149–155]. At cryogenic temperatures ($T = 4\text{-}10\text{ K}$), the neutral bright exciton emission blueshifts, with reported values of 1.71-1.75 eV or 708-725 nm [163–168]. The electronic band gap of monolayer WSe₂ is substantially larger than the optical band gap with reported values ranging from 2.02-2.63 eV [151, 152, 159, 169] due to the strong Coulomb interactions between electron-hole pairs, leading to the observed strong exciton binding energy with reported values ranging from 0.37-0.89 eV [151, 152, 159]. The exciton binding energies reported are about an order-of-magnitude larger than those of conventional bulk semiconductors and even bulk TMDs, where exciton binding energies for GaAs can be less than 5 meV and exciton binding energies for bulk MoS₂ can be 40 meV [48, 151, 152, 170]. The large exciton binding energies in monolayer WSe₂ stem from the spatial confinement of the electron-hole pairs which geometrically force them in proximity to each other and the significantly reduced dielectric screening compared to bulk WSe₂. Consequently, excitons in WSe₂ remain tightly bound to each other and dominate the optical absorption and emission properties up to room temperature (note that the exciton binding energies outweigh the thermal energy at room temperature where $k_bT \approx 25\text{ meV}$) [30, 48, 151].

Unique to tungsten-based TMDs like WSe₂ is the strong spin-orbit splitting at the K and K' points, and its inverted spin-orbit coupling, where the lowest sub-band of the conduction band has the opposite spin of the highest sub-band of the valence band, leading to the lowest energy or ground-state for electron-hole pairs being spin-forbidden and optically dark. Unlike molybdenum-based TMDs where the spin of the lowest sub-band of the conduction

band and highest sub-band of the valence band have matching spins, allowing for photon emission, the lowest energy states in WSe₂ are about 30-40 meV below the allowed radiative recombination energy state, or “bright exciton”, making the spin-forbidden electron-hole pair the ground state for the material, colloquially called the dark exciton. The lowest energy state being spin-forbidden for WSe₂ has led to some interesting optical responses compared to molybdenum-based TMDs, such as strong quenching of the photoluminescence at cryogenic temperatures, which is the opposite behavior seen in TMD monolayers like MoS₂. With the reduced thermal energy, more excitons in WSe₂ revert to energetically lower states, with the lowest being optically dark, reducing the bright PL emission. Although dark excitons do not interact with in-plane light, dark excitons can potentially be coupled with out-of-plane or z-mode fields due to weak band mixing [169, 171, 172]. This means that dark excitons can potentially be “brightened” through external magnetic fields, or even strong localized electric fields from localized surface plasmons.

4.3 Excitonic Species in Transition Metal Dichalcogenides and WSe₂

Excitons, which are quasiparticles of electron-hole pairs bound together by the Coulomb force, can be formed when radiation is absorbed, separating electrons and holes in semiconductors like TMDs. These quasiparticles eventually dissipate when the electron and hole inevitably recombine, with the electron transitioning the energy band gap in the semiconductor, generating an emission equal to the band gap energy. The amount of time that excitons can exist (exciton lifetime) before this occurs is related to the exciton binding energy. In monolayer TMDs, such as WSe₂ and MoSe₂, intralayer excitons possess relatively high exciton binding energies. The reported values for the exciton binding energy for WSe₂ range greatly from 0.37 eV to 0.89 eV, with varying methods of measurement and substrates or environments yielding vastly different results [151, 152, 159, 169, 173]. The exciton binding energy values reported for MoSe₂ range from 0.5 eV to 0.55 eV according to scanning tunneling spectroscopy [39, 152, 169]. In addition to high exciton binding energies, monolayer TMDs possess a diverse landscape of excitonic species due to a number of key properties they exhibit, including strong Coulomb interactions, reduced dielectric screening, and spin-valley locking. Like MoS₂, MoSe₂, and WS₂, bulk WSe₂ is an indirect band gap semiconductor, but transitions to a direct band gap semiconductor at the monolayer limit [4, 5, 38, 149, 153, 174, 175]. This greatly affects the photoluminescent behavior of WSe₂, which is greatly enhanced at the monolayer limit by multiple orders-of-magnitude compared to its bulk counterpart [4, 5, 48, 149].

At the cryogenic temperature of 4 K, a rich variety of excitonic species can be detected via photoluminescent emissions, including neutral excitons, trions, biexcitons, exciton-trions, indirect excitons, and even brightened dark excitons. The exciton population is capable of relaxing into lower dark energy states that possess long lifetimes and provides a reservoir for the formation of other complex excitonic species [48, 167, 172, 176]. At

higher temperatures, above 60 - 80 K, many of these excitonic species and localized excitons are no longer distinguishable in the PL emission spectra. Localized excitons are thermally quenched, as thermal energy is sufficient to activate trapped carriers, pushing them into delocalized bands [150, 163], and unstable multi-particle complexes, such as trion-excitons, and biexcitons, with relatively low binding energies thermally dissociate [132, 164, 167]. Additionally, thermal energy at higher temperatures allows radiative recombination of thermally active free bright excitons to dominate, washing out the finer features from dark states, defect or localized states, phonon replicas and multi-particle complexes [48, 150, 163, 174, 177].

4.3.1 Neutral Excitons

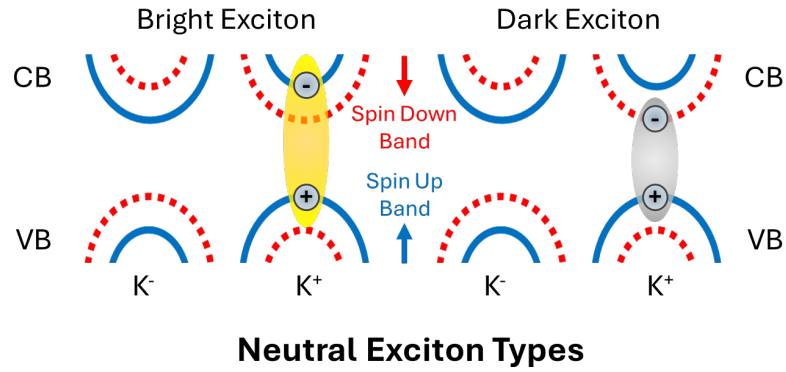


Figure 4.5: Simplified K^+ and K^- band illustration for neutral excitons including bright excitons and dark excitons, where CB represents the conduction band and VB represents the valence band, which each have sub-bands with a spin-up and spin-down sub-band due to the inverted spin-orbit splitting in WSe_2 , leading to dark excitons being the ground energy state.

Neutral excitons are two-particle bound states composed of electron-hole pairs bound together by Coulomb attraction, with the negative charge of the conduction-band electron and valence-band positive charge of the hole effectively canceling each other out from a charge perspective (also represented as X^0 in this thesis). Bright excitons are optically ac-

tive, where the electron and hole reside in the same valley (direct band gap) and possess opposite spins, which satisfies both momentum and spin conservation required for radiative recombination. For WSe₂, the bright exciton PL emission is temperature-dependent, with reported values ranging from 1.63 eV to 1.66 eV (or 747 nm to 761 nm) at room temperature [4, 43, 149–155], and from 1.71 eV to 1.75 eV (or 705 nm to 725 nm) [159, 163–168, 174, 178–180]. Additionally, other factors including substrate [153], dielectric screening/encapsulation [159, 164], and strain [153] can all modify the exciton binding energy and in consequence, the measured exciton PL emission spectrum.

Dark excitons are optically forbidden (no emission) and do not directly interact with light due to being either spin-forbidden (electron and hole have parallel spins, making the transition forbidden) or momentum-forbidden (electron and hole reside in different valleys such as K and K' or K and γ). Dark excitons can become visible in photoluminescence (PL) through multiple mechanisms such as external fields (both electric and magnetic), phonon coupling effects, defect assistance, and thermal activation, which effectively allow them to mix with bright exciton states. The result is the “brightening” of the dark exciton, allowing them to contribute to the PL emission [48, 50, 52, 167, 169, 171, 181–184]. In WSe₂ and WS₂, the spin-forbidden dark exciton is actually the energetic ground state, with transition energies that are 40-50 meV below the bright exciton in the case of WSe₂ [167, 177, 183]. In line with this research, electric field brightening or Rashba coupling can be caused by charged impurities in the substrate as well as an applied electric field to the monolayer TMD, which breaks the space inversion symmetry due to the out-of-plane electric field that it causes [181]. It has been postulated that spin-forbidden dark excitons possess a dipole moment that oscillates out of the monolayer plane (z-direction) and that it would be possible to couple to this mode using near-field and plasmonic coupling [48, 52, 169]. This suggests that it would be possible to brighten or activate the large population of dark excitons found in tungsten-based TMDs by coupling them to field-enhancing surface plasmon

polaritons using plasmonic resonance structures [48, 52]. A simplified band diagram to illustrate both types of neutral excitons is provided in Fig. 4.5.

4.3.2 Trions

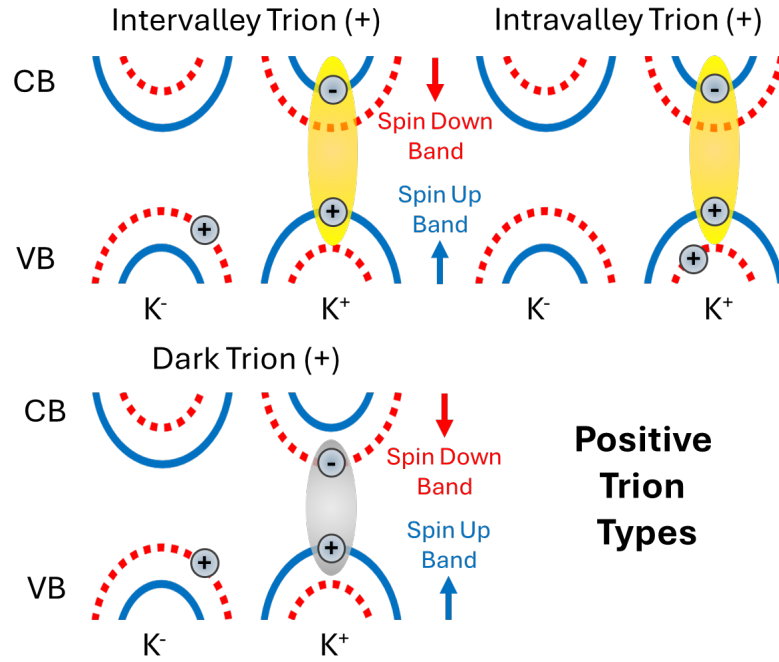


Figure 4.6: Simplified K^+ and K^- band illustration for positive trions including intervalley (triplet) trions, intravalley (singlet) trions, and dark trions, where CB represents the conduction band and VB represents the valence band, which each have sub-bands with a spin-up and spin-down sub-band due to the inverted spin-orbit splitting in WSe₂.

Trions are three-particle bound states composed of two electrons and one hole in the case of negatively-charged trions (X^-) or two holes and one electron in the case of positively-charged trions (X^+). They are also known as charged excitons since they are effectively a neutral exciton bound to an extra charge carrier [152, 185]. The probability of trion formation is typically related to the doping density of the material, with higher carrier concentrations allowing for increased opportunities of interaction between free carriers and excitons [153, 185]. Electrostatic doping through the use of electrical gating can be used

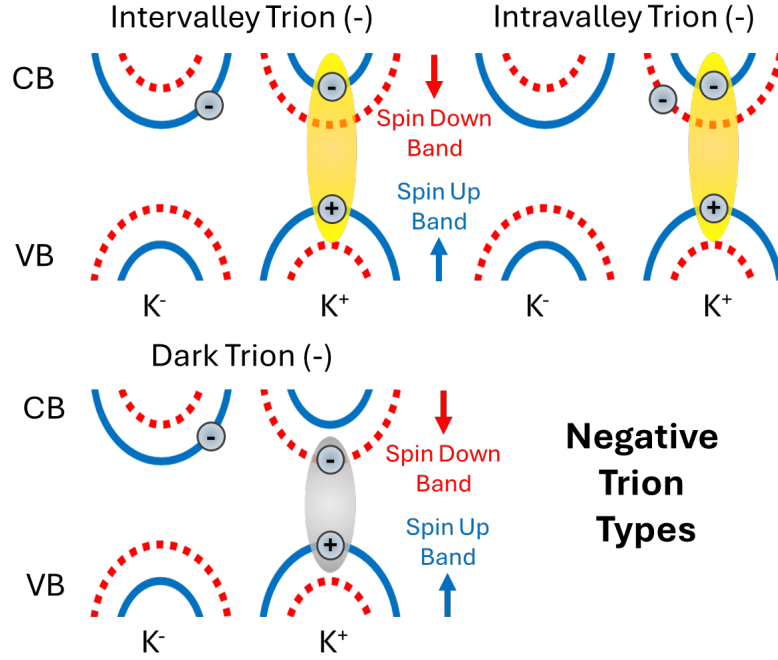


Figure 4.7: Simplified K^+ and K^- band illustration for negative trions including intervalley (triplet) trions, intravalley (singlet) trions, and dark trions, where CB represents the conduction band and VB represents the valence band, which each have sub-bands with a spin-up and spin-down sub-band due to the inverted spin-orbit splitting in WSe₂.

to tune the trion population by injecting the desired charge carriers into a monolayer TMD [152, 164, 169]. Even without doping, WSe₂, reported PL measurements have shown that exciton and trion species coexist at room temperature [162]. In tungsten-based TMDs, like WS₂ and WSe₂, negatively-charged trions can come in varieties due to spin-orbit splitting. Intravalley singlet trions come from two electrons that reside in the same valley but have opposite spins [166]. Intervalley triplet trions come from two electrons that reside in different valleys and have parallel spins [166]. The binding energy of the two types of negatively-charged trions differs as a result of the exchange interactions. Dark trions also exist at lower energies but are optically inactive, although they can be observed through phonon coupling (phonon replicas at low temperature) and through magnetic field coupling [171, 182, 184]. Trions are observed to have PL peak positions that are on the order of 20 meV to 37 meV

lower than the neutral exciton PL peak position [164, 166, 167, 171, 179], and have large binding energies on the order of 20 meV to 35 meV [169, 184]. Reported MoSe₂ trion PL peak positions are similarly located between 27 meV and 30 meV below the neutral exciton PL peak position [169, 186, 187]. Simplified band illustrations for positive and negative trion types are provided in Fig. 4.6 and Fig. 4.7, respectively.

4.3.3 Biexcitons

Neutral biexcitons are four-particle bound states composed of two neutral excitons (represented as XX^0 in this thesis). Specifically, for WSe₂, according to Chen et al. [167], biexcitons consist of a bound bright exciton and a dark exciton. This was postulated due to the observed negative or inverted valley polarization compared to the bright exciton, which indicated the involvement of a dark exciton in the valley opposite to the bright exciton [164, 167]. From previous PL measurements, the peak located between 17 meV and 18 meV below the bright exciton peak (X^0) is typically attributed to neutral biexcitons [164, 167, 179]. For photoluminescence, biexcitons have been found to have a quadratic dependence on the excitation source power where the intensity of the PL signal is proportional to the square of the excitation power ($I \propto P^2$ where I is the PL intensity and P is the excitation power) [164, 167, 168].

