RICE UNIVERSITY

Creation and Optical Characterization of Functional Defects in Two-Dimensional Materials

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

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HOUSTON, TEXAS
August 2018
ABSTRACT

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The optical properties of two-dimensional materials change with the introduction of defects into the lattice. In this work, we characterize some of the optical properties of a binary alloy, Mo_{x}W_{1-x}S_{2}, and hexagonal boron nitride (h-BN) as they change in the presence of defects. Under laser illumination and optical heating, we find that damage to the binary alloy leads to brightening in the photoluminescence intensity, and with increased exposure, oxidation of the material. It is also possible to induce sub-bandgap emission in h-BN when the lattice is damaged. Using electron beam lithography techniques, we are able to controllably induce defects into the material and, consequently, create sub-bandgap fluorescent emitters that follow the lithographically patterned array. Under the right conditions, some of these emitters show single-photon emission, which is observable at room temperature. These properties can be used advantageously to create areas of bright emission in optoelectronic devices.
Acknowledgments

I would like to thank Professor Junichiro Kono, Professor Jacob Robinson and Professor Gururaj Naik for their support and service as members of my thesis committee. My thanks to my colleague Ali Mojibpour for his support and collaborator Sandhya Susarla for growing the binary alloy samples. Thanks also to Jordan Hachtel who performed the HAADF-STEM and STEM-EELS measurements at Oakridge National Laboratory. Thank you to the Department of Electrical and Computer Engineering for funding this work.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>SPE</td>
<td>Single-photon Emitter</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>h-BN</td>
<td>Hexagonal Boron Nitride</td>
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<tr>
<td>Mo_xW_{1-x}S_2</td>
<td>Molybdenum Tungsten Disulfide</td>
</tr>
<tr>
<td>SAS</td>
<td>Stokes Anti-Stokes</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical Aperture</td>
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<tr>
<td>HBT</td>
<td>Hanbury-Brown and Twiss</td>
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<tr>
<td>APD</td>
<td>Avalanche Photodiode</td>
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<tr>
<td>TMDC</td>
<td>Transition Metal Dichalcogenide</td>
</tr>
<tr>
<td>ZPL</td>
<td>Zero Phonon Line</td>
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<td>EL</td>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>g^{(2)}(t)</td>
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Chapter 1

Introduction

This thesis will cover two topics: (i) optothermal study of molybdenum and tungsten disulfide binary alloys, and (ii) electron beam induced defect creation in hexagonal boron nitride. For ease of reading, the introduction will cover the background and our experimental equipment that was used for both studies. In the subsequent chapters, I will cover the specific background for each of the materials and any difference in their methods.

1.1. Introduction to Work on Two Dimensional Materials

Two dimensional materials have a host of advantageous properties that can allow for the fabrication of new devices with smaller footprint and improved performance. In the context of this work, we are looking at defect induced fluorescence changes in transition metal dichalcogenide (TMDC) binary alloys to be used in thermoelectric devices, and hexagonal boron nitride (h-BN) for the
development of single-photon sources. Such thin systems are ideal for integration into conventional electronics, while minimizing the total device footprint.\textsuperscript{1,2} Even single point defects can have a large effect on not just the morphological structure of the system, but also its optical and electronic properties.

TMDCs demonstrate extraordinary properties in the thin and monolayer limit that differ from the bulk material. MoS\textsubscript{2} and WS\textsubscript{2} have changes in the band structure from indirect to direct bandgap semiconducting materials in the monolayer limit.\textsuperscript{3,4} Also, the thermal conductivity of these compounds is relatively low 34.5 W/(m K) for MoS\textsubscript{2}, as reported by Yan et al.\textsuperscript{5} Alloying MoS\textsubscript{2} and WS\textsubscript{2} has the potential to maintain the advantageous high electrical conductivity, while lowering the thermal conductivity due to the inherent disorder in the crystal lattice caused by the growth conditions.\textsuperscript{6} Also, it has been shown that the thermal behavior and phonon dispersion changes greatly from bulk to monolayer samples. Due to the weak interlayer bonds and strong, covalent in-plane bonds, TMDCs like MoS\textsubscript{2} have been shown to have different thermal transport and dissipation properties in bulk and thin samples with a strong layer dependence on thermal conductivity.\textsuperscript{7,8} However, in order to reliably use these materials for thermal devices, it is necessary to first measure the thermal conductivity and understand the overall dissipation of heat stability in thin and monolayer samples.

It has been recently shown that h-BN can host single-photon emitting defects in both bulk and monolayer crystals.\textsuperscript{9,10} These single-photon emitting defects show promise in the development of stable single-photon sources for use in quantum
photonic circuits and quantum computing.\textsuperscript{11,12} H-BN single-photon emitters (SPEs) are optically active at room temperature and have a narrow spectral emission near 630 nm with short excited state lifetimes of around 2.5 ns, which makes them a competitive candidate for easy integration with existing circuit technologies.\textsuperscript{12,13} However, there are still challenges in the reliable and scalable fabrication of SPEs in thin layered materials like h-BN.

The morphology of h-BN SPEs is still under debate and the emission lines vary with the local environment and the fabrication method.\textsuperscript{13–17} There are a number of proposed solutions for deterministic fabrication methods; most of which rely on existing defects in the sample to be activated after annealing. Other methods use pillar structures to create a local strain environment that activates the defects.\textsuperscript{14,17} However, deterministic placement of defects in pristine samples still poses challenges.

Here, we present one method for defect creation using the electron beam in the scanning electron microscope based on standard electron beam lithography techniques on pristine h-BN. This method can yield fluorescent emitters in an array similar to a lithographic pattern. The emitters are often broad-spectrum emitters centered around 630 nm. Some of the emitters show single-photon emission with spectral and time-resolved properties similar to those reported in literature. This method demonstrates a small advancement towards deterministic creations of room temperature single-photon sources.
1.1.1. TMDC Alloys

Transition metal dichalcogenides (TMDCs) demonstrate extraordinary properties in the thin and monolayer limit that differ greatly from the bulk material. MoS$_2$ and WS$_2$ have changes in the band structure from indirect to direct bandgap semiconducting materials in the monolayer limit.$^3$ This means that single layer devices can show bright photoluminescence (PL) and form bright diode junctions and transistors with much less material than traditional bulk semiconducting materials. Pure TMDCs follow an MX$_2$ formula, where the M is the transition metal, most commonly, molybdenum or tungsten, and X is an element from the chalcogen family, such as sulfur, selenium or tellurium. At room temperature, defects in these materials have shown to broaden the PL spectrum and to increase the PL yield by the addition of emission from bound excitons occurring at defect sites.$^{18,19}$ Defects in TMDCs created by strain have also been shown to form quantum emitters and have separately demonstrated electroluminescence (EL).$^{20,21}$ Understanding the properties of these defects presents exciting potential for engineering devices to take advantage of these properties.

In chemical vapor deposition (CVD) growth of TMDCs, it is possible to mix multiple transition metals or chalcogen elements in a compound to form binary and quaternary alloy compounds. Mixing the alloys at controllable ratios allows for tuning of the material bandgap at the monolayer and engineering the optical properties.$^{22,23}$ Many of the properties of these compounds are unknown, but it is thought that they exhibit favorable thermal and electronic transport properties for
the design of thermoelectric devices. Recent reports have demonstrated that BiSbTe alloys had a lower thermal conductivity than the component materials due to increased scattering at grain boundaries and defect sites.\textsuperscript{24,25}

Alloying of TMDCs has the potential to combine beneficial properties of the constituent parts and create new thermoelectric materials. The thermal conductivity of MoS\textsubscript{2} is around 34.5 W/ (m K). However, alloys may have an even lower thermal conductivity due to phase segregation that occurs during the growth process.\textsuperscript{6} The Mo and W tend to grow in groups similar atoms adjacent to each other. Through this study we have investigated the like to investigated some of the effects of varying alloy composition and layer thickness, and its effects on thermal dissipation.

With layer and composition dependent behavior of thin layer alloys, one can envision designer thermal surfaces based on the choice of material thickness and composition, where the phonon dispersion and thermal conductivity is engineered based on thickness and composition of the material.\textsuperscript{3,7,26–28} A first step to creating these devices is measuring the any changes in the material over long term exposure to intense heat and light, which is what we have examined in this chapter.

The second chapter of this thesis focuses on our study of the optothermal properties of the Mo\textsubscript{x}W\textsubscript{1–x}S\textsubscript{2} alloy. We optically heated the system using the confocal microscope system and found that monolayer and bilayer samples experience an increase and then decrease in PL with increasing power. Using Raman spectroscopy and high angle annular dark field scanning transmission electron microscopy
(HAADF-STEM) measurements, we attribute these changes to a change in
temperature induced by the laser and the incorporation of oxygen from the
environment as the sample is heated. Also, the laser induced optothermal damage to
the sample seems to remove upper layers of the material, which reveals a bright
monolayer underneath. The monolayers are preferentially oxidized before
darkening.

1.1.2. Hexagonal Boron Nitride

Hexagonal boron nitride is a wide bandgap semiconductor with an indirect
bandgap in the UV, emitting at 5.95 eV.\textsuperscript{29–31} In its pristine form, the material is
chemically inert and inactive under visible illumination. The bulk material has a
layered van der Waals crystal structure similar to graphite. The weak interlayer
bonds can be easily broken using mechanical tape exfoliation to create single layers
of atoms that retain many of the properties of the bulk material.