4.3.4 Charged Biexcitons/Exciton-Trions

Charged biexcitons, also called exciton-trions, are five-particle bound states composed of a trion bound to an exciton represented as XX^- in this thesis). Charged biexcitons have been observed in doped material systems, with electrostatic gating as a means to generate charged biexcitons and quench neutral biexcitons [167, 168]. In the case of WSe₂, charged biexcitons have been determined to be composed of a bright trion and a dark exciton due

to the fact that the emissions with valley polarization have opposite signs compared to the bright exciton [164, 167]. The PL intensity of charged biexcitons has been estimated to have an excitation source power dependence of approximately $I \propto P^{1.5}$ where I is the PL intensity and P is the excitation power [168]. The reported PL peak location of charged biexcitons has been reported to be approximately 49 meV below the bright exciton [164, 167]. The observation of these biexcitonic species are made possible in materials like WSe₂ and WS₂ because dark excitons are the energetic ground state, providing a supply of the dark excitons for bright excitons and bright trions to bind or couple to for the production of biexcitons and charged biexcitons [167].

4.3.5 Interlayer Excitons

In addition to intralayer excitons that exist within a single molecular layer of a TMD, it is possible to create TMD-based heterostructures with engineered interfaces that allow for new energetic minima based on the varying combinations of conduction and valence bands of neighboring TMD layers. This leads to the potential for interlayer excitons, where electrons and holes are capable of tunneling to the respective lower energy conduction or valence band of the neighboring TMD layer. Several studies and reviews have been published [160, 170, 188–194], with some indicating that interlayer excitons can possess lifetimes up to a microsecond [188]. The energy band alignment of stacked TMD heterostructures can be engineered to generate interlayer excitons at varying wavelengths or energies. The ability to engineer pairings of TMD monolayers for stacking to design for a particular interlayer exciton has potential applications for radiation detectors in the visible and infrared spectrum ranges where many of these interlayer excitons exist, and for the tailoring of excitonic properties.

4.4 Addressing Practical Fabrication Concerns with Plasmonic Resonance Structures on TMDs

To pattern these low dimensional films into channels and devices, electron-beam lithography is a common method to achieve structural dimensions on the nanometer scale. Using an energy-sensitive polymer like polymethyl methacrylate (PMMA), high-resolution patterns can be etched into the polymer using an electron beam. This technique for patterning structures has been used with TMDs for the fabrication of field effect transistors, plasmonic structures [19], and sensors [30, 38, 39, 48, 129, 195]. Although useful for creating structures and patterns in transition metal dichalcogenides, it has been observed that electron-beam lithography and the associated irradiation of the TMD can generate defects in the TMD in the form of chalcogen vacancies and shallow traps. Although the effects of electron beam irradiation have been studied for a number of van der Waals materials [13, 15, 196–208], the effect of electron beam irradiation on different vdW heterostructures using TMDs is not fully understood, and few studies have looked at their effect on hBN-encapsulated TMDs in detail, with our results from Section 4.1 coming to a different conclusion from recent studies [19].

The use of hexagonal boron nitride (hBN) as a substrate and as an encapsulation material has become common with mono- and few-layer TMD devices and structures because they are low-defect van der Waals materials that spatially separate the TMDs from common substrates such as SiO_2 , which typically possess trap charges that introduce spatial inhomogeneities and substrate-induced disorder [124, 135, 209]. While it has been observed that in some cases, encapsulated $MoSe_2$ have been able to resist damage and defect generation even when exposed to electron beam irradiation [19], further investigation is warranted as excitonic populations beyond neutral bright exciton have not been studied before and after

electron beam irradiation. Furthermore, monolayer WSe₂ that is used for this study possesses a distinct band structure from the MoSe₂ previously studied, with inverted spin-orbit splitting leading to dark excitons populating the energy ground state of the tungsten-based dichalcogenide.

Chapter 5: Effects of E-beam Irradiation on 2D WSe₂ and hBN-encapsulated WSe₂

Looking beyond low-yield, prototypical TMD-based stacks and devices, the implementation and application of vdW TMDs in scalable, reproducible technologies require that TMD materials be produced at scale with reproducible properties and with minimal variability in key properties when processed or manipulated during device fabrication. Understanding how fabrication and processing methods affect monolayer TMDs and associated heterostructures, as well as understanding to what extent current mitigation techniques minimize impacts, will be necessary to ensure critical properties and responses of the material behave within expectations. This chapter examines the impact of electron-beam lithography on the optical properties of monolayer WSe₂. We evaluated its response at cryogenic temperatures, comparing a bare monolayer to one encapsulated in hexagonal boron nitride (hBN); a technique frequently used to shield the material from external defects.

5.1 Defect Generation and Exciton Populations in TMDs

In previous studies, the impact of electron-beam irradiation, which typically occurs during lithographic processes, has been modeled and experimentally shown to cause significant structural modifications to exposed TMD monolayers due to the generation of defects from ballistic displacement of chalcogen atoms and ionization damage [13, 18–20, 156, 196, 200, 203, 207, 210]. Defects such as chalcogen vacancies are typically formed due to their lower displacement threshold energy compared to the heavier transition metal atoms [13, 15, 156, 196, 204]. Quenching of the photoluminescence (PL) intensity has been observed by up to two orders of magnitude and with broad defect emission bands appearing due to the significant crystal defects generated from the irradiation [19, 156]. At higher electron energies beyond what is typical for electron-beam lithography (typically 100 keV or less), high energy electron beams at 1 MeV have been observed to induce a phase transition in WSe₂ from the semiconducting 2H phase to the metallic 1T phase through the generation of Se vacancies that introduce tensile strain, altering the d-orbital filling states [198].

Electron-beam irradiation has been shown to modify the chemical, optical, and electronic properties of monolayer TMDs. The generation of defects in the lattice in the form of chalcogen vacancies can serve as reactive sites for chemical functionalization on the surface of the TMD [21, 207]. Optically, defect-bound excitons associated with chalcogen vacancies are generated that exhibit relatively long lifetimes on the order of tens and even hundreds of nanoseconds compared to delocalized excitons, which generally have lifetimes on the order of picoseconds [156]. Additionally, it has been observed that the valley polarization can be maintained for more than one microsecond in defect-bound excitons, which spatially localize them, mitigating intervalley scattering [20, 156]. Electron-beam irradiation can also cause the red-shifting of the PL emission peaks, typically attributed to

defect-induced band structure modifications [21]. Electronic properties can be modified by electron-beam irradiation, affecting the effective doping of the TMD monolayer through charge trapping in the substrate or around generated defects such as chalcogen vacancies and changing the threshold voltage of TMD-based transistor channels [205, 208]. Chalcogen vacancies in monolayer TMDs degrade the carrier mobility due to increased scattering [205], and the functionalization of those vacancies can also lead to modifications of the work function [21]. The contact resistance for devices based on a monolayer TMD channel is typically reduced, with lower Schottky barriers between metal contacts and the TMD from interfacial reactions and atomic diffusion [202].

The use of hexagonal boron nitride (hBN) as a substrate and as an encapsulation material has become common with mono- and few-layer TMD devices and structures because it is a low-defect van der Waals material that spatially separates and provides a large barrier that electrically isolates the TMD from common substrates such as SiO_2 that typically possess trap charges that introduce spatial inhomogeneities and substrate-induced disorder. The reduction of trap charges at the substrate interface between commonly used substrates like SiO_2 on Si and TMDs by using a hBN interstitial layer to screen charge defects has been reported by multiple research groups [124, 134, 135, 209, 211]. In some cases, encapsulated TMDs have been shown to be able to resist damage and defect generation even when exposed to electron-beam irradiation [19]. More specifically, encapsulating monolayer TMDs with a thin insulator like hexagonal boron nitride (hBN) has been experimentally demonstrated to alter the electron-beam interactions with the TMD, preventing or significantly reducing the effects of chalcogen atom displacement and other defect generation in the monolayer TMD [18, 19, 51]. Important optical properties such as PL emission linewidths and spectral ranges are preserved when encapsulated in hBN, even under high-electron energy e-beam lithography (more than 80 keV), avoiding PL quenching and broad defect PL emissions observed in unencapsulated TMD monolayers [13, 19]. It has been

postulated that hBN can act as a sacrificial barrier layer that prevents the displacement of chalcogen atoms from escaping the lattice, increasing the displacement threshold energy required beyond the typical electron-beam lithography energy settings [18, 19]. Additionally, hBN could potentially facilitate both charge and heat dissipation, which mitigates ionization damage [18].

5.2 WSe₂ Synthesis and Stacking

Both encapsulated and bare unencapsulated WSe₂ exfoliated onto hBN, were acquired from collaborators at the University of Wisconsin-Madison (UWM). WSe₂ bulk crystals were synthesized based on a liquid salt chemical vapor transport process first reported by Cevallos et al. [212]. A stoichiometric quantity of tungsten (W) powder was mixed with an excess of selenium (Se) powder in an evacuated and sealed quartz ampoule, which was subsequently heated and cooled according to Cevallos et al. [212]. The subsequent WSe₂ crystals were then extracted from the ampoule and characterized, with single crystal flakes grown to a few millimeters per side. Monolayer WSe₂ flakes were mechanically exfoliated from the grown bulk crystals onto 1 cm × 1 cm (100) silicon (Si) coupons with 285 nm of thermally-grown dry oxide (SiO₂) and a marker layer of gold (Au) 50 nm in thickness were used as substrates for the WSe₂-based stacked heterostructures. Hexagonal boron nitride (hBN) films with thicknesses ranging from 4 to 40 nm were transferred onto the substrates to provide a substrate that reduces the charge impurities and scattering centers at the interface with the monolayer WSe₂ [125, 134, 137, 195], ensures a relatively atomically flat, dangling-bond-free contact surface to minimize strain [131, 134, 137, 213, 214], and possesses dielectric properties that reduce dielectric screening and enhance excitonic effects [215].

Collaborators from UWM performed atomic force microscopy to determine and verify the thicknesses of WSe₂ using an Oxford Instruments Asylum Cypher-S AFM. At UWM, WSe₂ stacks were fabricated using a standard dry transfer method with polycarbonate (PC) stamps. To assemble the encapsulated WSe₂ structures, hBN was initially picked up at 110 °C in ambient conditions. Subsequently, a monolayer of WSe₂ and a bottom layer of hBN were picked up at 65°C. The resulting structure was dropped onto a Si substrate with 285 nm of SiO₂ and a Au marker layer at 100°C and ramped to 200°C over the course

of 30 minutes. Any residual PC was removed with chloroform, and a final surface cleaning was performed via contact imaging in the Cypher-S AFM. Note that this stacking and transfer method for producing atomically thin heterostructures based on van der Waals materials produces stacks that have relatively high variability in terms of optical and electronic properties, even when produced to the same specifications and from the same original crystal/material sources. Due to the extreme surface sensitivity of 2D materials, any change in the strain, presence of residues (like PC or other polymers), or even small aberrations between layers can cause variability in the optical and electronic properties of the material stack from sample to sample.

5.3 Experimental Methodology

To determine the effects of electron-beam lithography (EBL) and its associated processes on WSe₂ monolayers with and without hBN-encapsulation, samples acquired from our collaborators at the UWM were characterized prior to exposure to EBL processes. Various methods were performed to confirm the presence of monolayer WSe₂, quantify the impact of defects in the films, and to understand the exciton populations in monolayer WSe₂ before electron-beam irradiation and processing. The WSe₂ films were then processed using a conventional EBL process flow typically used to pattern device structures such as channels, contacts, and gates. After processing and cleaning, WSe₂ samples were reviewed in a post-irradiation characterization study to determine how exciton populations changed due to the EBL process and the potential generation of defects from it. This procedure was performed on a set of WSe₂ samples composed of one hBN-encapsulated WSe₂ monolayer and one unencapsulated, exposed WSe₂ monolayer on a substrate stack composed of a thin exfoliated hBN film on top of 285 nm of SiO₂ grown on a (100) Si substrate. It should be noted that other sets were provided, but due to the lack of a low-temperature photoluminescence measurement setup early in the project performance period, measurements performed on those samples were unable to provide enough detail in the spectra to extract the variety of exciton populations discussed in Section 4.3. Additionally, other sets provided did not possess PL or Raman signatures, indicating that the transfer or stacking process damaged or removed the WSe₂ or somehow quenched the optical and/or vibrational response of the WSe₂.

5.3.1 Pre-Electron-beam Irradiation WSe₂ Characterization

Atomic force microscopy (AFM) was performed on the WSe₂ samples as described in Section 5.2, with the results in the first set and the second set shown in Fig. 5.1 and

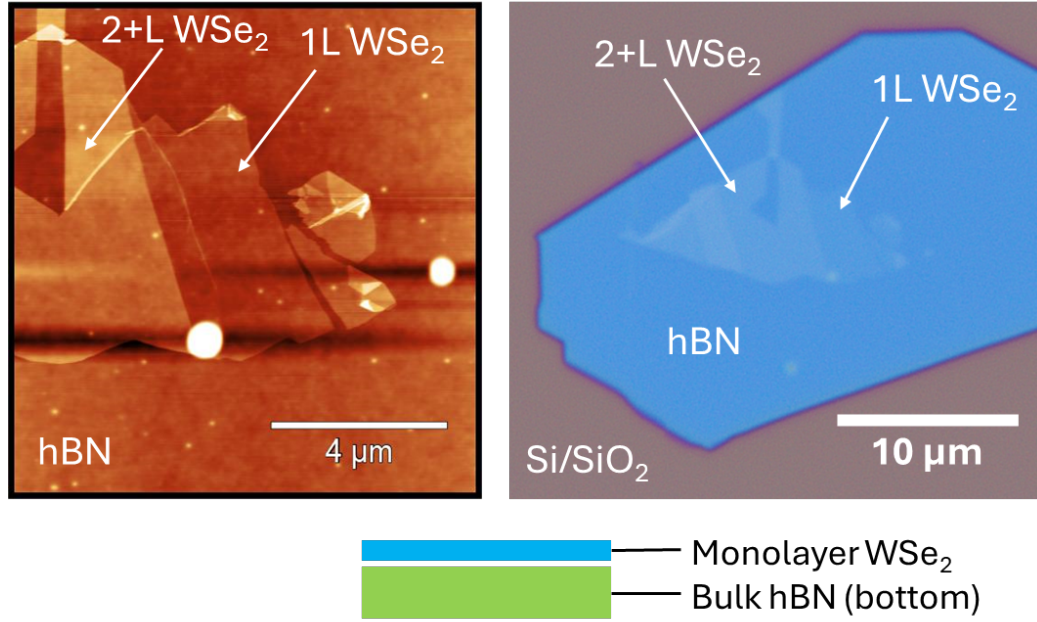


Figure 5.1: Atomic force micrograph (left) and optical micrograph (right) of unencapsulated monolayer WSe₂ sample on bulk hBN flake transferred onto a Si substrate with a 285 nm SiO₂ thermally grown layer.

Fig. 5.2, respectively. The AFM confirmed the thicknesses of the WSe₂ monolayers, the thicknesses of the encapsulating hBN layers, and the relative positions of the stacked layers to one another, ensuring proper coverage and contact of the WSe₂ with only hBN. The cross-sectional measurements for the WSe₂ were approximately 0.7 nm, which is within the expected thickness range of a monolayer.

Raman spectroscopy and PL mapping measurements were performed using a WiTec alpha300R Raman/PL confocal microscope. WSe₂ samples were mounted inside a Janis cryostat on a cold stage cooled with liquid nitrogen to between 77.6 and 77.9 K. The sample was kept under vacuum with a pressure of $2.1 - 6 \times 10^{-7}$ hPa. A continuous wave (CW) laser with an excitation wavelength of 532 nm and with an incident power ranging between 100 μW and 500 μW was fiber-coupled into the Raman and PL microscope. Light was focused onto the sample through the cryostat window using a Zeiss 63x objective (NA =

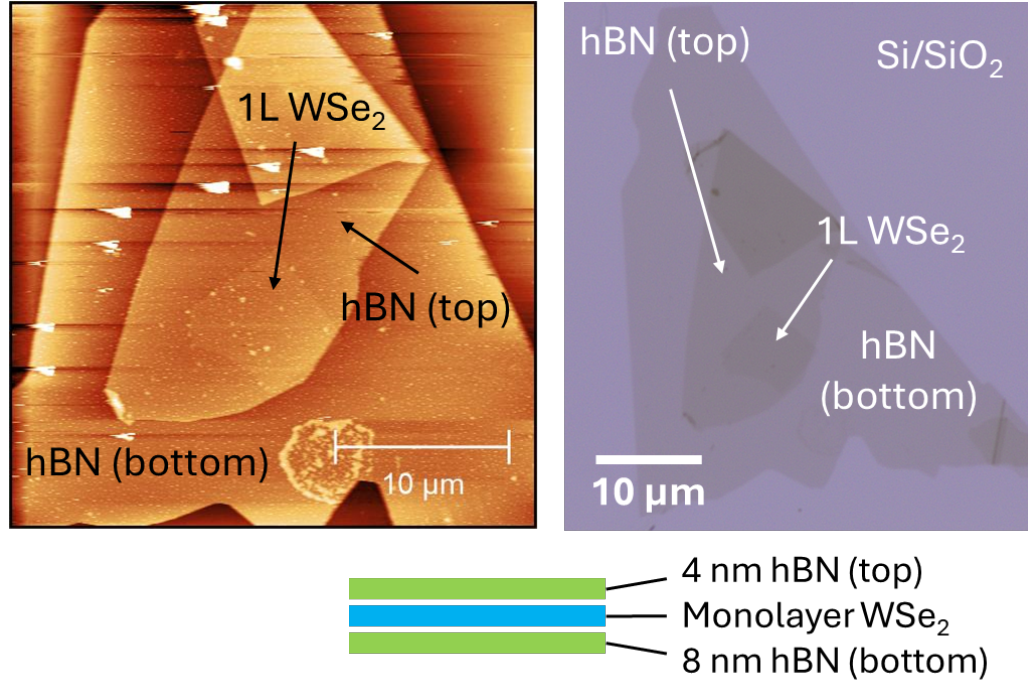


Figure 5.2: Atomic force micrograph (left) and optical micrograph (right) of hBN-encapsulated monolayer WSe₂ sample with 4 nm thick hBN top layer and 8 nm thick hBN layer transferred onto a Si substrate with a 285 nm SiO₂ thermally grown layer.

0.75). A Witec UHTS VIS series spectrometer was used with a cooled EM CCD camera, equipped with a 600 g/mm grating for PL measurements and an 1800 g/mm grating for Raman measurements. An integrated motorized stage with sub-micron step accuracy was used for performing the PL mapping.

Raman spectra were used to confirm the presence and layer count of the WSe₂ through confirming the presence of the in-plane E' and out-of-plane A'_1 vibrational modes typically 250 cm⁻¹ from the Rayleigh scattering point [149, 155, 216–220], and the absence of the out-of-plane B_{2g}^1 mode that appears around 310 cm⁻¹ from the Rayleigh scattering point in few-layer WSe₂ (two to five layers) [43, 149, 216]. For bulk WSe₂, the in-plane E_{2g}^1 and out-of-plane A_{1g} vibrational modes are typically degenerate, but as the WSe₂ thickness is decreased, these vibrational modes can potentially be distinguished from one another in separate peaks due to increased substrate interactions and strain from reduced rigidity of

the WSe₂ [155, 159]. Crystal quality and defects can also be surmised through the Raman spectra by looking at the linewidths and the full-width at half-maximum (FWHM) of the Raman peaks. Typically, linewidths are narrower for less defective crystals as phonon scattering is reduced [220]. Oxidation and photodegradation of the WSe₂ can also be determined from the Raman spectra with the emergence of a Raman peak between 810 and 820 cm⁻¹ with respect to the Rayleigh scattering point, which corresponds to the formation of WO₃ [38].

Raman spectra from the unencapsulated WSe₂ monolayer and the hBN-encapsulated WSe₂ monolayer are shown in Fig. 5.3. The unencapsulated sample possessed a single Raman peak at ~ 250.5 cm⁻¹, while the hBN-encapsulated sample possessed four distinct Raman peaks with the middle peak at ~ 251.5 cm⁻¹, similar to the unencapsulated sample's single peak in location and in line with the reported locations of the primary A'_1 and E' vibrational modes (~ 248 - 251 cm⁻¹) [217–220]. The other three Raman peaks observed in the Raman spectra for the hBN-encapsulated sample matched well with Raman peaks reported by others and attributed to second-order phonon modes, including a peak between 260-264 cm⁻¹ attributed to longitudinal acoustic phonon modes at the M-point of the Brillouin zone (2LA(M)) [217, 219, 220], a peak between 239-242 cm⁻¹ attributed to a combination of longitudinal acoustic phonon and out-of-plane acoustic phonon modes at the M-point of the Brillouin zone (LA(M)+ZA(M) by [218, 220] or attributed to the E-symmetry optic branch phonon mode at the M-point of the Brillouin zone by [217, 219], and a peak between 223-225 cm⁻¹ attributed to a E-symmetry optic branch phonon mode at the K-point of the Brillouin zone by [217, 219]. The appearance of these peaks could be attributed to Brillouin zone folding caused by lattice mismatch between the top layer hexagonal BN and the WSe₂, where the generated moiré pattern acting as a new periodic potential, bringing acoustic phonons from the edge of the original zone to the center or Γ -point. While second-order phonon modes were not observed in the Raman spectra of

the unencapsulated WSe₂ sample, the presence of the A'_1 and E' vibrational modes in both samples provided a strong indication of the presence of monolayer WSe₂.

PL mapping was used to confirm which areas where monolayer WSe₂ was present. The PL emission from monolayer WSe₂, which has a direct band gap, exhibits the bright or neutral exciton peak at shorter wavelengths compared to bilayer or multilayer regions of the WSe₂, allowing precise mapping of layer counts and distinguishing areas with and without WSe₂ present [4, 149]. Additionally, spatial charge doping can also be mapped through the spatial PL measurements by comparing the neutral exciton and trion peak ratio, with higher trion concentrations indicating localized electron or hole doping typically caused from trapped interfacial charges, defects, or metallic structures [135, 136]. It should be noted that measurements were taken at 78 K due to the temperature range of the cryostat, so peak or Lorentzian broadening is quite high compared to Raman and PL measurements performed at lower cryogenic temperatures, washing out some features, but enough information can be extracted even at liquid nitrogen temperatures to confirm WSe₂ monolayer presence and general quality level.

PL maps were taken for both the unencapsulated and the hBN-encapsulated WSe₂ samples at an incident laser power of 100 μ W, and an integration time of 1 s. For the unencapsulated WSe₂ sample, a mapped window of 20 μ m x 20 μ m with measurements taken in 0.5 μ m increments in both x- and y-directions (for a total measurement grid of 40 x 40). The map shown in Fig. 5.4 was taken and averaged at $\sim$ 734 nm or 1.69 eV, where the neutral exciton peak appeared strongest across the region where monolayer WSe₂ was expected to be. It should be noted that the neighboring bilayer and few-layer regions of this sample did not possess a strong PL emission with the same signature as the monolayer region, with a weak side maximum shifted to $\sim$ 780 nm or 1.59 eV in those bilayer regions and few-layer regions. For the hBN-encapsulated WSe₂ sample, a mapped window of 30 μ m x 30 μ m with measurements taken in 0.5 μ m increments in both x- and y-directions

(for a total measurement grid of 60 x 60). The map shown in Fig. 5.5 was taken and averaged at ~ 721 nm or 1.72 eV, where the neutral exciton peak appeared strongest across the region where monolayer WSe₂ was expected to be. In both samples, the mapped PL emission intensity at the expected neutral bright exciton wavelength corresponded well with the expected monolayer regions when compared to the optical micrographs.

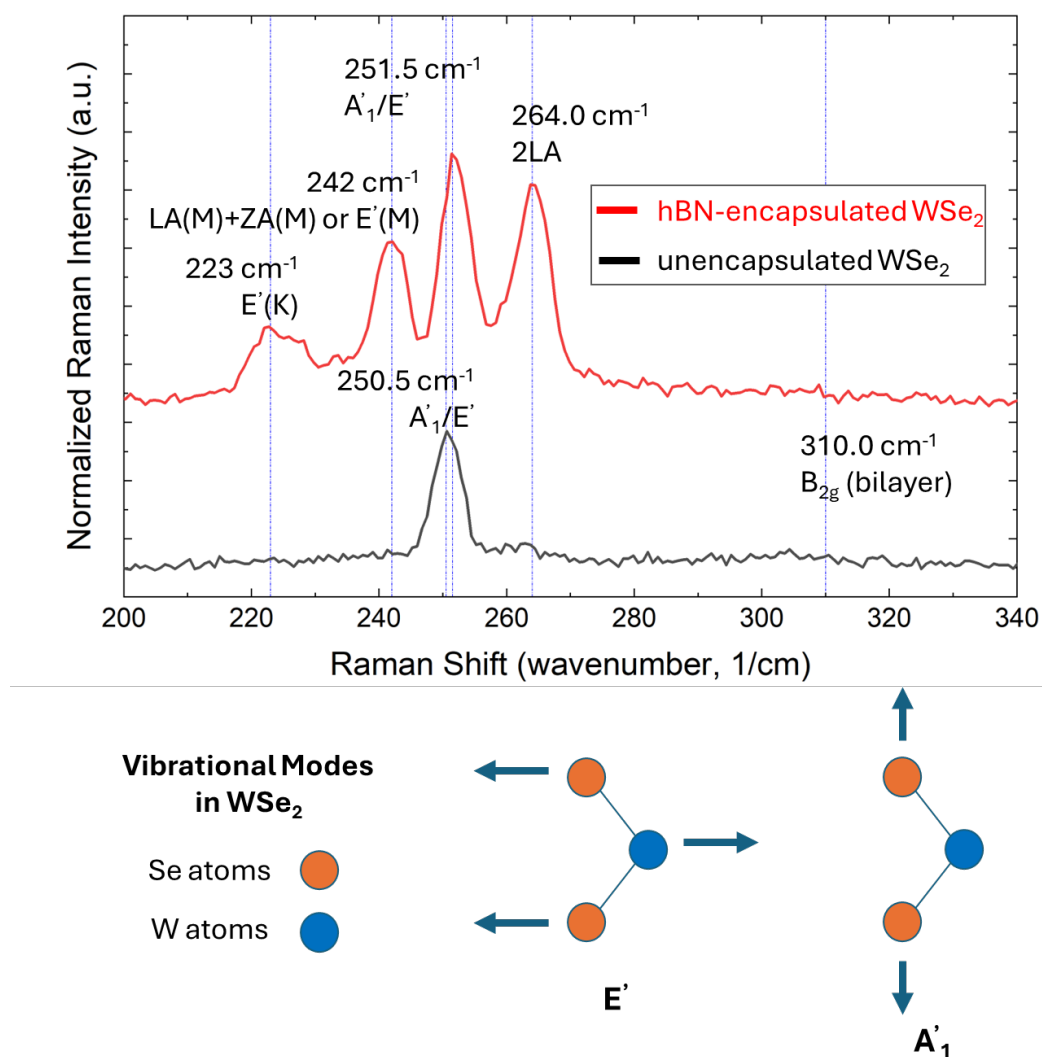


Figure 5.3: Raman spectra taken at $T = 78\text{ K}$ with a 532 nm CW excitation laser for both unencapsulated and hBN-encapsulated monolayer WSe_2 samples. The Raman measurements indicate the presence of monolayer WSe_2 in both cases, with the expected A'_1 and E' combined vibrational mode peak present. Illustrations of the two primary vibrational modes are also provided.

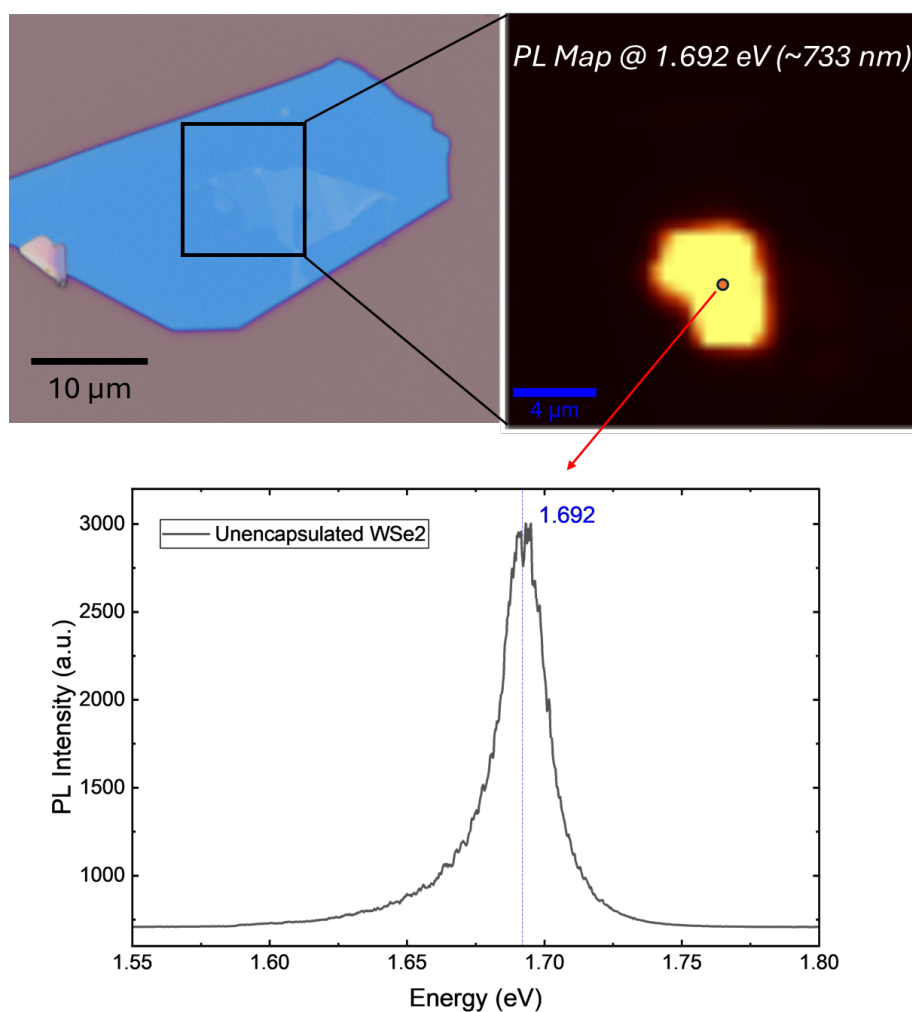


Figure 5.4: PL map of the unencapsulated WSe₂ mapped at the neutral bright exciton peak of 1.692 eV (733 nm) at $T = 78$ K with an 532 nm CW excitation laser source is shown in the top-right. An example PL spectrum measured at the point indicated is provided below the PL map. The illuminated areas of the PL map indicate the presence of monolayer WSe₂, which is in line with the expected region shown in the top-left optical micrograph.