Recent reports have found that h-BN can host fluorescence defects that emit
from sub-bandgap energy levels. Under the right conditions, some of these defects
can even become single-photon emitting quantum dot structures, which can even be
supported in the monolayer.\textsuperscript{9,10} The exact morphology of these SPEs is still under
debate, but they are generally thought to be caused by vacancy and substitutional
defects, which can also be activated by strain in the local environment.\textsuperscript{9,14}

H-BN single-photon emitting defects are stable emitters with a range of
wavelength emission properties.\textsuperscript{13} It presents an exciting platform for the creation
of single-photon sources that can be integrated into existing electronic materials, with a small footprint.\textsuperscript{1} As a stable insulator with preferential chemical properties, h-BN is reliable and reproducible of single-photon sources. Stable, reproducible, identical single-photon emission is widely understood to be a prerequisite for quantum computing, quantum key encryption and quantum optics experiments.\textsuperscript{32}

However, current research has only been able to show SPEs and fluorescent defects that rely on activation of existing defects created during the growth process and activated to become single-photon emitting.\textsuperscript{9,10,12,14–16,33,34} Depending on the technique, these defects occur with greater or lesser frequency. Activation is often performed by high-temperature annealing at temperatures upwards of 800 °C.\textsuperscript{9,10,13} Strain has also been proposed as the primary cause and activation method for these defects, but still relies on the use of less than pristine material to start.\textsuperscript{14,17}

The third chapter of this thesis focuses on our method of creating sub-bandgap fluorescent emitters in thin exfoliated boron nitride samples using electron beam lithography techniques. We present deterministic placement of defects in pristine h-BN flakes that follow a lithographically patterned arrangement. Using the confocal microscope, we were able to see emission in the visible range and, separately using $g^{(2)}(t)$ measurements, confirm that some of defects demonstrate single-photon emission.
1.2. Experimental Equipment Setup

The primary tool for optical characterization for all of these experiments was a custom-built confocal microscope, which gave us the ability to take optical spectra and fluorescence mappings of any sample loaded into the system. We designed this system specifically to accommodate the types of signals and sensitive detection limits needed to see narrow Raman lines of just a few wavenumbers and SPEs with just a few nanosecond lifetimes. A diagram of the system can be found in Figure 1-1.
Figure 1-1 Confocal microscope schematic showing the 532 nm laser excitation beam path and 2 signal collection paths with the inline filters: Hanbury-Brown and Twiss interferometer, and liquid nitrogen cooled CCD spectrometer
Our system was based on Nikon Ti Microscope, with a custom machined platform designed to accommodate a scanning probe, which will eventually be used to expand the microscope and become part of a near-field scanning optical microscope (NSOM). The platform was used to hold the sample on piezoelectric scanning motors that can have a minimum step size of 0.1 nm. The microscope was configured to accept a 532 nm continuous wave laser excitation from a Coherent sapphire single frequency laser source, which provided 532 nm light with 0.1 nm wavelength accuracy and a max power of 50 mW of power. This type of stable single frequency light source was selected wavelength precision in our Raman spectroscopy experiments.

The beam path was designed to minimize aberrations and provide a cleanly polarized output beam. This clean beam is required for the variable spiral plate to form a radial mode, which was ideally suited for mapping the orientation of the absorption dipole emitters in the sample due to its in plane and out of plane polarizations. The radially polarized mode was ideal for probing defects and mapping the orientation of the absorption dipole on any emitters in the sample.

In the beam path, the output of the laser was first fed through a 532 nm narrow bandpass filter and a polarizer to clean up the frequency and polarization profiles of the beam. The beam was then expanded to 1 cm in diameter using several short focal length aspherical lenses and passed it through a variable spiral plate rotator from ARCoptix. The spiral plate was a liquid crystal device that converts the vertically polarized Gaussian beam into a radially polarized mode.
After the spiral plate, the radially polarized beam was spatially filtered with a 30 µm pinhole and bounced into the back aperture of a high numerical aperture (NA) objective. Any changes in polarization introduced by the objective, dichroic and periscope steering mirrors were preemptively corrected using a Berek variable waveplate, which was necessary to preserve the radial mode polarization. The microscope could be either used with a dichroic mirror for increased filtering or a 50/50 beamsplitter in our Raman spectroscopy measurements. A series of ND filters was used to adjust the input power of the beam, which was measured after the ND filters and just before the entrance to the microscope.

On the collection path, there were several possible detectors for mapping, spectroscopy, and time correlated measurements. Output light could be collected using either our Princeton Instruments spectrometer system or our Hanbury-Brown and Twiss (HBT) interferometer, which also could be used to create integrated fluorescence maps of the sample.

To demonstrate the measurement capability of the optics and measurement system, the R9 control system and the avalanche photodiodes (APDs) were used to measure CdSe 6 nm quantum dots. Figure 1-2 shows an example integrated fluorescence mapping of the quantum dots drop cast on silicon substrate. The R9 system was able to raster the sample over the beam while collecting the fluorescence signal from the APDs. This mapping process located the flakes under the microscope and helped us to get an idea of the point spread function of our system, which resembles an Airy disc pattern.
Figure 1-2 Test image for the confocal microscope R9 integrated fluorescence mapping system. A dilute solution of CdSe quantum dots was scanned at 10 µW of power using the same 50x objective that was used in all of the experiments mentioned. The radial mode beam was used here as a method for emitter structure of the quantum dots.

When the APDs were connected to the PicoHarp (PicoQuant GmbH), they formed the HBT interferometer setup. See Figure 1-1 for a diagram of the HBT. The beam passed through a series of optical filters and a thin pellicle beamsplitter before being focused onto 2 avalanche photodiodes (APDs). The PicoHarp collected the delay time between photons arriving on each of the APDs and created a histogram of the delay times, which gave a time-resolved measurement of the second-order correlation function.³⁷
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Overall, the system had a few drawbacks that could affect our timing resolution. The APDs were susceptible to timing jitter of 350 ps, which placed a lower bound on the signals that could be reliably measured. The HBT interferometer setup could be subject to an after-pulsing artifact inherent to the design of the system. Light arriving on the APD could cause the detector to re-emit light due to the sensitive avalanche bias conditions. This light could enter the optical path and land on the second APD, which leads to a correlated bunching signature in the $g^{(2)}(t)$ histogram. To eliminate this effect, a band pass filter was placed directly in front of each APD with the pass-band centered on the wavelength range of interest.
For our spectral measurements, we used several lenses to collimate and focus the output beam of our spectrometer onto the entrance slit of a Princeton Instruments Acton2300i spectrometer. The spectrometer could be used with any of 3 gratings: 300 g/mm, 1200 g/mm and 1800 g/mm. The spectrometer focuses the output light onto a liquid nitrogen cooled Pylon CCD camera with a 1400x512 pixel array. The camera was cooled to -120 °C. See Figure 1-1 for a diagram of the spectrometer collection path.

To improve detection capabilities and signal to noise ratio, we used the two 532 nm longpass filters in series from Semrock that provided up to 12 ODs of rejection for most PL measurements. For the Stoke and Anti-Stokes (SAS) Raman measurements, we had 3 532 nm notch filters in series that removed the laser line and light up to +/- 300 cm⁻¹ around the laser line. This allowed us to see both the lower and higher energy Raman modes close to the laser. We could also use the longpass filters in the Raman spectroscopy setup to measure signals down to 100 cm⁻¹ to the red of the laser.

Overall, this optical setup was the ideal tool for optical investigation of fluorescent defects in two dimensional materials. It provided us with a high spatial and spectral resolution, with also the ability to measure time-resolved signals.
Chapter 2

Optothermal Raman and Photoluminescence Study of Molybdenum Tungsten Disulfide Binary Alloys

2.1. Introduction

In this chapter, we present an investigation on the thermal stability and changing fluorescence properties of the TMDC alloy, Mo$_x$W$_{1-x}$S$_2$. As mentioned in Section 1.1.1, this alloy material presents some exciting possibilities for the design of new devices. Binary, tertiary and quaternary alloys of TMDC compounds provide a tunable bandgap that depends greatly on the composition and increases the number of possibilities for device design in this area.\textsuperscript{6,22} For Mo$_x$W$_{1-x}$S$_2$, the bandgap varies from 1.82 to 1.99 eV.\textsuperscript{6,23} Although the thermal stability of these materials has not been studied in great detail.

The process of alloying TMDCs can combine properties of the constituent materials to have beneficial effects. However, the intrinsic disorder in the lattice due to phase segregation during the CVD growth process leads to a decrease in the
thermal conductivity due to increased scattering in the sample. This type of alloying has been shown to successfully engineer bulk BiSbTe alloy materials, by reducing their thermal conductivity\textsuperscript{24,25} A decrease in thermal conductivity could be beneficial for the construction of designer thermal interfaces. Thin layers materials have also been demonstrated to have very different thermal conductivities in the in-plane and out-of-plane directions. It has even been predicted MoS\textsubscript{2} would have an increased thermal conductivity between thin and few layer samples, but careful experimental investigation of this is still necessary\textsuperscript{8,38} The thermal conductivity of MoS\textsubscript{2} has been reported to be 34.5 W/ (m K). It may be possible to further vary the thermal conductivity with varying alloy composition and material thickness. But before effective devices can be made from these materials, it is necessary to understand the overall heat dissipation in these materials as well as the tolerance for heat exposure.