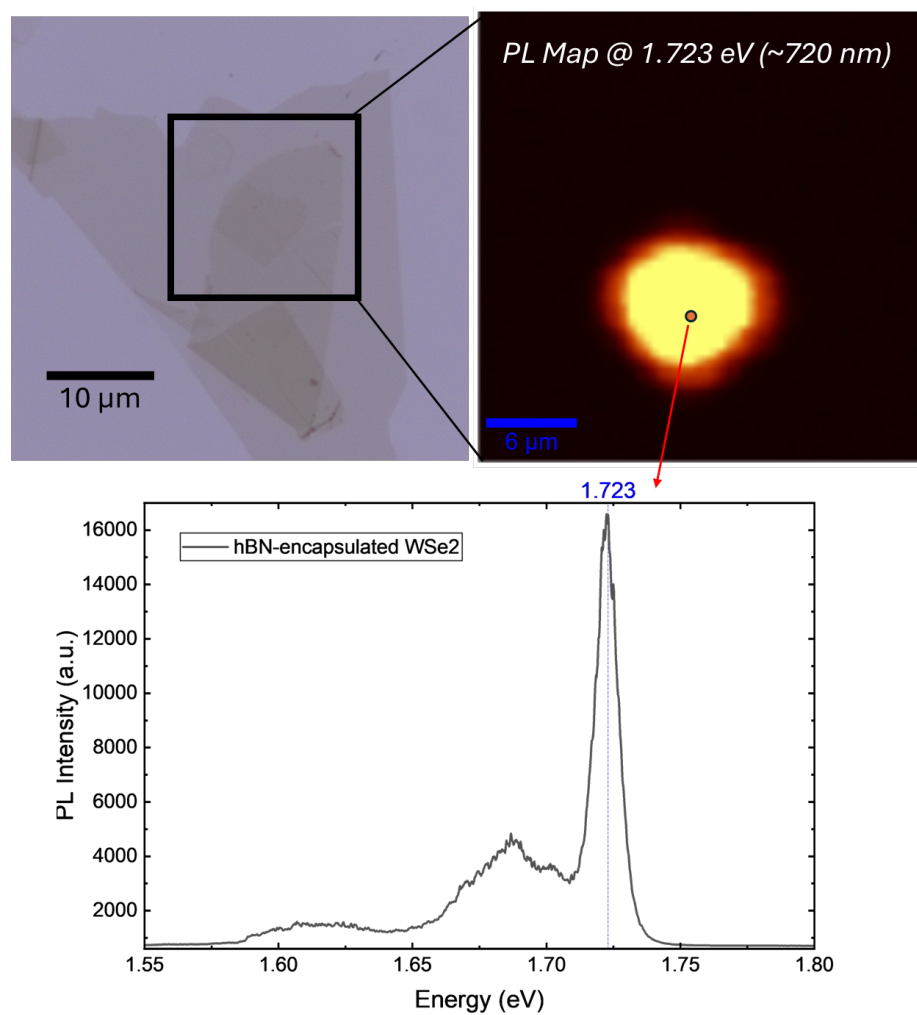


Figure 5.5: PL map of the unencapsulated WSe₂ mapped at the neutral bright exciton peak of 1.723 eV (720 nm) at $T = 78$ K with an 532 nm CW excitation laser source is shown in the top-right. An example PL spectrum measured at the point indicated is provided below the PL map. The illuminated areas of the PL map indicate the presence of monolayer WSe₂, which is in line with the expected region shown in the top-left optical micrograph.

Low-temperature PL was used to study the excitonic complexes in the unencapsulated and hBN-encapsulated WSe₂ monolayer samples, with the goal of understanding how their populations, outlined in Section 4.3, change before and after electron-beam lithography processing, and to also understand how well protective layers like hBN inhibited changes to the optical properties of WSe₂. Many excitonic complexes, including biexcitons, higher-order complexes, and localized/defect-bound excitons, have lower binding energies and/or trap depths, making them susceptible to thermal dissociation or spectral broadening [163, 167, 178, 221]. A custom-built cryogenic PL setup was used to perform these measurements based on a Montana Instruments S50 Cryostation that kept the samples cooled to $T = 4.2$ K at a pressure of $\sim 1 \times 10^{-4}$ Torr. A CW 633 nm HeNe laser was used as the excitation source with a focused beam spot diameter of $\approx 1 \mu\text{m}$ using a microscope objective, and with a circularly variable neutral density filter wheel used to control the incident power between 100 nW and 100 μW . A Teledyne Princeton Instruments Acton spectrometer and cryogenically cooled PyLoN CCD camera were used to collect the PL spectra. A combination of free space optics and fiber-coupled optics was used to direct the excitation laser source onto the samples in the cryostat and collect the resultant radiative PL emissions from the sample.

Power-dependent measurements were collected for each WSe₂ sample to determine the excitonic complexes and to identify defect-bound or localized excitonic states present in the PL spectra. The integrated PL intensity of different excitonic populations scales with the excitation power according to a power law, can be described by the proportionality: $I \propto P^\alpha$, where I is the PL intensity, P is the excitation power, and the exponent α , provides insight into excitonic population. Bright excitons and trions generally exhibit a linear or near-linear dependence ($\alpha \approx 1$) with respect to the excitation power [150, 164, 179, 221]. Biexcitons and charged biexcitons (trion-excitons) generally exhibit a superlinear or near-quadratic dependence ($\alpha \approx 2$) with respect to the excitation power [164, 167]. Defect-bound and

localized excitonic states generally exhibit a sublinear dependence ($\alpha < 1$) with respect to excitation power, typically saturating at higher power levels [184, 221]. Power-dependent PL measurements were taken at each discerned PL peak location and plotted on a log-log scale for PL intensity vs. power. A curve fitting tool was used to estimate the linear fit and slope of the plot to extract α .

5.3.2 Pre-Electron-beam Irradiation Characterization of Excitonic Populations in WSe₂

For the unencapsulated WSe₂ sample, measurements were performed with a slit width of 100 μm , a center wavelength of 750 nm, an integration time of 15 s, and an accumulation count of 10. PL spectra were collected from the center of the WSe₂ monolayer at various excitation source power levels including: 100 nW, 500 nW, 1 μW , 5 μW , 10 μW , 50 μW , 100 μW , and 500 μW . The results have been compiled in Fig. 5.6. Discernible peaks were identified and then plotted with respect to the excitation power to determine if the power dependence was approximately linear, superlinear, or sublinear. PL peaks were identified at ~ 717 nm (~ 1.730 eV) and ~ 737 nm (~ 1.683 eV), which correspond well to the neutral bright exciton (X^0) and trion (X^-) peak respectively. The results were tabulated and are shown in Table 5.1.

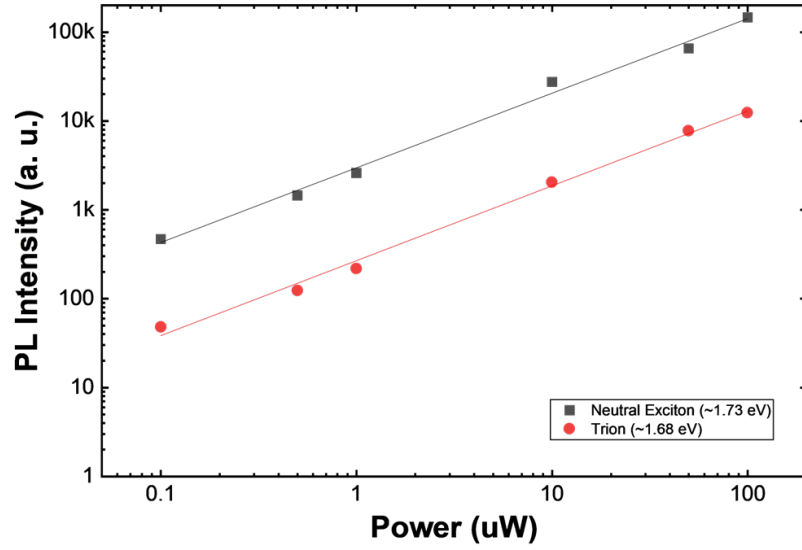
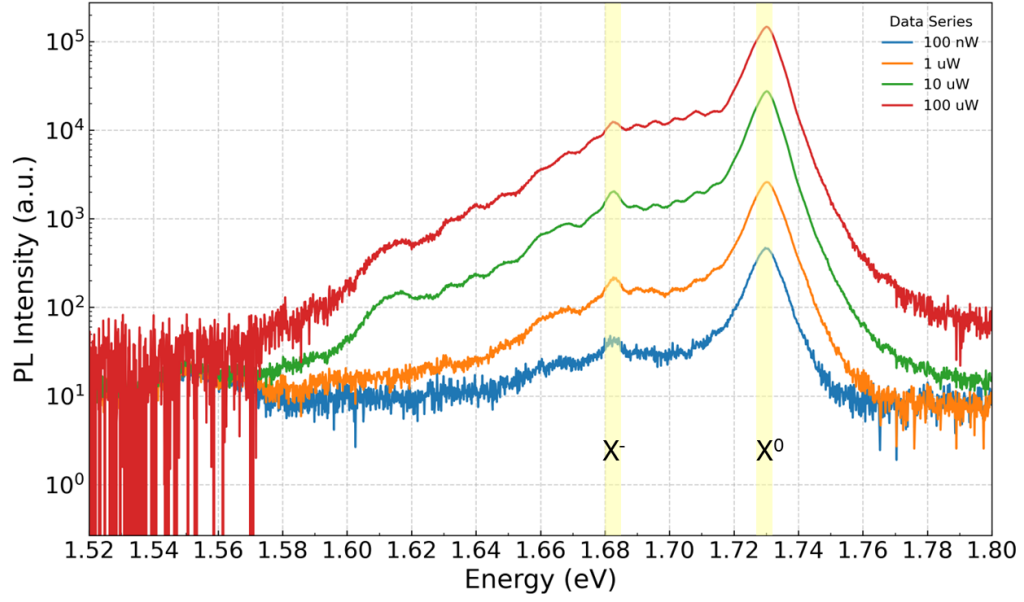


Figure 5.6: Power-dependent low-temperature ($T = 4$ K) PL for unencapsulated sample before electron-beam lithography processing. PL peaks were identified, with that information provided in Table 5.2. The power dependence of the PL peaks were plotted using a log-log scale, where linear curve fitting was used to determine the power law scaling exponent (α).

Table 5.1: Tabulated results from measured PL emissions at $T = 4$ K from an unencapsulated WSe₂ monolayer before electron-beam lithography processing. Excitonic populations were attributed to each PL peak based on peak position and considerations from the literature. The power law scaling exponents were also reported based on the fitted slope of the log of the PL intensity with respect to the log of the incident power.

	Peak Position (eV)	Plot Label	Offset from X^0 (meV)	Power Dependence
Neutral Exciton	~ 1.730	X^0	0	$\alpha \sim 0.84$
Trion	~ 1.683	X^-	47	$\alpha \sim 0.84$

No biexciton or higher-order complexes were discerned, which could be due to a combination of factors. For unencapsulated WSe₂, due to the dielectric environment mismatch between the side in contact with the hBN and the other being in contact with vacuum, and due to the higher probabilities of charge- or environment-induced defects on the bare, unprotected WSe₂, inhomogeneous broadening can cause the biexciton and higher-order excitonic complex peaks to be unresolvable [164, 168]. Historically, it has been difficult to find these multi-body excitonic complexes on bare WSe₂. The power law scaling exponent (α) for both the neutral exciton and trion peaks matched at $\alpha \sim 0.84$ which indicates a sublinear dependence, which was not expected for these two excitonic populations where a linear dependence ($\alpha \sim 1$) is typically expected. A potential explanation for this could be some form of quenching due to being in a relatively high-density regime, where the exciton population is high enough that mechanisms such as exciton-exciton annihilation (EEA), other Auger-like processes, Pauli blocking, and high dielectric screening become dominant. These processes limit radiative recombination by a combination of increasing the probability of non-radiative decay processes, reducing the binding energies of excitons and trions, as well as reducing the oscillator strength of excitonic transitions [52, 169, 186, 222, 223]. It should be noted that since both the neutral exciton and trion have the same power scaling ($\alpha \sim 0.84$), it appears that the trion intensity scales with the exciton, suggesting that the

trion population is limited by the exciton population rather than free carriers in the material.

For the hBN-encapsulated WSe₂ sample, measurements were performed with a spectrometer slit width of 100 μm , a center wavelength of 750 nm, an integration time of 5 s, and an accumulation count of 20. PL spectra were collected from the center of the WSe₂ monolayer at various excitation source power levels including: 100 nW, 500 nW, 1 μW , 5 μW , 10 μW , 50 μW , 100 μW , and 500 μW . Discernible peaks were identified and then plotted with respect to the excitation power. The power law scaling exponent (α) was ascertained from the power dependence of each identified peak and estimated from the slope of the log of the PL intensity with respect to the log of the incident power. The results have been compiled in Fig. 5.7. PL peaks were identified at ~ 720 nm (~ 1.721 eV), ~ 729 nm (~ 1.701 eV), ~ 739 nm (~ 1.677 eV), ~ 745 nm (~ 1.665 eV), ~ 748 nm (~ 1.657 eV), ~ 761 nm (~ 1.630 eV) and ~ 781 nm (~ 1.588 eV). The identified peaks were given tentative assignments based on the peak positions from the literature. The results are shown in Table 5.2.

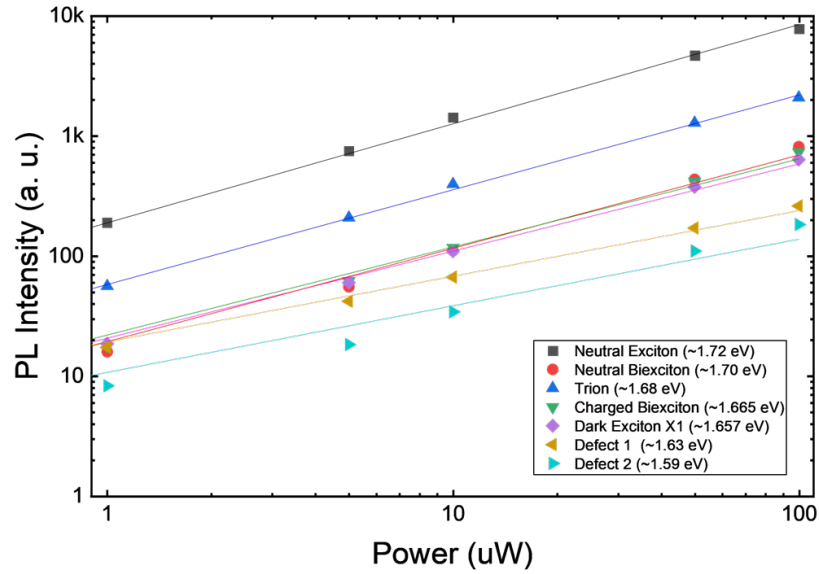
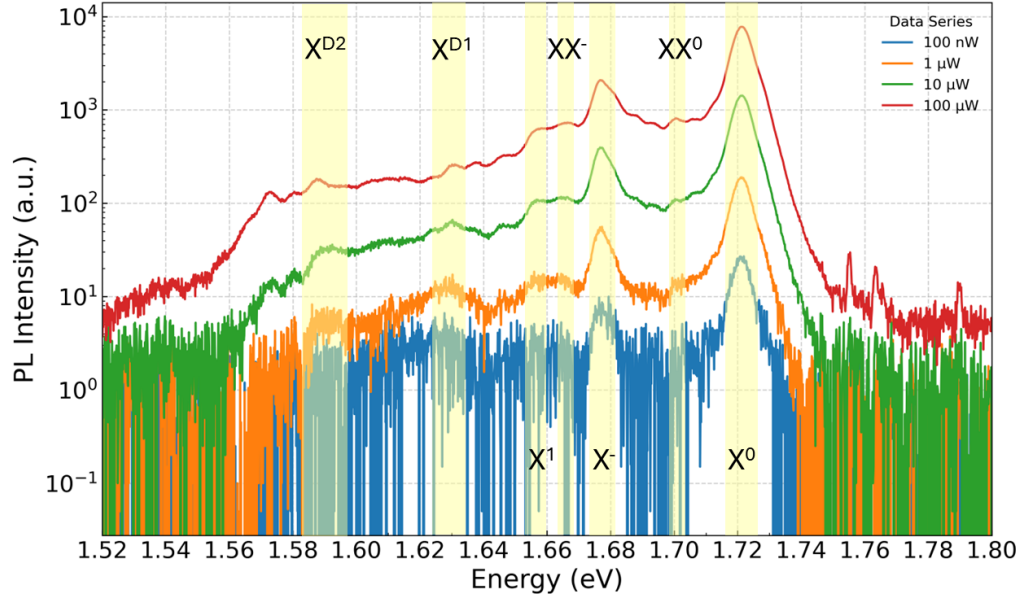


Figure 5.7: Power-dependent low-temperature ($T = 4$ K) PL for hBN-encapsulated WSe_2 sample before electron-beam lithography processing. PL peaks were identified, with that information provided in Table 5.2. The power dependence of the PL peaks were plotted using a log-log scale, where linear curve fitting was used to determine the power law scaling exponent (α).