Damage due to laser radiation can also significantly change the properties of TMDCs. Increases in PL yield from damaged TMDCs has been reported to happen when the materials are exposed to laser irradiation under atmospheric conditions\textsuperscript{18} This brightening has been attributed to creation of defect sites, which allow for the creation of bound excitons at the defect sites\textsuperscript{18,19}

While monitoring the Raman and PL signatures, we found that samples that started out as mostly bilayers were damaged by increasing laser power. The samples at first brighten with an initial increase in temperature of 50-100 K above room temperature and then darken with another increase in temperature of 50 K or
more. We also found that in this batch of samples the PL peak shows a slight blue shift of 20 meV. This is attributed to the damage process lifting the bilayer and revealing a monolayer underneath of different composition.

Our experiments show that under laser illumination, these TMDC alloy compounds exhibit some brightening with characteristics similar to those shown for pure TMDCs by Chow et al. However, the changes in brightness also spread across even though the beam is always in the center of the sample, which suggests that the damage is a thermal effect moving through the sample. The Raman spectra and damage found in HAADF-STEM images suggests a process similar to the laser thinning, where the top layer of the sample is damaged by the beam in such a way that the underlying monolayer is revealed.

In our case, the bilayer areas are first damaged, which reveals the monolayer underneath. The monolayer shows bright PL but is also more susceptible to oxidation. Under further heating, the monolayer oxidizes fully, causing it to darken again.

2.2. Methods

2.2.1. Sample Preparation

The binary alloy samples were grown on a silicon and silicon dioxide substrate using CVD techniques described in Susarla et al. Then, the TMDC alloy flakes were lifted from the substrate and transferred to a holey silicon nitride
membrane on a TEM grid by using a wet PMMA transfer technique. PMMA was spun onto the surface of a silicon/silicon dioxide wafer and dried so that the PMMA holds onto the TMDC flakes. This was set to dry overnight to ensure strong adhesion to the flakes.

Next, the wafer was submerged in a dilute solution of KOH to lift the PMMA membrane from the top surface of the substrate and float it on the top of the solution. The PMMA membrane was then carefully washed and scooped onto a TEM grid. We used silicon nitride hole array membrane TEM grids with 5 µm diameter and 5 µm pitch.

### 2.2.2. Measurement Theory

Suspending our thin samples over a circular aperture allowed us to probe the sample in the center of an aperture and use a heat diffusion model described by Faugeras et al. and Yan et al. to calculate the temperature of the sample during illumination. Assuming a known geometry for the sample, the paper presents an analytical model for heat spreading through the sample, when supplied by a Gaussian beam illuminating the sample at the center of the membrane. We also assume that the sample diameter is large enough and the material conductivity is low enough that the edge of the aperture is at room temperature, 295 K. Then we calculate the temperature at the center of the membrane using the Stokes and Anti-Stoke Raman data.
Generally in Raman Spectroscopy, we know that the phonon population follows the Boltzmann distribution and that a measure of the Stokes and Anti-Stokes phonon populations is a direct measure of the temperature of the system.\textsuperscript{42,43}

Equation 2-1 below shows the relationship between the Stokes and Anti-Stokes intensities, which can be used to find a measurement of the temperature at the center of the membrane. This equation has been adapted from Sullivan et. al. to use the $A_{1g}$ optical phonon modes as extracted using our MATLAB code for the Mo and W bonds in the alloy system.\textsuperscript{42} This calculation is performed on each of the power dependent spectra to calculate temperatures based on the Mo and W optical phonon modes separately.

\[
\frac{I_{AS}}{I_S} = C \left( \frac{\omega_L + \omega_{A_{1g}}}{\omega_L - \omega_{A_{1g}}} \right)^4 \exp \left( \frac{-\hbar \omega_{A_{1g}}}{k_B T_o} \right)
\]

\textbf{Equation 2-1} Relates the Stokes and Anti-stokes intensity ratio to the temperature at the center of the focal spot.\textsuperscript{42} $\omega_L$ is the excitation laser frequency. $\omega_{A_{1g}}$ is the frequency of the measured Raman line in question, in this case $A_{1g}$. $T_o$ is the temperature at the center of the membrane and $C$ is a constant used to account for the collection efficiency of the system.

A constant $C$ is used to include the collection efficiencies of the system and the Raman cross section of the respective modes. Using this method, we were able to gain optical information and temperature information about the sample at the same time, without the need for complex device fabrication and without directly contacting the sample.
This process extracts all the information about the Raman peaks including the peak positions. The peak position can be used to calculate a separate measure of temperature by tracking the shift in the peak position of the $A_{1g}$ Raman modes with increasing power. From these two methods, we were able to verify our temperature measurement through separate processes.

2.2.3. Measurement Setup

Using the confocal microscope in Figure 1-1, we first took integrated intensity and fluorescence maps of the sample as depicted in Figure 2-1 (C). The different apertures are labeled sequentially as they are investigated. Then, we measured the samples through PL and SAS Raman spectroscopy. Between each SAS measurement, we also took low power PL mappings to look for changes in the PL intensity using 50 µW and scan rates of 20 µm/s to map with minimal exposure during the mapping. After completing the optical experiments, the treated sample were studied using HAADF-STEM and STEM-EELS under 60 kV beam.

2.2.4. Analysis

The full calculations used can be found in the MATLAB data processing code in Appendix A. All graphs were created using MATLAB. The image processing code was used to calculate the relative difference in PL intensities.
2.3. Results and Discussion

Figure 2-1 gives a basic layout of our samples. The TMDC alloy is suspended across an electron microscopy grid, to give optical access to the suspended membrane with the ideal geometry for our optical heating studies. In Figure 2-1 (B), we see a brightfield image of the binary alloy sample taken with a basic inspection microscope. The TMDC alloys shows a small amount of contrast with the silicon nitride background. Each of the apertures has been labeled with numbers, sequentially during the investigation process. Figure 2-1 (C) shows a fluorescence mapping of the sample for the same region as in panel (B). The numbering system was used to identify the apertures across figures. The sample was suspended across the open apertures but showed little fluorescence until the sample was exposed to some light. This image is taken in a reflection geometry with 2 longpass filters used to remove the laser line from our image. Here, the edges of the silicon nitride holes appear as bright rings on. Most of the membrane showed count rates of approximately 100 kHz and some had bright spots. Overall, the sample was as dark as the background area. See Section 2.2 for more description of the sample prep and measurement setup.
To test thermal stability using the Stokes and Anti-Stokes (SAS) Raman spectroscopy technique described in Section 2.2.2, we first varied the input power into the sample and measured the ratio of Stokes and Anti-Stokes Raman intensities. The result of our SAS measurements yielded several interesting facts about our sample. There are four peaks visible for the compound: two $A_{1g}$ peaks and two $E_{2g}$ peaks. The $A_{1g}$ peaks correspond to the energy of out-of-plane bonds between Mo-S
and W-S, which can be found around 410 cm\(^{-1}\) and 420 cm\(^{-1}\), respectively. The E\(_{2g}\) peaks correspond to the in-plane bond energies for Mo-S and W-S, which are 383 cm\(^{-1}\) and 353 cm\(^{-1}\), respectively.

In MATLAB, we extracted the position of these peaks and fit a Lorentzian line shape to each individual peak. From this data, we found two independent signals of the temperature at the center of the membrane: the peak position and the SAS intensity. Using the first method, we were able to compare the ratio of the SAS intensities and determine a direct measurement of the temperature. As a result, in Figure 2-2 (A) and (B), we plot the temperature using both the Mo A\(_{1g}\) modes and W A\(_{1g}\) modes throughout the range of input powers. Both the Mo and W peaks show that the temperature increases to at least 500 K, begins to plateau around this temperature.

By comparing the shift in relative peak positions with input power, we were also able to determine the increase temperature in from a starting temperature. We plot the temperature using the shift in the peak position in Figure 2-2 (A) and (B) next to the SAS method, which yielded a similar trend and the same general temperature profile.

These two different measurements operate on different physical principles and yet seem to confirm the behavior. The SAS method relies on a ratio of the phonon populations in the system. The peak shift method measures the change in bond energy with temperature. Both should provide accurate measures of temperature. This is a good indicator that the sample is really reaching this
temperature. In some later noisy measurements, the SAS information became
difficult to extract due to the damage to the sample, so the peak shift data because
the more reliable measurement.

To illustrate the difference in the Raman spectra with increasing power,
several Stokes and Anti-Stokes spectra are plotted together in Figure 2-2 (C). As the
power increases, the $A_{1g}$ modes trend toward the laser line and decrease in energy.
The peak intensities increase with power, and the ratio of Stokes to Anti-Stokes
decreases with increasing power. We use this information to calculate a value for
the thermal conductivity shown in Figure 2-2 (D). This is done using by modeling
the energy applied by a gaussian beam as heat diffusions through the membrane.
The membrane itself is approximated as a suspended cylinder with the edges
pinned at room temperature. The model can be found in the references here that
were used for temperature calculations.