Table 5.2: Tabulated results from measured PL emissions at $T = 4$ K from a hBN-encapsulated WSe₂ monolayer before electron-beam lithography processing. Excitonic populations were attributed to each PL peak based on peak position and considerations from the literature. The power law scaling exponents were also reported based on the fitted slope of the log of the PL intensity with respect to the log of the incident power. Note that (pr) stands for "phonon replica".

	Peak Position (eV)	Plot Label	Offset from X^0 (meV)	Power Dependence
Neutral Exciton	~ 1.721	X^0	0	$\alpha \sim 0.83$
Biexciton	~ 1.701	XX^0	20	$\alpha \sim 0.78$
Trion	~ 1.677	X^-	44	$\alpha \sim 0.79$
Charged Biexciton	~ 1.665	XX^-	56	$\alpha \sim 0.73$
Dark exciton (or pr)	~ 1.657	X^1	64	$\alpha \sim 0.73$
Defect 1	~ 1.630	X^{D1}	91	$\alpha \sim 0.55$
Defect 2	~ 1.588	X^{D2}	133	$\alpha \sim 0.56$

For comparison, Table 5.3 provides published peak positions in (eV) for 5 publications that identify various excitonic complexes in hBN-encapsulated WSe₂ at low-temperature via PL. Variations in the PL wavelengths are expected due to the differences in material quality and local dielectric environment of the material stacks.

Based on the literature, the peaks found are in good agreement with what has been reported for the bright exciton, biexciton, and trion, respectively. Their peak locations are in line with those that were published in prior studies [164–168]. The peak order assigned to the charged biexciton and dark exciton, respectively, are reversed compared to what has been previously published. This is due to the fact that the reported dark exciton ground state sits approximately 40-42 meV below the neutral bright exciton [166, 167, 169], and when coupled to the zone-center chiral E'' phonon, the necessary angular momentum/spin-flip can be provided to allow for radiative decay [171]. This phonon has been observed to have an energy of 21-22 meV, and when subtracting this phonon energy from the dark exciton ground state, one would expect to see this dark exciton-based phonon replica between 61-64 meV below the neutral bright exciton, which matches the peak location found at 1.657 eV.

Table 5.3: Published peak positions (eV) for different identified PL spectral emissions at $T = 4$ K for hBN-encapsulated WSe₂ monolayers. The referenced sources include [164–168]. Note that (pr) stands for "phonon replica".

Peak Position (eV)	Yang [166]	Strasbourg [165]	Barbone [168]	Chen [167]	Li [164]
Bright Exciton	1.707	1.733	1.728	1.708	1.74
Biexciton			1.711	1.690	1.723
Intervalley Trion	1.680	1.705	1.699	1.680	1.712
Intravalley Trion	1.674	1.697	1.692	1.672	1.70
Dark Exciton	1.669		1.685	1.668	1.697
Charged Biexciton		1.683	1.679	1.659	1.691
Dark Exciton 2 (pr)	1.648				
Indirect Exciton 1	1.678				
Indirect Exciton 2 (pr)	1.661				
Indirect Exciton 3 (pr)	1.653				

Likewise, based on the reported values, the charged biexciton tends to sit ~ 49 -50 meV below the neutral exciton, which would be ~ 1.67 eV. This value is quite close to the observed peak at ~ 1.665 eV. The PL peaks at ~ 1.630 eV and ~ 1.588 eV were attributed to defect-bound states or localized trapped excitonic states, primarily due to their very low power law scaling exponent values of $\alpha < 0.6$. This indicates high saturation behavior typically associated with trap charges from defects, vacancies, or impurities that can be populated at lower power intensities, but are quickly filled and saturated [163, 221]. Even though the WSe₂ was encapsulated, either the transferred WSe₂ monolayer possessed inherent defects before encapsulation, or surface defects (or impurities) were introduced during the hBN encapsulation process. Based on the estimated power law scaling exponent values for all identified peaks being sublinear ($\alpha < 1$), this encapsulated sample appears to be similar to the unencapsulated WSe₂ monolayer, where non-radiative processes such as Auger-like recombination processes (EEA, etc.) are dominant, and Pauli blocking actively restricts additional exciton formation at higher powers due to potentially high exciton densities in

the WSe₂. Only the dark exciton and defect peaks were expected to have a sublinear power law scaling exponent, with the dark exciton expected to have an $\alpha \sim 0.72$ to 0.77 [171]. The biexciton and charged biexciton PL peaks typically have super-linear power dependence of $\alpha > 1.5$ and ideally $\alpha \approx 2$, but the observed power dependence was sublinear. Since even the bright exciton is exhibiting sublinear ($\alpha \sim 0.83$) power dependence, there is strong evidence that all other higher excitonic complex peaks will be limited by the exciton density.

5.3.3 Electron-beam Irradiation Process

Electron-beam irradiation of the WSe₂ samples were performed in a Raith/Vistec EBPG electron-beam lithography (EBL) system with a high-tension voltage of 100 kV using a 400 μm aperture, a 1 nA beam current, and an electron dosage of 1,200 $\mu\text{C}/\text{cm}^2$. To mimic the process as close as possible to typical EBL pattern writing, a PMMA 950 A4 resist was spun on to a thickness of approximately 300 nm on top of the WSe₂ samples. The resist was baked at 185 °C for 120 s to remove the solvent, and after electron-beam irradiation, the samples were developed in a solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) with a ratio of 1:2.5 for 75 s before being dried with nitrogen gas. An example image of the electron-beam exposure post-resist development is shown in Fig. 5.8. The PMMA resist was removed using an acetone submersion process heated to 80 °C for 10 minutes, and then immersed in IPA for 1 min at room temperature, with the samples subsequently dried using dry nitrogen gas. For both the hBN-encapsulated WSe₂ sample and the unencapsulated WSe₂ sample, the entire exfoliated monolayer region of the WSe₂ was irradiated. Once the electron irradiation process was complete, the WSe₂ (encapsulated and unencapsulated) samples were placed back under a 1×10^{-5} hPa vacuum environment within 30 minutes to minimize ambient air exposure.

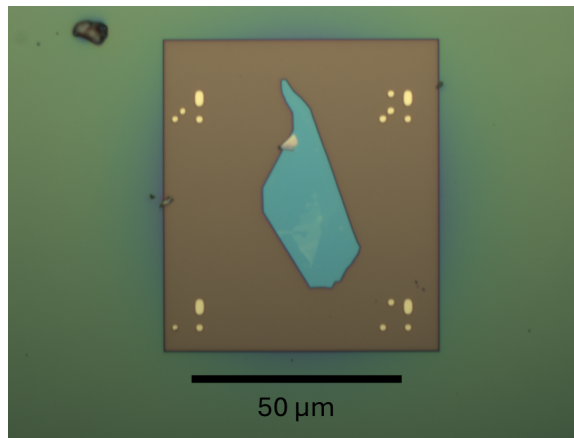


Figure 5.8: Optical micrograph of the unencapsulated WSe₂ sample with PMMA resist that has been both exposed to electron-beam irradiation and developed in an MIBK:IPA solution. The entire WSe₂ flake and the associated 50 μm x 50 μm area was irradiated with a 100 keV electron-beam with a dose of 1,250 μC/cm².

5.3.4 Post-Electron-beam Irradiation Characterization of Excitonic Populations in WSe₂

Low-temperature PL was performed after the EBL processing to determine and understand any changes in the excitonic complex populations in the unencapsulated and hBN-encapsulated WSe₂ monolayer samples compared to before the electron-beam irradiation process. Additionally, a comparison between the two WSe₂ samples helped elucidate the impacts of hBN-based protective layers on monolayer WSe₂ used for defect mitigation as described in the literature [19, 51, 125, 131, 133, 214, 219].

For the unencapsulated WSe₂ sample, post-EBL measurements were performed using a spectrometer slit width of 100 μm , a center wavelength of 750 nm, an integration time of 5 s, and an accumulation count of 20. PL spectra were collected from the center of the WSe₂ monolayer at various excitation source power levels including: 100 nW, 500 nW, 1 μW , 5 μW , 10 μW , 50 μW , 100 μW , and 500 μW . The results have been compiled in Fig. 5.9. As with the pre-EBL PL measurements, discernible peaks were identified and then plotted with respect to the excitation power to determine if the power dependence was approximately linear, superlinear, or sublinear. The results are shown in Table 5.4. No PL peaks associated with multi-particle excitonic complexes such as biexcitons or charged biexcitons were observed.

Table 5.4: Tabulated results from measured PL emissions at $T = 4$ K from an unencapsulated WSe_2 monolayer after electron-beam lithography processing. Excitonic populations were attributed to each PL peak based on peak position and considerations from the literature. The power law scaling exponents were also reported based on the fitted slope of the log of the PL intensity with respect to the log of the incident power. *Power dependence was taken at 1.600 eV for X^D as reference point due to the broadband nature of the defect band.

	Peak Position (eV)	Plot Label	Offset from X^0 (meV)	Power Dependence
Neutral Exciton	~ 1.706	X^0	0	$\alpha \sim 0.91$
Defect Band	$\sim 1.54\text{-}1.65^*$	X^D	50-170	$\alpha \sim 0.68^*$

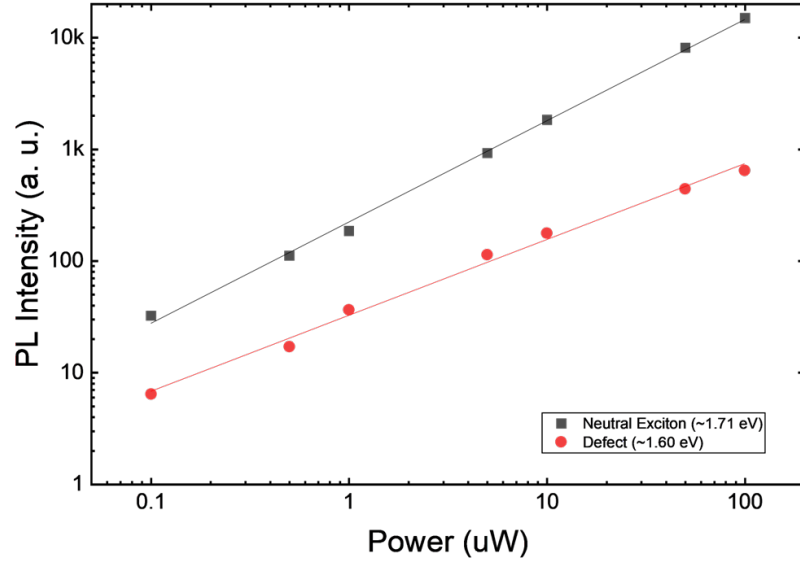
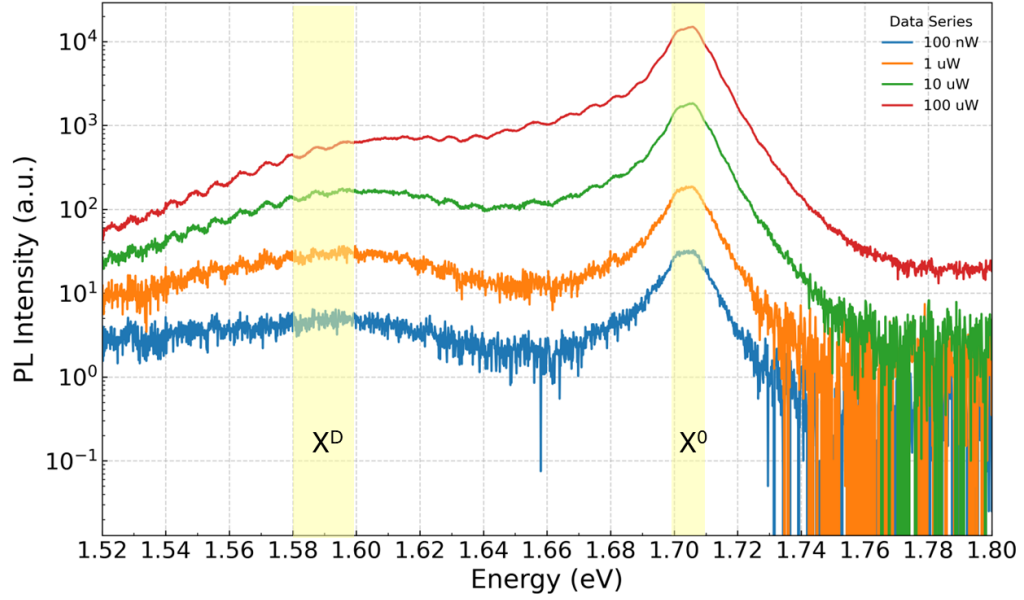


Figure 5.9: Power-dependent low-temperature ($T = 4$ K) PL for unencapsulated sample after electron-beam lithography processing. PL peaks were identified, with that information provided in Table 5.5. The power dependence of the PL peaks were plotted using a log-log scale, where linear curve fitting was used to determine the power law scaling exponent (α).

For the hBN-encapsulated WSe₂ sample, the post-EBL measurements were performed using the same settings and parameter values as was done before electron-beam irradiation process were performed on the sample, as described in Section 5.3.2. PL spectra were collected from the center of the WSe₂ monolayer at various excitation source power levels including: 100 nW, 500 nW, 1 μ W, 5 μ W, 10 μ W, 50 μ W, 100 μ W, and 500 μ W. As before, peaks were identified and then plotted with respect to the excitation power. The power law scaling exponent (α) was determined from the power dependence of each identified peak and estimated from the slope of the log of the PL intensity with respect to the log of the incident power. The results have been compiled in Fig. 5.10. The identified peaks were given tentative assignments based on the peak positions from the literature. The results were tabulated and are shown in Table 5.5. Similar to the unencapsulated sample, the neutral exciton peak location has red-shifted to 1.709 eV, which is still in line with the expected range of values observed in the literature for the peak location of the neutral exciton (please refer to Table 5.3 for literature comparison).

Table 5.5: Tabulated results from measured PL emissions at T = 4 K from a hBN-encapsulated WSe₂ monolayer after electron-beam lithography processing. Excitonic populations were attributed to each PL peak based on peak position and considerations from the literature. The power law scaling exponents were also reported based on the fitted slope of the log of the PL intensity with respect to the log of the incident power.

	Peak Position (eV)	Plot Label	Offset from X^0 (meV)	Power Dependence
Neutral Exciton	~ 1.709	X^0	0	$\alpha \sim 0.85$
Trion	~ 1.664	X^-	45	$\alpha \sim 0.83$
Defect 1	~ 1.607	X^{D1}	102	$\alpha \sim 0.49$
Defect 2	~ 1.552	X^{D2}	157	$\alpha \sim 0.25$

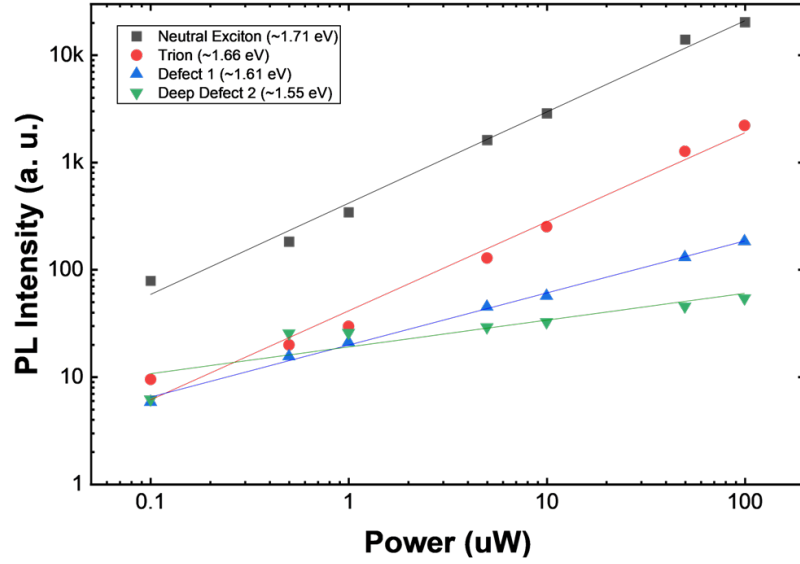
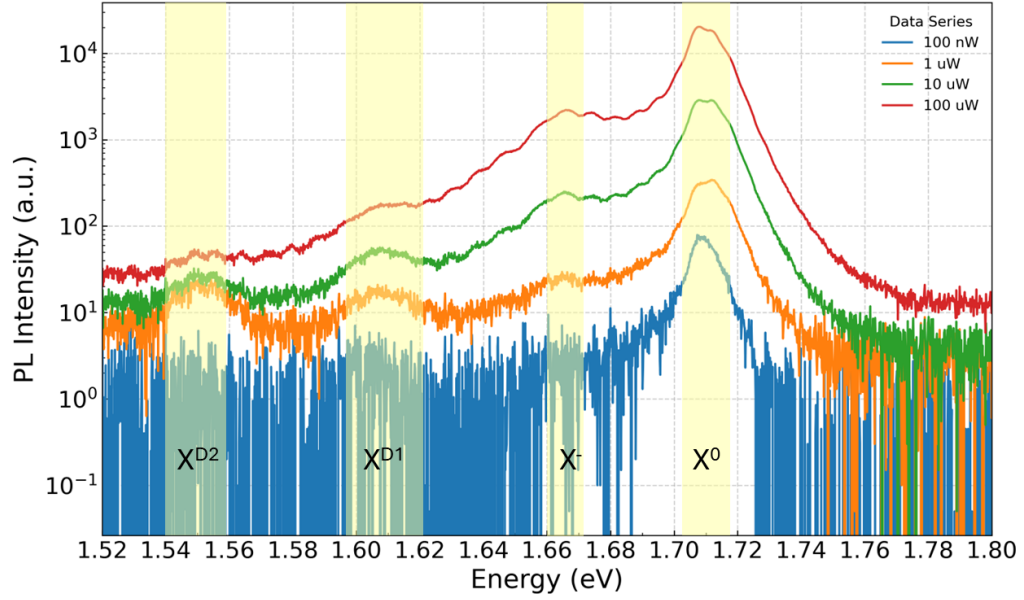


Figure 5.10: Power-dependent low-temperature ($T = 4$ K) PL for hBN-encapsulated sample after electron-beam lithography processing. PL peaks were identified, with that information provided in Table 5.5. The power dependence of the PL peaks were plotted using a log-log scale, where linear curve fitting was used to determine the power law scaling exponent (α).

5.4 Effects of Electron-beam Irradiation on WSe₂ and hBN-encapsulated WSe₂

To provide more direct comparisons, PL spectra were normalized to the neutral exciton PL intensity and then plotted together. Power levels were kept consistent between the two PL spectra being compared. Combinations reviewed include comparing pre-EBL and post-EBL normalized PL spectra for the bare, unencapsulated WSe₂ monolayer, the pre-EBL and post-EBL normalized PL spectra for the hBN-encapsulated WSe₂, the unencapsulated and hBN-encapsulated pre-EBL normalized PL spectra, and finally the unencapsulated and hBN-encapsulated post-EBL normalized PL spectra. Results are discussed pertaining to each set of PL spectra.

5.4.1 PL Spectral Comparison of Unencapsulated WSe₂ before and after Electron-Beam Irradiation

A set of PL spectra are shown in Fig. 5.11 comparing the PL before and after electron-beam lithography was performed on the unencapsulated WSe₂ monolayer on the same area of the WSe₂, with each of the three PL spectra representing different incident power levels (top: $P = 1 \mu\text{W}$, middle: $10 \mu\text{W}$, bottom: $100 \mu\text{W}$). Comparing low-temperature PL spectra taken on the unencapsulated WSe₂ sample before and after EBL and its associated processes were performed on the sample, a number of changes can be observed. There is a substantial red-shift of $\sim 24 \text{ meV}$ from $\sim 1.730 \text{ eV}$ (pre-EBL) to $\sim 1.706 \text{ eV}$ (post-EBL). This has been associated with a n-doping effect caused by induced trapped charges in the underlying dielectric layers and surface of the material, from injected electrons from EBL, which can modulate the carrier density in the WSe₂ monolayer [224]. Additionally, strain and substrate interactions caused by the associated EBL processes such as soft baking the

sample at 185°C and PMMA residue not removed by the acetone immersion, respectively, could also factor into the observed redshift [48]. Peak broadening is also observed as a change in the full-width-half-maximum (FWHM) from ~ 7.8 meV to ~ 12.5 meV. In previous studies, inhomogeneous linewidth broadening provides insights into the extent of disorder in the material due to local strain, charge doping, surface defects/impurities, and dielectric environmental changes [134–136, 186, 213, 225]. All of these disorder mechanisms could potentially be attributed to the associated EBL fabrication processes, but additionally, crystal damage and non-radiative recombination at defect sites generated by electron-beam damage have also been shown to contribute to inhomogeneous broadening [19, 156].

The trion peak appears to have completely disappeared post-EBL treatment, with no discernible PL feature found around 1.67-1.69 eV. In intrinsic WSe_2 , the relative intensity of the negatively-charged trion peak has been observed to drop by a factor of 5 due to the quenching of the neutral exciton from the creation of defects (interstitial defects and vacancies) diverting optical emission to the newly formed broad defect-band excitons [156]. This is supported by the observed order-of-magnitude reduction in PL intensity between the PL spectra presented in Fig. 5.6 and Fig. 5.9. This can put the trion PL emission below the noise floor, especially with the generation of the large, broadband defect band, which dominates much of the PL spectra at the lower energy levels between 1.54 and 1.65 eV. The appearance of a broad defect band post-EBL has been associated with the generation of Se vacancies and interstitial defects in the WSe_2 . Irradiation has been said to introduce mid-gap defect states in TMDs, which generate broad PL emissions located ~ 130 -150 meV below the neutral exciton PL peak [20, 156]. This is quite clearly seen relative to the neutral exciton peak with a clear and dramatic defect band appearing across much of the PL spectrum post-EBL. While the calculated transferred electron-beam energy does not reach the calculated displacement energy required to elastically eject a Se atom from the WSe_2 lat-

tice (calculated to be in the range of 5-7 eV for displacing a chalcogen atom in WSe₂ [13]), it has been found that 100 keV electron beams can break TMD covalent bonds through inelastic scattering and through electronic excitations that work to significantly lower the effective displacement threshold energy required for displacing a chalcogen atom, like the additional contribution from back-scattered secondary electrons [16, 19]. It should also be noted that the PL intensity of the unencapsulated WSe₂ before and after the electron-beam lithography processing, a reduction of over an order-of-magnitude is observed based on Fig. 5.6 and Fig. 5.9. This is expected as high-dose electron beam exposure has been shown to lead to quenching of the neutral exciton PL by up to two orders-of-magnitude at cryogenic temperatures [156].

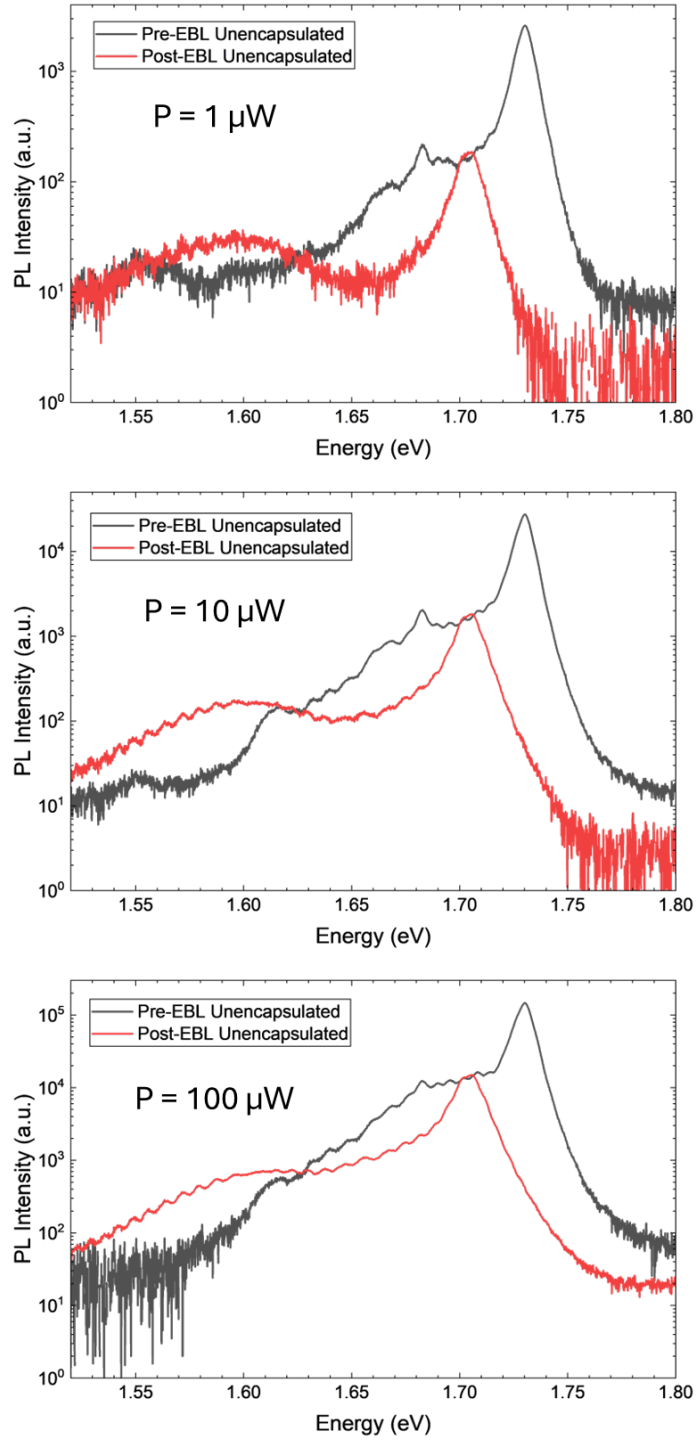


Figure 5.11: Comparison: Low-Temp ($T = 4$ K) PL comparison between before and after electron-beam irradiation process for an unencapsulated WSe₂ sample.

5.4.2 PL Spectral Comparison of hBN-encapsulated WSe₂ before and after Electron-Beam Irradiation

A set of PL spectra are shown in Fig. 5.12 comparing the PL before and after electron-beam lithography was performed on the hBN-encapsulated WSe₂ monolayer (performed as close as possible to the same spatial location on the sample), with each of the three PL spectra representing different incident power levels (top: $P = 1 \mu\text{W}$, middle: $10 \mu\text{W}$, bottom: $100 \mu\text{W}$). After the electron-beam lithography process, the low-temperature PL spectra of the hBN-encapsulated WSe₂ monolayer changed in a number of ways compared to the PL spectra collected before EBL processing. The neutral exciton peak location red-shifted from 1.721 eV before EBL to 1.709 eV after EBL, a 12 meV shift. This red-shift is approximately half the shift that occurred with the in the unencapsulated sample, indicating that the hBN encapsulation is possibly reducing or mitigating effective doping or carrier density modification of the WSe₂ [224]. The FWHM of the neutral exciton peak increased as well, from ~ 5.8 meV to ~ 10.3 meV, in line with what was seen in the unencapsulated sample pre- and post-EBL. The PL peak located at ~ 1.664 eV is attributed to the trion population as it matches similarly in energy offset to the trion peak identified on this sample before EBL, at ~ 44 meV, even though the peak location is similarly located where the charged biexciton peak was previously found. Compared to the PL pre-EBL though, the peak has substantially broadened more so than the neutral exciton peak and lost much of its definition due to the PL signal floor around this peak increasing. This could potentially be accounted for by the inhomogeneous broadening and spectral merging with other nearby features in the PL, such as the phonon-coupled dark exciton feature located 1.657 eV found in the pre-EBL PL spectra. Additionally, the trion-to-neutral exciton PL intensity ratio changes considerably, going from ~ 0.28 to ~ 0.10 , indicating that the sample became more charge-neutral after electron-beam exposure. This might indicate that some form of de-

doping occurred, moving some of the trion population to the exciton population. Note that the neutral exciton peaks of the post-EBL PL spectra are twice the PL intensity compared to the pre-EBL neutral exciton peaks, which does not come through in the normalized PL plots shown in Fig. 5.12. This seems counterintuitive, but could indicate that the de-doping due to the EBL might have moved a large enough portion of the trion population to boost the exciton population, but this is unlikely to justify a doubling of the exciton peak. This high post-EBL neutral exciton peak intensity could also indicate some form of inhomogeneity in the WSe₂ monolayer under the hBN where the post-EBL PL measurement was enhanced relative to the pre-EBL PL measurement due to spatial variations in the crystal quality.