The value appears to change with increasing power, which we know to be
unphysical and thus makes this calculation unreliable. However, it does provide
some separate indication that the sample is changing. The average value about 4 W/
(m K), which is promising, but requires further investigation.
Figure 2-2 (A) Power dependent temperature behavior of TMDC alloy sample. The top curve is calculated using the SAS intensity method. The bottom two curves are calculated by tracking the position of the $A_{1g}$ peak both the Anti-Stokes and side of the laser. This information is taken from the Molybdenum $A_{1g}$ mode. (B) The same temperature dependent profile is depicted, but for the Tungsten $A_{1g}$ mode. (C) Several Raman spectra examples are shown with for the TMDC alloy. The $A_{1g}$ and $E_{2g}$ peaks have been labeled. (D) Thermal conductivity in W/(m K) calculation based on the SAS peak ratios.

After each SAS measurement, we also took an integrated fluorescent map to track brightness changes in the sample. We found that with increasing power there is a change in the brightness in the part of the sample direct underneath the laser, which propagates to the surrounding area. The integrated fluorescence map for
aperture 22 is shown in Figure 2-3 (A), where the center portion has already undergone an irreversible oxidation process. There is a ring around the center dark area that has been brightened. Figure 2-3 (B) and (C) show the temperature calculations based on the peak position shift for several membranes that in which trend is repeated.

Figure 2-3 (A) The final integrated fluorescence map for aperture 22 taken after all measurements. (B) Temperature profiles based on shift in the peak position for aperture 21. (C) Temperature profiles shown for several apertures that show the same general trend of reaching 400 K and beginning to plateau in that range.
By combining the whole series of power dependent mapping images and the temperature curves, we can estimate the temperature at which the sample begins to brighten. Figure 2-4 shows the progressive increase in brightness for aperture 22, and the corresponding measured temperatures. Even from the initial laser exposure at low powers the sample begins to brighten. The ring of brightened area spreads as the input power increases although the beam is held in the center of the sample during the exposure process. This spread without scanning the beam indicated that the change appears to be heat induced. By the third exposure, the center area darkens at about 300 μW or a temperature of 500 K and above.

![Figure 2-4 Progression of integrated fluorescence maps from after each SAS Raman measurement for aperture 22.](image)

To highlight the change that occurs from one exposure to the next, Figure 2-5 shows a progression of the fluorescence images after some processing. The absolute
difference between each successive image was calculated and replotted as a map. In this image, we only have a relative scaling and all differences are plotted as positive values. In the first image, the sample brightens right in the center of the aperture after an exposure to low powers. By the third exposure, the sample darkens again. In subsequent images, one can see small changes in the brightness as heat spreads out from the center.

![Image of the membrane with different intensities and temperatures]

**Figure 2-5** The absolute difference between successive images in Figure 2-4 was calculated and plotted in order to highlight progressive increase brightness throughout the sample.

To characterize the initial, bright, and dark states of the membrane, we took several PL spectra from which we can try to explain the brightening phenomena found in the samples. In Figure 2-6, we can see that emission intensity brightens and darkens by an order of magnitude during this process. In the normalized graph of
the sample PL spectra, it can also be seen that the peak shifts by about 10 nm or 20 meV.

Figure 2-6 Photoluminescence spectra for aperture 11 in the initial, bright and dark states.

The increase in brightness change can be attributed to the creation of defects similar to reports for MoS$_2$ and other TMDCs by Chow et al.$^{18}$ The authors used an Ar plasma to create nonuniform defects throughout the lattice and found that a second peak arises at 0.1 eV below the central emission peak. They found that this is related to bound excitons localized to the defect site that contribute to the brightness of the emission. In this case, it is most likely the incorporation of oxygen from the local environment that begins to introduce defects in the sample. This is
also confirmed by the scanning transmission electron microscopy electron energy loss spectroscopy (STEM-EELS) measurements in Figure 2-8.

To analyze this phenomenon, each of the PL peaks was fit with 2 Lorentzian peaks. It was possible to fit the peaks with a 95% confidence level or better in each case. In each case, there is a central peak at the zero phonon line and a second peak approximately 20 meV below the principal line. This suggests that while defects may contribute to the brightening phenomena, the binary alloy does not respond in the same way as the pure TMDCs. While there is a contribution from a second peak at a difference of 20 meV, this value still seems to differ greatly from the 100 meV found by Chow et al.

In the PL data, we also found that there is a blue shift in the peak position of about 20 meV. In untreated binary alloy samples, PL can be used to characterize the chemical composition of the membrane. Using Equation 2-2, the peak position can be used to calculate the composition of the membrane. The values for peak position before and after exposure can be found in Table 2-1. The position of these peaks indicates that the samples are approximately a 60% Mo and 40% W composition. After significant damage and exposure, in this context a 20 meV shift corresponds to a change in composition to about 75% Mo and 25% W.

\[
E_{PL,Mo_{1-x}W_xS_2} = (1 - x)E_{PL,MoS_2} + xE_{PL,WS_2} - bx(1 - x)
\]

Equation 2-2 Equation for calculation of composition based on composition based on PL energy. 6
Table 2-1 Composition calculation based on PL energy measurements.

<table>
<thead>
<tr>
<th></th>
<th>Peak Position (eV)</th>
<th>Peak Position (nm)</th>
<th>Comp Mo</th>
<th>Comp W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.864</td>
<td>665</td>
<td>62%</td>
<td>38%</td>
</tr>
<tr>
<td>Bright</td>
<td>1.885</td>
<td>657</td>
<td>75%</td>
<td>25%</td>
</tr>
</tbody>
</table>

The overall composition of the alloy is unlikely to change unless there is some loss of material. Further investigation in STEM-EELS studies showed us that the sample is indeed changing, not only is incorporation of oxygen into the sample that were exposed, but also there is separation of the bilayer parts of the sample. It has also been shown that laser exposure of pure TMDC compounds can also be used to thin down thick samples and reveal a monolayer.\textsuperscript{39,40}

The STEM-EELS spectra also show that the bilayer seems to be damaged first and the monolayers are preferentially oxidized. Once the bilayer parts of the sample are separated, it reveals a monolayer sample of slightly different composition underneath. This separate monolayer has a 75% Mo and 25% W, which shifts the PL peak by 20 meV from the original peak position. Also, the exposure of the underlying monolayer changes the PL brightness without introducing a defect related change in the PL at 100 meV.
Figure 2-7 (A) HAADF-STEM Image of membrane number 8 of the TMDC alloy sample. We can see that the sample shows the 2H nearest neighbor configuration consistent with the semiconducting phase of the material. We can also see that there is a mix of Mo and W within the focal area, which generally means the sample is homogenous within the laser spot. (B) Same membrane as (A) but with a larger field of view. The dark region shows a mixed monolayer area. Patchy bright areas are indicative of carbon deposition on the sample.

From the HAADF-STEM images in Figure 2-7, we can first see that the sample is generally homogenous within the laser spot. There are a number of phase segregated regions of Mo and W, but they are much smaller than the diffraction-limited laser spot used in the optical experiments. This type of electron microscopy operates on contrast by atomic number and mass thickness contrast. Brighter atoms are heavier than the darker ones. It is difficult to see the lighter atoms such as oxygen or sulfur, but molybdenum and tungsten are visible. We can also see that the material is in the 2H phase from the position of the nearest neighbor atoms. The
white patches that slightly blur over the lattice structure are carbon contamination on the surface deposited during viewing in the TEM.

In Figure 2-8, the electron energy loss spectra are shown for samples 17 and 46. Our collaborator was able to first take dark-field images of a small region of the sample. Then using energy filtering and spectroscopy techniques in the TEM, they were able to filter the electron beam for the absorption peaks that correspond to sulfur and oxygen. Those energy filtered images are also plotted for each of the corresponding areas. The energy filtered images show that the oxygen concentration is highest in the small monolayer triangles found in the samples. There is also significant damage to the membrane which can be seen in some of the large chunks of materials on the surface.
Figure 2-8 STEM-EELS investigation of samples 17 and 46. Each sample shows a representative high angle annular dark field image and the electron energy loss absorption spectra taken for the same region. The spectra measurements show the concentration of sulfur and oxygen in the sample.

To explore further the claim of loss of material, studies of laser thinning of TMDC compounds can also use the difference between the $A_{1g}$ and $E_{2g}$ modes as a measure of the thickness of MoS$_2$.\textsuperscript{39,40} They find that MoS$_2$ samples will show a difference in Raman modes that tends to decrease by about 2 cm$^{-1}$ with each layer: 19.4 cm$^{-1}$ for monolayer, 21.2 cm$^{-1}$ for bilayer and 23.2 cm$^{-1}$ for three layers.

In Figure 2-9, we show the difference between the $A_{1g}$ and $E_{2g}$ peaks plotted for sample 22. The difference in the Mo peaks trends downward by about 1 cm$^{-1}$ at maximum. While this trend is enticing, the overall measurement shows only a small change, which may be smaller than the inherent error in the system. For W, the
difference decreases by about 2 cm\textsuperscript{1}. This level of change is measurable in the system. From this data, we can posit that the sample thickness is decreasing slightly. However, the HAADF-STEM images have some sulfur particles on the surface along with some other contamination, which could disrupt this measurement.

![Figure 2-9](A) Power dependent difference between both the Mo A\textsubscript{1g} and E\textsubscript{2g} Raman modes (B) Power dependent difference for the W A\textsubscript{1g} and E\textsubscript{2g} Raman modes.