The biexciton and charged biexciton PL features that were already faint in the pre-EBL PL spectra are no longer distinguishable in the post-EBL PL spectra. The loss of these peaks could be an indication of the point defect creation, which act as scattering centers, reducing the exciton lifetime and diffusion length, leading to a reduced probability of radiative exciton-exciton interactions or exciton-trion interactions. This is further supported by the emergence of the defect peaks located at ~ 1.607 eV and ~ 1.552 eV. The power law scaling exponents of these two defect peaks with $\alpha > 0.5$ in both cases, indicate that these are localized deep traps that are likely due to Se vacancies or interstitial defects pertaining to Se dislocations [156, 204, 221]. The two defect peaks found in the PL pre-EBL are no longer present in the PL post-EBL. The PL features pre-EBL that were attributed to potential defects located at peak positions of ~ 1.630 eV and ~ 1.588 eV are unlikely to be the same defect features post-EBL at ~ 1.607 eV and ~ 1.552 eV, respectively, due to the fact that for defect-bound excitons, the emission energy is tied to the local atomic configuration, and will not shift to the extent required for the pre-EBL and post-EBL results to line up. There is a possibility that the previous defect peaks found in the pre-EBL PL spectra are either spectrally buried due to the increase in PL emission across the entire spectral range in the post-EBL measurement, or that the new defects that appear after electron-beam irra-

diation are quenching the PL from all other localized states around them due to them being deeper in the band gap with lower energy required, effectively hoarding exciton populations. While it has been postulated that hBN encapsulation provides a level of protection against defects from irradiation processes [18, 19, 51], evidence here suggests that some level of change is occurring, with evidence of vacancy or interstitial defect generation.

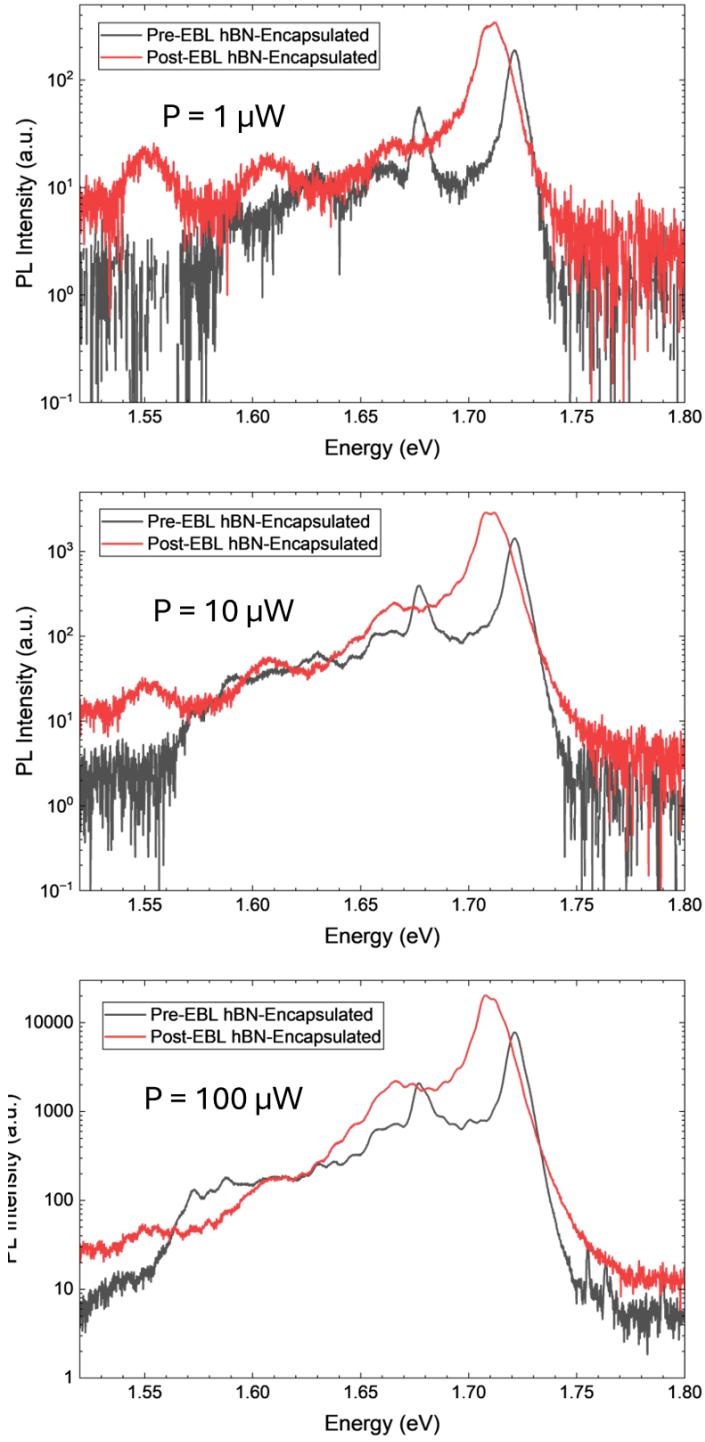


Figure 5.12: Comparison: Low-Temp ($T = 4 \text{ K}$) PL comparison between before and after electron-beam irradiation process for a hBN-encapsulated WSe₂ sample.

5.4.3 PL Spectral Comparison of Unencapsulated and hBN-encapsulated WSe₂ before Electron-Beam Irradiation

A set of PL spectra are shown in Fig. 5.14 comparing the PL of the unencapsulated WSe₂ with the PL of the hBN-encapsulated WSe₂ monolayer before electron-beam lithography, with each of the three PL spectra representing different incident power levels (top: $P = 1 \mu\text{W}$, middle: $10 \mu\text{W}$, bottom: $100 \mu\text{W}$). Comparing the unencapsulated and hBN-encapsulated WSe₂ monolayers, there is a distinct difference in the peak location for the neutral exciton, where the hBN-encapsulated sample is red-shifted by $\sim 9 \text{ meV}$ due to the difference in dielectric screening [214]. The red-shift is smaller than the reported comparison between an hBN-encapsulated WSe₂ sample and WSe₂ on SiO₂ since the unencapsulated WSe₂ used in this work sits on a hBN flake. While the profiles of the PL are similar, the hBN-encapsulated sample has a richer set of features visible in the PL emission spectrum compared to the unencapsulated sample. This is typically attributed to the suppression of inhomogeneous broadening as stated in previous sections, which also has the benefits of reducing the linewidths and FWHM of PL features too. In this case, the difference between the FWHM of the neutral exciton peak between the two samples pre-EBL was $\sim 2 \text{ meV}$, where the hBN-encapsulated sample had a neutral exciton PL peak FWHM of $\sim 5.8 \text{ eV}$ compared to the unencapsulated sample's $\sim 7.8 \text{ eV}$. Another distinguishing feature was the trion-to-neutral exciton PL intensity ratio, with the hBN-encapsulated sample having a substantially higher ratio of ~ 0.28 compared to the unencapsulated sample of ~ 0.09 . This indicates that the hBN-encapsulated sample was not as charge-neutral at the start as its unencapsulated counterpart.

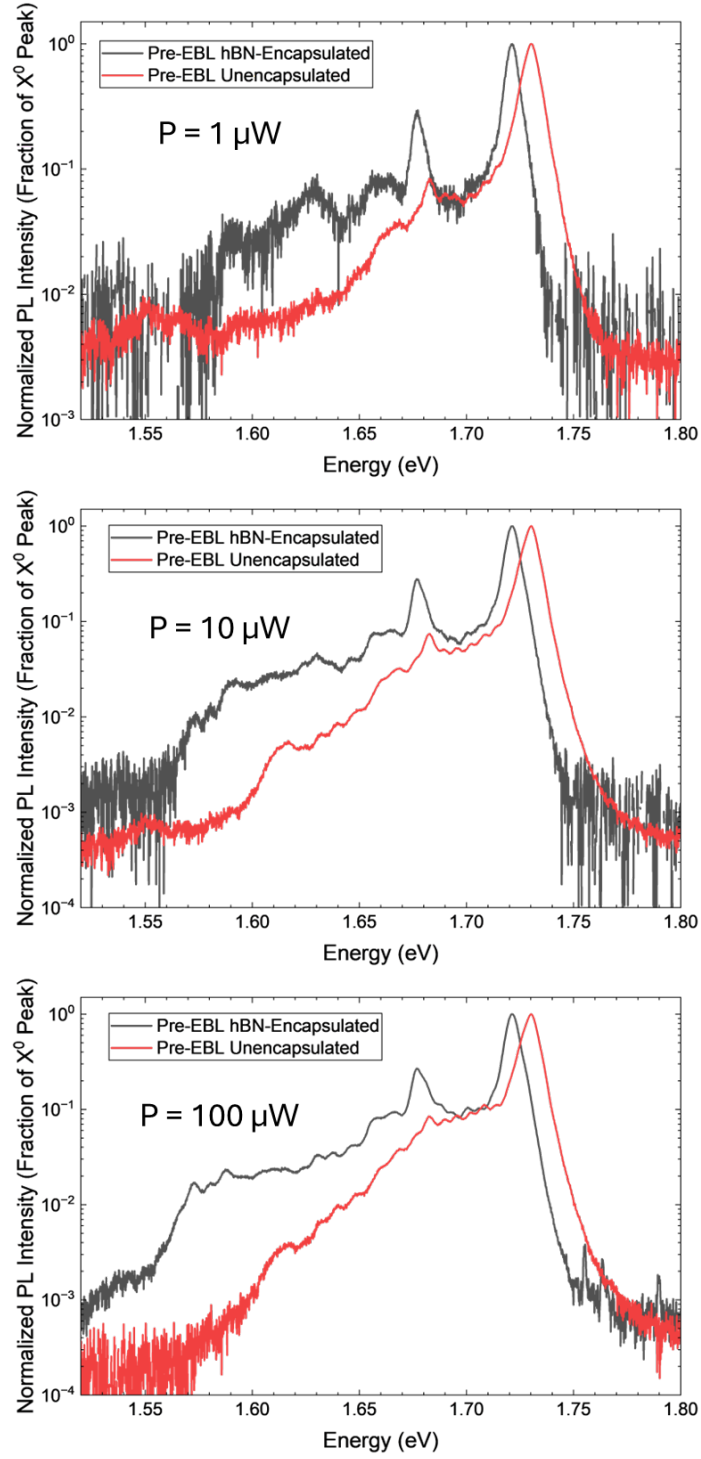


Figure 5.13: Comparison: Low-Temp ($T = 4 \text{ K}$) PL comparison between bare WSe_2 and hBN-encapsulated WSe_2 samples before electron-beam irradiation process.

5.4.4 PL Spectral Comparison of Unencapsulated and hBN-encapsulated WSe₂ after Electron-Beam Irradiation

A set of PL spectra are shown in Fig. 5.14 comparing the PL of the unencapsulated WSe₂ with the PL of the hBN-encapsulated WSe₂ monolayer after electron-beam lithography, with each of the three PL spectra representing different incident power levels (top: $P = 1 \mu\text{W}$, middle: $10 \mu\text{W}$, bottom: $100 \mu\text{W}$). A dramatic difference after electron-beam irradiation can be seen between the unencapsulated and hBN-encapsulated WSe₂ monolayer samples. The largest difference between the post-EBL PL is in the very large defect band that appears in the unencapsulated WSe₂ PL spectra. This defect band is one order of magnitude lower than the PL intensity of the neutral exciton and is more than one order of magnitude higher than the noise floor. The defect band spans from 1.54 eV to 1.66 eV (120 meV) and has been previously attributed to chalcogen vacancies (Se in this case) that give rise to localized mid-gap states that inhomogeneously broaden the defect emission [156]. In contrast, while the hBN-encapsulated sample also had additional defect peaks emerge post-EBL, both peaks are more localized. This is where the benefits of hBN-encapsulation can be seen, where defect generation can be minimized by raising the displacement threshold of chalcogen atoms in the lattice [19]. hBN encapsulation, however, does not provide complete protection, as emergent defects were observed in the PL post-EBL. Additionally, an overall reduction in PL intensity was observed in the hBN-encapsulated sample post-EBL. Even so, compared to the unencapsulated sample, more of the fine structure features were observable post-EBL, with the trion peak still discernible.

As an aside, post-EBL, the neutral exciton peaks become aligned with only about 1 meV on average separating the two samples. This is probably coincidental that the exciton peak locations were so well matched, but the difference in the red-shifting of the two was probably not, with the unencapsulated sample's neutral exciton peak position red-shifting ~ 24

meV compared to the ~ 12 meV that the hBN-encapsulated sample red-shifted. The difference probably stems from the difference in charge doping, and the different charge densities each of these samples started off at. As mentioned previously the hBN-encapsulated sample had a substantially higher trion-to-exciton ratio (~ 0.26) compared to the unencapsulated sample (~ 0.09) pre-EBL. Post-EBL, the trion peak effectively disappeared in the unencapsulated sample, while the hBN-encapsulated sample had its trion-to-exciton ratio reduced to ~ 0.10 . The electron-beam lithography process most likely introduced surface charges and resist residues directly on the WSe_2 leading to a substantial doping jump to the charge-sensitive WSe_2 surface. As described earlier, this effective doping can lead to a large red-shift [224]. In comparison, the relatively protected hBN-encapsulated WSe_2 sees less of a shift. The linewidth difference between the two neutral exciton peaks shows a ~ 2 meV difference at the FWHM, with the hBN-encapsulated WSe_2 sample having the narrower linewidth (with a FWHM of ~ 10 meV) compared to the unencapsulated WSe_2 neutral exciton linewidth (with a FWHM of ~ 12 meV).

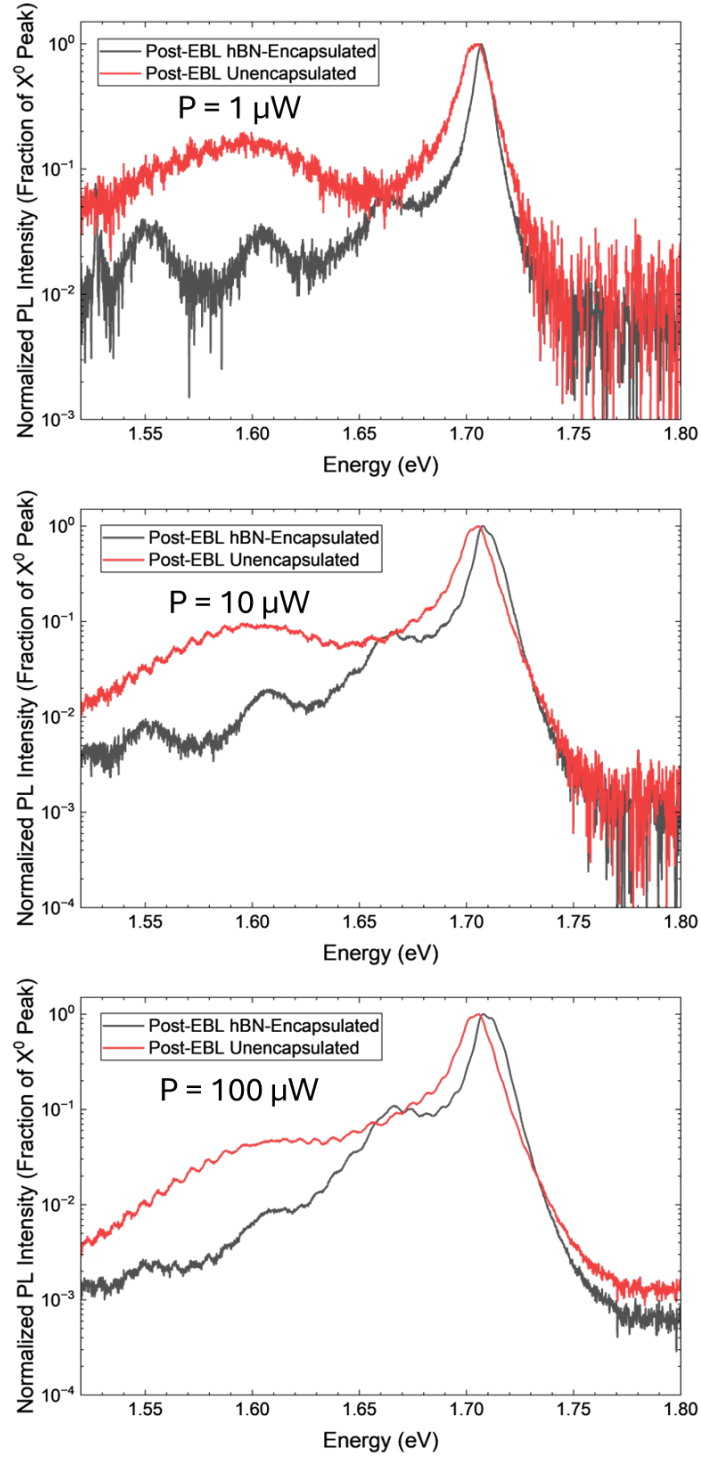


Figure 5.14: Comparison: Low-Temp ($T = 4$ K) PL comparison between bare WSe₂ and hBN-encapsulated WSe₂ samples after electron-beam irradiation process.