2.4. Conclusion

These TMDC binary alloy samples undergo a series of interesting changes during optical heating. When taken together, these measurements show that laser induced heating of the sample under atmospheric conditions damages the sample significantly.
From the Raman measurements and fluorescence maps, we can see that as the temperature of the bilayer sample rises, it goes from a dark state, brightens and then irreversibly darkens again. Raman measurements demonstrate that these changes begin with as little as an increase of approximate 50 K and then spreads across the sample. With an increase of another 100 K, the sample darkens again.

We ascribe the brightening effect to two mechanisms: (1) the creation of nonuniform defects that localize excitons at the defect sites, and (2) laser thinning of the bilayer sample, which reveals a monolayer sample. The final darkening can be ascribed to a permanent oxidation of the sample at temperatures from 450-500 K. From HAADF-STEM and STEM-EELS measurements, we can conclude that the monolayer parts of the sample are preferentially oxidized.

The described behavior presents interesting possibilities for optothermal design of bright features in devices using this TMDC alloy. However, more investigation is required to properly characterize the thermal conductivity of the sample and the behavior of the sample at high temperatures.
Chapter 3

Electron Beam Induced Defect Creation in Hexagonal Boron Nitride

3.1. Introduction

In this chapter, we present our method for defect engineering in hexagonal boron nitride (h-BN). Our goal was to deterministically place and optically activate the defects. Most of the emitter we created show broad fluorescence, and some showed narrow emission lines with single-photon emission.

H-BN is a layered wide bandgap insulator with stable chemical and electrical properties. Because of its strongly insulating properties, h-BN is a good complement to many of the other direct bandgap semiconducting two-dimensional materials. It is well suited for use in thin insulating gate oxide in two dimensional transistors or as tunnel barriers in electron tunneling applications.
Aside from its insulating electronic and chemical properties, h-BN is inactive in the visible spectrum. H-BN has a bandgap of 5.95eV indirect, which means that is optically active in the UV.\textsuperscript{29,31} Recent reports have shown that under the right conditions damage and defects to h-BN can create stable, localized emitters embedded in the lattice structure.\textsuperscript{9,10}

Localized dipole like SPEs have also been found in SiC, diamond, carbon nanotubes and many other materials.\textsuperscript{12} In many fields researchers are still developing methods to create and characterize the emitters more reliably, with the goal of developing quantum emitter technologies that can be seamlessly integrated into quantum computers or quantum key inscription systems.\textsuperscript{12} However, there are

<table>
<thead>
<tr>
<th></th>
<th>Maximum Count Rates (Counts/s)</th>
<th>Lifetime (ns)</th>
<th>Operation Temperature</th>
<th>Spatially Targeted Fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defects in BN</td>
<td>$3 \times 10^6$</td>
<td>3</td>
<td>RT</td>
<td>No</td>
</tr>
<tr>
<td>Defects in SiC</td>
<td>$2 \times 10^6$</td>
<td>1-4</td>
<td>RT</td>
<td>No</td>
</tr>
<tr>
<td>SiV in Diamond (Diamond)</td>
<td>$3 \times 10^6$</td>
<td>1</td>
<td>RT</td>
<td>Yes</td>
</tr>
<tr>
<td>NV in Diamond</td>
<td>$1 \times 10^6$</td>
<td>12-22</td>
<td>RT</td>
<td>Yes</td>
</tr>
<tr>
<td>CNTs</td>
<td>$3 \times 10^3$</td>
<td>0.4</td>
<td>RT</td>
<td>No</td>
</tr>
<tr>
<td>2D TMDCs</td>
<td>$3.7 \times 10^5$</td>
<td>1-3</td>
<td>4K</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 3-1 Comparative table to H-BN emitters to other existing SPE technologies. H-BN compares well on speed and maximum count rates, but as of yet has not reliable deterministic fabrication method.\textsuperscript{12}
still roadblocks to determining the exact morphology and the best fabrication methods. See Table 3-1 for a comparison of h-BN SPEs to other materials. This table was adapted from Aharonovich et al. While h-BN single emitters are competitive due to their high count rates and easy of integration with other layered technologies, but as of yet there is no consistent, reliable fabrication method.

The exact morphology of h-BN defects is still yet to be determined, but there have been several proposed mechanisms and activation methods. It has been shown that the defects could be optically activated and stabilized under electron beam irradiation followed by high temperature annealing.\(^9,^{13}\) This method relied on a point defect structure thought to be a nitrogen vacancy and boron substitution (N\(_B\)V\(_N\)) site. Figure 3-1 (A) shows a schematic version of the defect site.

Other studies have shown that large amounts of strain applied to thin h-BN stretched over a pillar structure could form arrays of single-photon emitting defects in the potential wells created at the points of maximum strain.\(^{14,17}\) This effect was not unlike the similar methods for generating SPEs in TMDC materials.\(^{20,21}\) But in the context of h-BN, these methods relied on the use of imperfect h-BN samples and the activation of preexisting defects. For more reliable and predictable placement of defects, it is important to determine reproducible methods for creating and activating these defects in pristine samples rather than relying on defects randomly occurring in samples. Here, we present a method for patterning h-BN to deterministically induce fluorescent defects using electron beam lithography.
For this project, we use pure crystalline h-BN produced by the research group of Taniguchi and Watanabe.\textsuperscript{30,31} This h-BN has been shown to have minimal defects and therefore is an ideal platform, ‘clean slate,’ for creating luminescent defects with minimal background radiation. Most of the emitters show broad band fluorescence with a peak near 630 nm. From additional reports, it would seem to indicate that we have created multiple emitters within a small focal spot, which cannot be separated with diffraction limited microscopy techniques.\textsuperscript{13,33}

3.2. Methods

3.2.1. Sample Preparation

In order to prepare thin h-BN flakes, we first mechanically exfoliated bulk material and found flakes of the appropriate thickness. We then used our Bruker Innova AFM tools to measure the thickness of the flakes. In general, all experiments were performed on flakes of a thickness of 4 nm or less.

After exfoliation and choosing the samples of the correct thickness, we first took optical images in the confocal microscope to determine the optical activity of the samples. We found that untreated flakes are not active, and there is only random optical activity due to surface contaminates that bleaches away with prolonged exposure. Images of this stage are not shown as they are essentially blank.
3.2.2. Electron Beam Exposure and High Temperature Annealing

Then the flakes are exposed to the electron beam in the JEOL SEM using the NPGS lithography system. We first measured the beam current using a Faraday cup and found an effective dosing current to be 5 nA. To organize the dosing, we used a dot array with a dosage of 2 C/cm². Each dot was a small circle with a diameter of just 1 nm, which will cause the NPGS dosing system to divide the pattern into single shot exposures.

After exposure to the electron beam, the sample was annealed at 800 °C for two hours under 400 sccm of Argon gas flow. This temperature has been reported by Tran et al. as the ideal temperature for creating SPEs. The authors annealed for 30 min, but we used additional time to ensure the removal of organic contaminates deposited either during the exfoliation or exposure processes. The high amount of Argon gas was used to purge the quartz annealing tube of any oxygen and to quickly sweep away any contaminates that were vaporized from the sample surface.

3.2.3. Intensity Maps and Spectroscopy

After dosage and annealing, the flakes were measured again in the confocal microscope shown in Figure 1-1. The result was a fluorescence mapping similar to those shown for the TMDC alloys in Chapter 2, but here we use much longer exposure and higher power to get accurate mappings. All fluorescence maps in this chapter were taken with 200 μW of power and 20 ms/pixel dwell time.
One key difference is that, since h-BN is optically inactive, it is difficult to see anything at all. Here we used much higher power and longer integration time per pixel to take these images.

To observe any optical structure to the emitter, we probed with a radial mode beam. The radial mode gaussian beam was created by passing vertically polarized light through the variable spiral plate in the confocal microscope. When focused in our 0.8 NA Nikon objective, the radial mode could be used to trace out the absorption dipole of point-like emitters. If we assume that the absorption and emission dipoles will have the sample orientation, these fluorescence images are expected to give a mapping of the emission dipole of the sample.

Photoluminescence measurements were performed using 200 uW of laser power for 2 minutes integration time, while binning all 400 rows on our CCD. All of the emitters showed some broad background luminesce. A separate background spectrum was taken at the same power and subtracted from the PL for each individual emitter in MATLAB.

3.2.4. Time Resolved Second Order Correlation Function Measurements

The single-photon emitting nature of our emitters was tested using the second-order cross correlation measurements of the pulse train coming from the emitter using an HBT interferometer. The HBT interferometer divides the output photon stream from our sample onto two different APDs using a pellicle beamsplitter. Each of the APDs produces a pulse train that is fed into our PicoHarp
time correlation measurement module, which performs a stop-start method of measuring the delay times between photon arrivals. Each delay time is counted and measured into 128 ps bins. Over the course of a long integration, a large histogram of delay times is built up, which approximates the second-order cross correlation of the two photon streams.

The HBT measurement gives a measure of the time between photon arrivals. Knowing something about the properties of single photon emitters, we can infer that perfectly anti-bunched light will have no two photons leaving the source at the same time. On the detection side of the measurement, we will see that there should be no light arriving simultaneously on both detectors. As we scan through possible delay times on our interferometer will have a ‘zero delay time’ $t = 0$, where the two arms of the HBT are equal in length. At $t = 0$, there should be no photons arriving simultaneous, which will lead to very few counts in that histogram bin.