5.5 Conclusions

The effects of electron beam irradiation and associated chemical processes on monolayer WSe₂ were examined in detail via low-temperature ($T = 4$ K) photoluminescence to study how fine structures associated with the excitonic complexes and populations in WSe₂ changed due to this common fabrication process. The PL spectra of a bare, unencapsulated WSe₂ monolayer on hBN and a hBN-encapsulated WSe₂ monolayer were compared before and after electron beam irradiation, with the hBN-encapsulated WSe₂ being included to determine how effective the claimed protection of such a thin dielectric was in mitigating changes in the WSe₂ properties. The excitonic populations of the two samples were compared before and after electron beam irradiation after confirming the quality of the WSe₂ monolayer films using AFM, Raman spectroscopy, and PL mapping at $T = 78$ K. It was found that electron-beam irradiation significantly changed the excitonic populations in both the unencapsulated WSe₂ sample and the hBN-encapsulated WSe₂ sample, but to very different extents. While not all excitonic species were located in this particular unencapsulated WSe₂ monolayer, the neutral exciton and trion populations were identified. After the electron-beam lithography the exciton population remained, but the trion population was no longer discernible, and in its place, a very large and broad defect band, ostensibly due to Se vacancies and lattice damage, was generated. The hBN-encapsulated WSe₂ monolayer possessed a richer fine structure of excitonic populations with the neutral exciton, biexciton, trion, charged biexciton, phonon-coupled dark exciton, and even a couple localized defect populations detected in the photoluminescence. After the electron-beam lithography a number of changes occurred in these excitonic populations, including the disappearance of the biexcitons, charged biexcitons, and the emergence of additional localized defect states. Even so, the exciton and trion populations could be discerned, albeit at a different ratio compared to before the electron-beam lithography (from 0.29 trion/exciton

to 0.10 trion/exciton). hBN encapsulation did indeed mitigate a number of changes in the observed excitonic populations in WSe₂ that could be ascertained from the photoluminescence compared to unencapsulated WSe₂, but was not able to maintain the excitonic populations present before electron-beam irradiation.

Chapter 6: Conclusions and Summary

In this chapter, a summary of this work is provided, including key results and conclusions of the two projects discussed in this dissertation. This is followed by a discussion of related future research efforts to build on the work described here, and final comments on the importance of this work and its follow-on research.

6.1 Summary and Conclusions

Chapter 1 introduces the field of 2D materials, focusing on the unique properties that emerge when materials are thinned to a single atomic or molecular layer. The dissertation explores the engineering of light-matter interactions within two material systems: graphene and tungsten diselenide (WSe_2). These materials exhibit novel characteristics, due to quantum confinement and reduced dielectric screening, which enhance light-matter interactions compared to their bulk counterparts. Although 2D materials offer significant potential for electronic and optoelectronic applications, there are practical barriers in processing and fabrication that must be addressed to fully utilize them at scale. The research objectives are divided into two distinct efforts, with both aiming to advance the understanding and application of their respective 2D material systems. The two projects can be summarized as follows.

(1) The exploration of the tunability of the strong thermal nonlinearity in patterned, SiC-sublimated bilayer graphene plasmonic disks in the presence of magnetic fields using THz

pump-probe spectroscopy.

(2) A comparison study of the effects that electron beam irradiation and the general electron beam lithography process have between hBN-encapsulated and unencapsulated TMD structures using photoluminescence.

In addition to defining the research objectives, Chapter 1 provides an overview of the 2D material families (including graphene, hexagonal boron nitride, transition metal dichalcogenides, MXenes and Xenes) and the fundamental principles of plasmonics (including bulk plasmons, surface plasmon polaritons, and localized surface plasmons). Finally, various characterization techniques used in these research efforts were outlined and described, including atomic force microscopy, Raman spectroscopy, photoluminescence, THz time-domain spectroscopy, and THz pump-probe spectroscopy.

The influence of an applied, external magnetic field on the optical nonlinearity observed in plasmons in graphene disk arrays fabricated from quasi-freestanding bilayer epitaxial graphene on SiC is investigated in chapters 2 and 3. The design, modeling, fabrication, and linear characterization of graphene plasmonic disk arrays on SiC were described, with the primary objective of engineering graphene structures to maximize light-matter interactions at a target frequency of ~ 3.5 THz. Utilizing EM field simulations, the optimal diameter of the disk was identified to be $1.45 \mu\text{m}$ with a periodicity of $1.85 \mu\text{m}$ to minimize EM coupling between neighboring disks. Fabrication involved patterning quasi-freestanding bilayer epitaxial graphene using electron-beam lithography and oxygen plasma etching. Atomic force microscopy and Raman spectroscopy were used to verify the bilayer graphene via its thickness of $0.6\text{--}0.7 \text{ nm}$ and its characteristic Raman peaks located at 1580 cm^{-1} and 2700 cm^{-1} , respectively. Linear transmission measurements via THz time-domain spectroscopy confirmed a peak extinction of $\sim 30\%$ at the designed resonant frequency of 3.5 THz .

The magnetic field-dependence and tunability of the nonlinear response in the graphene

disk arrays were then explored. THz pump-probe spectroscopy was used to investigate how external magnetic fields affected the transient optical properties of hot carriers. When strong THz radiation was pumped resonantly with the plasmon frequency of the graphene disks, the absorbed radiation raised the electron temperature in the graphene, which lowered the associated Fermi energy, causing the plasmon resonance to weaken and shift to a lower frequency. Without a magnetic field, the disks exhibited a pump-induced increase in transmission of $\sim 0.8\%$ due to the thermal redshift of the plasmon resonance. However, in the presence of magnetic fields of up to 7 T, this nonlinear response was dramatically altered and even inverted at fields as low as 3 T. It was found that applied magnetic fields introduce a cyclotron resonance that hybridizes with the plasmon resonance of the graphene disks. This splits the plasmon resonance into upper and lower frequency branches. By utilizing circularly polarized radiation, these individual branches could be selectively excited, allowing for precise control over the transmission characteristics based on the field strength and polarization direction. A Drude-based two-temperature numerical model was able to also successfully describe the experimental results that were observed, where the nonlinear optical response is governed by the heating of charge carriers, which leads to a red-shift of the plasmon frequency.

The effects of electron beam irradiation and associated chemical processes on excitonic complexes and populations in monolayer WSe₂ were examined in detail via low-temperature photoluminescence in chapters 4 and 5. The PL spectra of a bare unencapsulated WSe₂ monolayer on hBN and a hBN-encapsulated WSe₂ monolayer were compared before and after electron beam irradiation to determine how effective the claimed protection of such a thin dielectric layer was in mitigating changes to the optical properties of WSe₂. The motivation for this second research project stems from an attempt to study plasmon-exciton hybrid light-matter states through the coupling of exciton populations in TMD heterostructures with Au-based plasmonic disk arrays. However, initial

measurements revealed evidence that the electron-beam lithography process used to pattern the plasmonic disks altered the optical properties of the WSe₂, including spectral shifting and peak broadening. To understand these changes, an overview of the WSe₂ properties are covered with an emphasis on the excitonic landscape of TMDs. As a W-based TMD, WSe₂ has an inverted spin-orbit splitting where spin-forbidden "dark" excitons are at the ground state, which influences the population of other excitonic populations including neutral bright excitons, trions, and biexcitons.

An experimental comparison between an unencapsulated WSe₂ monolayer and a hBN-encapsulated WSe₂ monolayer was performed to determine how electron-beam lithography processes affect the excitonic populations in WSe₂. Low-temperature ($T = 4$ K) photoluminescence was used to characterize the excitonic properties of both samples before and after they were subjected to the same set of electron-beam lithography parameters and processes. The results demonstrated that hBN encapsulation provides significant, though incomplete shielding to the changes in excitonic populations caused by electron-beam irradiation and its related chemical processes. The electron-beam irradiation of the unencapsulated WSe₂ caused a dramatic red-shift of ~ 24 meV of the neutral exciton peak and the complete disappearance of the trion peak. A massive, broad defect-bound exciton band emerged, dominating the lower portion of the energy spectrum, signaling severe lattice damage. electron-beam irradiation of the hBN-encapsulated WSe₂ also caused a red-shift but was half of the unencapsulated sample at ~ 12 meV. While multi-particle excitonic complexes such as biexcitons (composed of two excitons) and charged biexcitons (composed of a trion and exciton) disappeared, the core neutral excitons and trion populations remained clearly discernible. Although hBN encapsulation raises the displacement threshold and provides a means to stand off both heat and surface charges to mitigate damage, it did not entirely prevent the emergence of new localized defect states as a result of the EBL process.

6.2 Future Work and Directions

The engineering of light-matter interactions in just graphene or transition metal dichalcogenides provides a wide range of potential directions that future research could take. This section will offer some experimental proposals in which future work can be performed to explore additional light-matter interactions in graphene and transition metal dichalcogenides.

6.2.1 Second-harmonic Generation in Graphene through Edge-Induced Symmetry Breaking

As a potential future direction for the graphene-based plasmonic research performed in the first project of this dissertation, a study of the design and implementation of graphene plasmonic structures that can break the centrosymmetry of graphene using geometric engineering and spatial confinement to induce a non-zero second-order nonlinear susceptibility ($\chi^{(2)}$) could be performed to demonstrate second harmonic generation using graphene. Studies looking at third harmonic generation in graphene plasmonics have shown that it can be boosted by several orders of magnitude through structural engineering of the graphene [226, 227]. Second harmonic generation is significantly more challenging to see in graphene due to its inherent centrosymmetry (from its hexagonal honeycomb lattice structure), which suppresses even-order processes. Some groups have broken this centrosymmetry in graphene through other means, including non-uniform straining of monolayer graphene [228] and charge doping of bilayer graphene [229], but geometrically or spatially breaking the centrosymmetry of graphene is an open area for exploration. The same quasi-freestanding bilayer epitaxial graphene used in the research presented in this dissertation tends to be AB-stacked, which is centrosymmetric. To break this centrosym-

metry, nanoscale geometries, such as triangles, lack an inversion center due to the edges of the graphene structure, creating gradient-induced nonlinearities. Such a study would make use of the fabrication and plasmonic structural modeling capabilities discussed in chapters 2 and 3.

6.2.2 Time-resolved Photoluminescence Study of Radiative and Non-radiative Recombination Mechanisms

To address some of the deficiencies in the understanding of the underlying non-radiative and radiative recombination pathways or mechanisms that drive the excitonic populations and, in some cases, limit the excitonic populations in WSe₂ monolayers, an experimental study based around time-resolve photoluminescence would be a prudent next step to the second project of this dissertation. This proposed study was motivated by the desire to understand the sublinear power dependence that was observed in the neutral exciton and trion populations for the WSe₂ samples used for the experiments performed in the second project of this dissertation. It was postulated that Auger-like processes or exciton-exciton annihilation along with other non-radiative recombination pathways could have been dominant factors for the observed power dependence of the excitonic populations. To quantify the Auger recombination rate and look at other non-radiative recombination pathways including dark exciton trapping or defect-mediated recombination, time-resolved photoluminescence measurements dependent on power and temperature are proposed in unencapsulated and hBN-encapsulated WSe₂. The power-dependence of the PL lifetimes can provide important details on loss mechanisms, including exciton-exciton annihilation/Auger recombination (if the lifetime gets shorter as power increases) and Pauli blocking (if the lifetime remains constant, but the PL intensity saturates as power increases). The temperature-dependence of the PL lifetimes can provide additional details on loss mechanisms, such as

dark state scattering (if the lifetime gets longer as temperature is increased), and phonon-assisted non-radiative decay (if lifetime gets shorter as temperature is increased). In addition, recombination mechanisms can also vary with temperature. Studying the localized defect peaks can shed light on defect-assisted/Shockley-Read-Hall recombination.

6.2.3 Photoluminescence Mapping with Electrostatic Gating for Studying Carrier Density

Spatial variations in the PL spectra of some of the larger WSe₂ monolayers and other TMD samples have been observed and ensuring that the same location is measured pre- and post-processing is crucial for the ability to be able to perform direct comparisons. The uniformity of the charge density across a large area of the WSe₂ monolayer is ideal and preferred, but is typically not guaranteed due to complications and contamination from transfer or stacking processes and strain in the case of as-grown films that are not transferred. Localized doping from surface contaminants or charge trapping and strain are potential causes for some of this variation. To understand the spatial distribution of the doping or carrier density across a WSe₂ monolayer, a gate underneath the monolayer and an electrical feedthrough to allow for gate voltage sweeping would be required. This provides the ability to sweep the gate and tune the WSe₂ PL to find the charge neutrality, where there are minimal background carriers to form trions with. A motorized XY stage would be required to perform the spatial mapping, ideally with positional precision down to the tens or hundreds of nanometers. This proposed study would involve both the spatial mapping and electrostatic mapping (gate voltage sweep) of the photoluminescence at low temperatures across a WSe₂ sample. This would generate a plethora of information about the entire sample, providing a five-dimensional map that includes spatial position X, spatial position Y, gate voltage, PL intensity, and PL energy/wavelength). These modifications to

the low-temperature PL setup could be merged with the ability to perform time-resolved photoluminescence for an even wider variety of information to be collected.

6.3 Final Comments and Thoughts

In materials research, one of the ultimate goals of studying novel materials and understanding their underlying properties and physics is to be able to use them to further innovative technologies. To be able to produce designs, processes, devices, or systems that can improve the world is an overarching objective of studying materials science and engineering. A key practical consideration in achieving this goal is the ability to scale material synthesis while understanding and maintaining a consistent set of properties across both space and time, as is typically needed to consistently fabricate devices and products with yields acceptable for commercial feasibility. While two-dimensional material research has been an increasingly popular area of study as the promise of material properties and responses have started to be realized, and the ability to produce these atomically-thin materials at scale has improved, there is still a large gap of understanding the causes and mechanisms for the large variation in properties that are observed for some of these 2D material systems. There is a strong need for continued focus to address the underlying effects of fabrication processes on the optical properties and physical mechanisms of transition metal dichalcogenides and other 2D material systems to truly be able to bring this class of material into greater adoption for use in commercial applications.

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