The number of counts at $t = 0$, is a key metric in the creation of SPEs and actually provides an assessment of the purity of the single-photon source quality. In the ideal case, the value at $t = 0$ will go to zero. Usually, there is some background in the measurement setup and therefore we can say that if the value at zero delay goes at or below 0.5, then we can consider it a SPE. However, higher purity single-photon streams will give a value closer to zero. If the sample has just a few emitters, the number of emitters in the focal spot can be calculated separately using equation Equation 3-1.32,36 This calculation is only an approximation in that it may give a fractional number, where only whole emitters would be considered physical. In this
case, discrepancies in value may be pointing to the presence of a 3 level or 4 level system, or emission from a nearby shelving state that would otherwise reduce the purity of a single photon emitter.\textsuperscript{45}

\[ g^2(t = 0) = 1 - \frac{1}{n} \]

**Equation 3-1** The value measured at zero time delay of the second-order correlation measurement can be used to approximate how many emitters are within the focal spot of a measured region using this equation.

### 3.3. Results and Discussion

Our method for defect fabrication centers around exposing thin h-BN flakes to the electron beam over a small area in the sample. Figure 3-1 gives a brief outline of this process for a 4 nm flake on a silicon and silicon dioxide substrate. Figure 3-1 (B) shows a brightfield optical image taken with a general inspection microscope. This is part of the first step of sample preparation, identifying thin flakes by optical contrast and measuring them with the atomic force microscope. Thin flakes below 10 nm in thickness appear to be very pale or almost transparent, with little contrast to the background substrate.

Next, the flake was viewed under the electron microscope and exposed to a controlled dosage. Figure 3-1 (C) shows the same flake as in (B) but under the FEI Helios 660. After exposure, the flake is annealed at 800 °C under 300-400 sccm of Ar gas flow. Finally, the flake was viewed with the confocal microscope system using
the radial mode beam, an example of which is shown in Figure 3-1 (D). Any created emitters appear as a bright spot and above the background.

Figure 3-1 (A) Schematic diagram showing light emission from Nitrogen Vacancy Boron Substitution Structure in Hexagonal Boron Nitride Lattice. (B) Optical Image taken of h-BN flake on silicon support substrate. (C) SEM image of the same flake shown in (B) during the SEM dosing procedure. (D) Integrate intensity mapping of the same flake in (B) and (C) showing light emission from the treated areas.

Under the Helios, we were able to use a dosage based on the findings of Tran et al.\textsuperscript{13} In that study, the authors exposed an area of 600 \( \mu \text{m}^2 \) to the electron beam for 1 h used a beam of 15 kV and 1.4 nA under some flow of water vapor. However, by using the same beam conditions and a smaller viewing area, we were able to apply sufficient dosage in much shorter time. Also, the authors found that their
bright emitters were often localized to the edges of the flakes. In our case, they
stayed right underneath the viewing spot.

For control experiments throughout this work, each electron beam dosage
was also applied to an adjacent area of bare silicon dioxide substrate. Since the
flakes were very thin, there was little material to interact with the electron beam
during exposure. The supporting substrate sunk most of the energy applied by the
beam. Despite this in all cases, the silicon substrate remained inactive when treated
by the dosing process.

In order to make this process more precise, we moved to the electron beam
lithography system in the JEOL 6500 electron microscope and used a dosage value
of 2C/cm$^2$ on a 5x5 array of 1 nm spots. This dosage was very high compared to
values used in conventional electron beam lithography, but in this case, we were not
trying to use any resist. This technique was purely trying to damage the h-BN lattice
with a high electron flux.

An example of the results of this technique are shown in Figure 3-2. In Figure
3-2 (A), we find a flake that is about 4 nm thick the edge region and 10 nm thick in
the center and expose that flake to a dosage of 2 C/cm$^2$. Figure 3-2 (B) shows the
same flake as in (A). After treatment, there are large bright spots that stand out from
the background the pattern of which mirrors the electron beam lithography design.
Large portions of the flake have brightened uniformly, and the luminescent spots
can now be seen clearly within the outline of the h-BN flake. Some of the spots show
a dipole like structure while others show only large bright areas. For reference purposes, the emitters are labeled numerically.

Figure 3-2 (C) and (D) show the PL spectra taken on the background and emitters. The background has both bright and dark areas. The dark areas of h-BN show the same features as the clean silicon background, which only have Raman peaks visible for silicon near 520 cm\(^{-1}\) and 900 cm\(^{-1}\) for silicon dioxide. In the bright areas of h-BN that are not localized emitters, two peaks at 575 nm and 585 nm show up on the areas that have brightened uniformly along with some low intensity broad peaks near 630 nm.

Figure 3-2 (D) shows the bright spectra for the localized bright emitters found in the same. In general, any of the localized bright spots found in (B) show the same type of broad PL spectra found in (D), which has a large broad peak that blurs over most the visible range. While they appear as bright over the background, each emitter has relatively low brightness.
Figure 3-2 (A) Optical image of h-BN flake with a thickness of about 4 nm. (B) Integrated intensity mapping of same flake in panel (A) after SEM treatment. The upper flake shows a relatively ordered array of fluorescent spots in the same area that was treated with the electron beam. (C) Spectra taken from the silicon and silicon with h-BN areas of the sample. The silicon has relatively flat background spectra with narrow peaks for the raman lines of silicon at 550 nm and silicon dioxide at 560 nm. The hBN shown some general broadband emissions most likely arising from collateral damage caused the by SEM. Two peaks are consistently seen at 575 and 580 nm. Another broad peak can be found at 630 nm. (D) Broad band PL emission at the defect centers. This peak is centered around 630 nm and is most likely caused by the a collection of many emitters caused by the higher concentration of damage to that area.

To improve the exposure method and refine the dosage, we repeated the sample exposure technique with higher and lower doses. On the higher end, doses of
up to 3.8 C/cm² were used and had similar results with large broad emitters. Doses much lower than 2 C/cm² brighten the flake uniformly and showed the bright h-BN background spectra shown in Figure 3-2 (C). However, they did not show localized bright spots as in (B).

Figure 3-3 (A) Brightfield optical images taken of an hBN flake on silicon dioxide substrate. (B) Integrated intensity map of the same flake shown in (A) after exposure to the electron beam. Most of the flake has brightened uniformly, with some localized dipole-like emitters at the center. (C) Photoluminescence spectra for the brightest emitter at the center of the flake. The spectra shows narrow band emission at 640 nm with a phonon side band appearing approximately 700 nm. The inset shows the background for this flake, which has been subtracted from the main data. The background spectra and intensity are comparable to those found in other flakes and similar to that shown above. (D) $g^2(t)$ measurement on the emitter measured in (C) after normalizing by the mean the value $t = 0$ is shown to be 0.5, which demonstrates that this is a SPE.
The thin flakes in Figure 3-3 and Figure 3-4 were exposed using 2 $C/cm^2$, and both had defects with single-photon emission in addition to defects with broad emission. These emitters showed narrow emission lines with a full width at half maximum of 30 meV. The 4 nm flake in Figure 3-3 (C) showed emission centered at 640 nm with a sideband located at 700 nm. This sideband is separated from the zero phonon line by 166 meV, which is the same energy value reported by other studies. The background shows the same features and has been subtracted from the PL spectra. The single-photon emitting nature of this defect center was confirmed by the $g^2(t)$ measurement in Figure 3-3 (D). The minimum value at $t = 0$ is 0.5, which demonstrates that this is indeed a SPE.

However, there is significant background light coming into the $g^2(t)$, which seems to significantly decrease the signal-to-noise ratio. In Figure 3-3 (D), there is a discontinuity evident at $t = 0$, but the data is overall noisy, which makes it hard to apply an exponential fit to the data. The same can be said about the $g^2(t)$ in Figure 3-4 (D). In this case, if we did not know the location of $t = 0$ prior to measurement, it would be hard to find a dip in counts that would be statistically significant when compared to the background.

Figure 3-4 shows a 10 nm flake with a zero phonon emission line at 565 nm and a phonon side band at 610 nm. This emitter structure is brighter than the SPE1. The $g^2(t)$ measurement shows a value of $g^2(t = 0) = 0.8$. We can calculate that this indicates the presence of 5 emitters in the focal region.
Figure 3-4 (A) Optical image for the hBN flake. (B) Integrated intensity mapping on this flake after exposure to the electron beam. (C) PL spectra for the bright emitter shown at the corner of the flake. The background shown in the inset has been subtracted from the spectra. The bright dipole-like emitter shows predominate spectral features at 565 nm. The phonon sideband appears at 605 nm along with several other peaks coming from other emitters in the same focal spot of the beam. (D) $g^2(t)$ measurement on the same emitter. The after normalizing to the mean, the minimum value is $g^2(t = 0) = 0.8$. This indicates the presence of 5 emitters in the same area.

To further characterize these emitters, several small area scans were taken. Under our microscope, the emitter spot maps to a diameter of about 1 $\mu$m. At this level, the radial mode beam also provides some information about the dipolar
structure of the emitter. SPE1 in Figure 3-5 (A) is adjacent to several other broad emitter spots that do not show single-photon emission. Single-photon stream is only measured at the brightest lobe. In Figure 3-5 (C), SPE 2 shows a two lobed dipole like shape, with some faint side lobes appearing below it.

To test the power dependent behavior, we also measured the count rate while varying the excitation power into the microscope. Figure 3-5 (B) and (D) plot the signal counts, background count, and then the difference of the signal and background. SPE1 has a linear dependence on input power but is not very bright. SPE2 shows brighter emission, which saturates around 1.4 mW and 100 kHz count rate, which is an order of magnitude less than what has been shown in several other groups.13
Figure 3-5 (A) Shows an integrated fluorescence intensity map of sample 1 shown above. (B) Here we plot the power dependence of the output fluorescence counts, with the background counts. The center line shows that the data with the background substrate. Overall the output of the sample increases linearly with the input power. However, the sample output is low, showing only 20 kHz count rates at excitation powers of powers up to 4 mW. (C) Shows the SPE found in sample 2 above. The intensity maps shows an overall dipolar like structure. (D) Power dependence of SPE 2 shown in (C). This emitter saturates at about 1.4 mW at about 100 kHz. The count rates seem to increase again around 4 mW.

3.4. Conclusion

From these fluorescence mapping measurements, we can definitely see that defects can be created in h-BN from a high electron flux. High energy electrons
impinging on the sample can break bonds and destroy the crystalline nature of the sample. The arrangement of the defects can be lithographically patterned and deterministically activated. It is even possible to create fluorescent defects, which under the right conditions can have single-photon emitting states.

The optical emission frequencies suggest that we are creating the same type of emitters as found in literature, which are most likely vacancy and substitutional defects. Under the right conditions, these point-like defects can indeed form a countable number of SPEs, as shown by our second-order correlation measurements. We have also shown that it is possible to create these defects within a relatively ordered array, which present exciting possibilities for future design and engineering of devices using this same type of emitters.

Future work on this technique would entail further refinement of the dosing pattern and electron dose in order to create more SPEs with narrow zero phonon lines. The ideal procedure would use the minimum dosage required to create just SPEs in the location desired. A more successful method might use a lithographically defined pattern and heavy ion exposure, which would still have enough energy to break bonds, but minimize the overall damage to the sample.
Notes

All optical measurements were performed by James Kerwin. The binary alloy sample growth and transfer was done by Sandhya Susarla in the Ajayan Group at Rice University. All of the HAADF-STEM and STEM EELS measurements were done by Jordan Hachtel at Oakridge National Laboratories.
References


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Appendix A: Raman Peak Processing Code

The data processing was done in 3 parts. The first program extracted the peaks from our Raman data and performed the intensity and peak shift temperature calculations. Two other smaller programs were called in order to perform the peak fitting with a least squares regression model and separately plot any data necessary. PL and $g^{(2)}(t)$ data were graphed using simple plotting and labelling code not shown here.

```
%% Aperture 11 Stokes Anti-Stokes Processing Code

clear
clc
close all

%%
load('powerdeptdata')
%%

cntrfrq=5.319e-5;%cm
cntrwv=cntrfrq^-1;

x1=December111500441800g9uw5min(1:1340,2);
y1=December111500441800g9uw5min(1:1340,5);
x1=cntrwv-((10^-7*x1).^(-1));
xAS1=x1(200:350,1);
yAS1=y1(200:350,1);
xS1=x1(1000:1200,1);
yS1=y1(1000:1200,1);

x2=December111500441800g25uw10min(1:1340,2);
y2=December111500441800g25uw10min(1:1340,5);
x2=cntrwv-((10^-7*x2).^(-1));
xAS2=x2(200:350,1);
yAS2=y2(200:350,1);
xS2=x2(1000:1200,1);
yS2=y2(1000:1200,1);
```
x3=December111500441800g120uw5min(1:1340,2);
y3=December111500441800g120uw5min(1:1340,5);
x3=cntrwv-((10^-7*x3).^(-1));
xAS3=x3.(200:350,1);
yAS3=y3.(200:350,1);
xS3=x3.(1000:1200,1);
yS3=y3.(1000:1200,1);

x4=December111500441800g190uw3min(1:1340,2);
y4=December111500441800g190uw3min(1:1340,5);
x4=cntrwv-((10^-7*x4).^(-1));
xAS4=x4.(200:350,1);
yAS4=y4.(200:350,1);
xS4=x4.(1000:1200,1);
yS4=y4.(1000:1200,1);

x5=December111500441800g360uw2min(1:1340,2);
y5=December111500441800g360uw2min(1:1340,5);
x5=cntrwv-((10^-7*x5).^(-1));
xAS5=x5.(200:350,1);
yAS5=y5.(200:350,1);
xS5=x5.(1000:1200,1);
yS5=y5.(1000:1200,1);

x6=December111500441800g630uw2min(1:1340,2);
y6=December111500441800g630uw2min(1:1340,5);
x6=cntrwv-((10^-7*x6).^(-1));
xAS6=x6.(200:350,1);
yAS6=y6.(200:350,1);
xS6=x6.(1000:1200,1);
yS6=y6.(1000:1200,1);

x7=December111500441800g860uw2min(1:1340,2);
y7=December111500441800g860uw2min(1:1340,5);
x7=cntrwv-((10^-7*x7).^(-1));
xAS7=x7.(200:350,1);
yAS7=y7.(200:350,1);
xS7=x7.(1000:1200,1);
yS7=y7.(1000:1200,1);

x8=December111500441800glmw1min(1:1340,2);
y8=December111500441800glmw1min(1:1340,5);
x8=cntrwv-((10^-7*x8).^(-1));
xAS8=x8.(200:350,1);
yAS8=y8.(200:350,1);
xS8=x8.(1000:1200,1);
yS8=y8.(1000:1200,1);

power=1e-6*[9 25 120 190 360 630 860 1000];
power1=[9 25 120 190 360 630 860 1000];
```
%%

ramanplotter(x1,y1,...
  20,3,'S/AS Raman',...
  'Aprt 11 50uW','Raman Shift (cm^-1)','Intensity (Counts)',...
  [-600 600 0 max(y1)+100])

%%

ramanplotter(x2,y2,...
  20,3,'S/AS Raman',...
  'Aprt 11 100uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y2)+100])

%%

ramanplotter(x3,y3,...
  20,3,'S/AS Raman',...
  'Aprt 11 150uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y3)+100])

%%

ramanplotter(x4,y4,...
  20,3,'S/AS Raman',...
  'Aprt 11 200uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y4)+100])

%%

ramanplotter(x5,y5,...
  20,3,'S/AS Raman',...
  'Aprt 11 250uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y5)+100])

%%

ramanplotter(x6,y6,...
  20,3,'S/AS Raman',...
  'Aprt 11 300uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y6)+100])

%%

ramanplotter(x7,y7,...
  20,3,'S/AS Raman',...
  'Aprt 11 400uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y7)+100])

%%

ramanplotter(x8,y8,...
  20,3,'S/AS Raman',...
  'Aprt 11 500uW','Raman Shift (cm^-1)','Counts',...
  [-600 600 0 max(y8)+100])

%% fit 1

% fitparamsAS.Indices=[1:20 120:151 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
  16 17 18 19 20 21 22 56 57 58 84 85 86 114 115 116 117 118 119 120 121
  122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139
  140 141 142 143 144 145 146 147 148 149 150 151];```
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf 421 -415 -390 -360 -Inf -Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf 414 -407 -375 -340 Inf Inf Inf Inf]
fitparamsAS.StartPoint = [150 150 150 150 -420 -407.4 -380 -350 ...
10 10 10 10 ... 10];

classparamsAS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
41 42 82 94 108 109 151 152 153 154 155 156 157 158 159 160 161 162
163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180
181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198
199 200 201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf -Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ...
351 383 409 418 ...
10 10 10 10 ... 10];

[TA1gW1,TA1gMo1,TE2gMo1,TE2gW1,coef1AS,coef1S] = ramanfitter(x1,y1,fitparamsAS,fitparamsS);

%% fit 2

fitparamsAS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
41 42 82 94 108 109 151 152 153 154 155 156 157 158 159 160 161 162
163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180
181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198
199 200 201];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf 421 -415 -390 -360 -Inf -Inf -Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf 414 -407 -375 -340 Inf Inf Inf Inf Inf]
fitparamsAS.StartPoint = [150 150 150 150 ...
-420 -407.4 -380 -350 ...
10 10 10 10 ... 10];

classparamsAS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
41 42 82 94 108 109 151 152 153 154 155 156 157 158 159 160 161 162
163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180
181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198
199 200 201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf -Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ...
351 383 409 418 ...
10 10 10 10 ... 10];
[TA1gW2,TA1gMo2,TE2gMo2,TE2gW2,coef2AS,coef2S] = ramanfitter(x2,y2,fitparamsAS,fitparamsS);

%% fit 3

fitparamsAS.Indices=[1:20 120:151 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 93 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -421 -415 -390 -360 -Inf -Inf -Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf -414 -400 -375 -340 Inf Inf Inf Inf Inf];
fitparamsAS.StartPoint = [150 150 150 150 -420 -407.4 -380 -350 ... 10 10 10 10 ... 10];

fitparamsS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf -Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 -351 -383 -409 -418 ... 10 10 10 10 ... 10];

[TA1gW3,TA1gMo3,TE2gMo3,TE2gW3,coef3AS,coef3S] = ramanfitter(x3,y3,fitparamsAS,fitparamsS);

%% fit 4

fitparamsAS.Indices=[1:20 120:151 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -421 -415 -390 -360 -Inf -Inf -Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf -414 -400 -375 -340 Inf Inf Inf Inf Inf];

fitparamsAS.StartPoint = [150 150 150 150 ...
-420 -407.4 -380 -350 ...
10 10 10 10 ...
10];

fitparamsS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65
66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90
91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111
112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130
131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148
149 150 151];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf
-Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf
Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ...
351 383 409 418 ...
10 10 10 10 ...
10];

[TA1gW4,TA1gMo4,TE2gMo4,TE2gW4,coef4AS,coef4S] = ramanfitter
(x4,y4,fitparamsAS,fitparamsS);

%% fit 5

% fitparamsAS.Indices=[1:20 120:151 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65
66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90
91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111
112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130
131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148
149 150 151];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -421 -415 -390 -360 -Inf -Inf
-Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf -414 -400 -375 -340 Inf Inf Inf Inf
Inf Inf];
fitparamsAS.StartPoint = [150 150 150 150 ...
-420 -407.4 -380 -350 ...
10 10 10 10 ...
10];

fitparamsS.Indices=[1:20 171:201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf
-Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf
Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ...
351 383 409 418 ...
10 10 10 10 ...
10];
[TA1gW5,TA1gMo5,TE2gMo5,TE2gW5,coef5AS,coef5S] = ramanfitter(x5,y5,fitparamsAS,fitparamsS);

%% fit 6

% fitparamsAS.Indices=[1:20 120:151 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
16 17 18 19 20 21 22 23 24 25 26 121 122 123 124 125 126 127 128 129
130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147
148 149 150 151];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -421 -415 -390 -360 -Inf -Inf
-Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf -414 -400 -375 -340 Inf Inf Inf
Inf Inf];
fitparamsAS.StartPoint = [150 150 150 150 ...
-420 -407.4 -380 -350 ...
10 10 10 10 ...]
fitparamsS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 81:83 155 156 157
158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175
176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193
194 195 196 197 198 199 200 201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf -340 375 400 414 -Inf -Inf -Inf
-Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf
Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ...
351 383 409 418 ...
10 10 10 10 ...]

[TA1gW6,TA1gMo6,TE2gMo6,TE2gW6,coef6AS,coef6S] = ramanfitter(x6,y6,fitparamsAS,fitparamsS);

%% fit 7

% fitparamsAS.Indices=[1:20 120:151];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -421 -415 -390 -360 -Inf -Inf
-Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf -414 -400 -375 -340 Inf Inf Inf
Inf Inf];
fitparamsAS.StartPoint = [150 150 150 150 ...
-420 -407.4 -380 -350 ...
10 10 10 10 ...]
fitparamsS.Indices=[1:20 171:201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ... 351 383 409 418 ... 10 10 10 10 ... 10];

[TA1gW7,TA1gMo7,TE2gMo7,TE2gW7,coef7AS,coef7S] = ramanfitter(x7,y7,fitparamsAS,fitparamsS);

%% fit 8

fitparamsAS.Indices=[1:20 120:151];
fitparamsAS.Lower = [-Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf];
fitparamsAS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf];
fitparamsAS.StartPoint = [150 150 150 150 ... -420 -407.4 -380 -350 ... 10 10 10 10 ... 10];

fitparamsS.Indices=[1:20 171:201 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201];
fitparamsS.Lower = [-Inf -Inf -Inf -Inf 340 375 400 414 -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf -Inf];
fitparamsS.Upper = [Inf Inf Inf Inf 360 390 415 430 Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf Inf];
fitparamsS.StartPoint = [350 350 350 350 ... 351 383 409 418 ... 10 10 10 10 ... 10];

[TA1gW8,TA1gMo8,TE2gMo8,TE2gW8,coef8AS,coef8S] = ramanfitter(x8,y8,fitparamsAS,fitparamsS);

%%
tempA1gW = [TA1gW1 TA1gW2 TA1gW3 TA1gW4 TA1gW5 TA1gW6 TA1gW7 TA1gW8 ];
tempA1gMo = [TA1gMo1 TA1gMo2 TA1gMo3 TA1gMo4 TA1gMo5 TA1gMo6 TA1gMo7 TA1gMo8 ];
tempE2gW = [TE2gW1 TE2gW2 TE2gW3 TE2gW4 TE2gW5 TE2gW6 TE2gW7 TE2gW8 ];
tempE2gMo = [TE2gMo1 TE2gMo2 TE2gMo3 TE2gMo4 TE2gMo5 TE2gMo6 TE2gMo7 TE2gMo8 ];

%% Plotting Temperature Calculation

figure(101)
plot(power1, tempA1gW,'r', power1, tempA1gMo,'k',...
    'LineWidth',2)
%    'MarkerSize',10,...
%    'MarkerEdgeColor','b',...
%    'MarkerFaceColor',[0.5,0.5,0.5])
%text(power,tempW,labels1)
%title('Calculated Temp','FontSize', 18)
xlabel('Input Power (uW)','FontSize', 18)
ylabel('Temperature (K)','FontSize', 18)
legend('A1gW','A1gMo','location','southeast')
axis([0 1100 200 700])

set(gca,'fontsize',18)
print('A1g E2g Difference','-dtiffn')
saveas(gcf,'A1g E2g Difference')

%% extracting alpha

Tedge=295;       %room temp
a=.5*1.22*532e-9/.8;
R=2.5e-6;
d=5e-9;         %membrane thickness
rho=R/a;

delTMO=tempA1gMo-Tedge;
delTW=tempA1gW-Tedge;

eg=0.5772;        %euler constant

alphaMoAlg=(2*delTMO)./(log(rho)+eg/2);
alphaWA1g=(2*delTW)./(log(rho)+eg/2);

% alphaMoAlgS=(2*delTMOs)./(log(rho)+eg/2);
% alphaWA1gS=(2*delTWS)./(log(rho)+eg/2);

%% extracting kappa

P=.1*.25*power;  %assume the total power absorbed is 10% 25%actually on sample

kappaMo=P./(alphaMoAlg*d*pi);
kappaW=P./(alphaWA1g*d*pi);
% kappaMoS=P./(alphaMoA1gS*d*pi);
% kappaWS=P./(alphaWA1gS*d*pi);

kmo=mean(kappaMo);
kW=mean(kappaW);

% kmos=mean(kappaMoS);
% kws=mean(kappaWS);

figure(102)
plot(power1, kappaW,'--or', power1, kappaMo,:xk',... 'LineWidth',2)
title('Calculated Thermal Conductivity','FontSize', 20)
xlabel('Input Power (\mu W)','FontSize', 20)
ylabel('Thermal Conductivity [W/(m K)]','FontSize', 20)
legend(['A1gW','A1gMo'],'FontSize', 18,'location','northwest')
axis([0 1100 0 10])
set(gca,'fontsize',18)
print('thermal conductivity','-dtiffn')
saveas(gcf,'thermal conductivity')

%% Plotting Peak Shifts

coeffAS= [coeff1AS coeff2AS coeff3AS coeff4AS coeff5AS coeff6AS coeff7AS]
coeffS= [coeff1S coeff2S coeff3S coeff4S coeff5S coeff6S coeff7S coeff8S ];

ASpW=coeffAS(5,:);
ASpMo=coeffAS(6,:);
SpW=coeffS(8,:);
SpMo=coeffS(7,:);

SpMoE2g=coeffS(6,:);
SpWE2g=coeffS(5,:);

figure(103)
plot(power1, ASpW,'--or', power1, ASpMo,:xk',... 'LineWidth',2)
title('Peak Positions AntiStokes','FontSize', 20)
xlabel('Input Power (\mu W)','FontSize', 20)
ylabel('Raman Shift (cm^-1)','FontSize', 20)
legend(['A1gW','A1gMo'],'FontSize', 18,'location','southeast')
axis([0 1100 -420 -400])
set(gca,'fontsize',18)
print('peak shift Mo','-dtiffn')
saveas(gcf,'peak shift W')

figure(104)
plot(power1, SpW,'--or', power1, SpMo,':xk',... 
     'LineWidth',2)
title('Peak Positions Stokes','FontSize', 20)
xlabel('Input Power (\muW)','FontSize', 20)
ylabel('Raman Shift (cm^{-1})','FontSize', 20)
legend({'A1gW','A1gMo'},'fontsize',18,'location','southeast')
axis([0 1100 400 420])
set(gca,'fontsize',18)
print('peak shift W','-dtiffn')
saveas(gcf,'peak shift W')

%% Peak Shift with Temperature Shift Mo

Tr=295;
xt=-.013; % in cm^{-1}/K Alg linear temperature coefficient taken from paper

peakshiftASMo=diff(ASpMo);
tempshiftASMo=[0 peakshiftASMo/xt];

peakshiftSMo=diff(SpMo);
tempshiftSMo=[0 peakshiftSMo/xt];

l=length(power1);
tempMoAS=[Tr zeros(1,l-1)];
tempMoS=[Tr zeros(1,l-1)];

for i=1:length(power1)
    if i==1
        tempMoAS(i)=tempMoAS(i)+tempshiftASMo(i);
        tempMoS(i)=tempMoS(i)+tempshiftSMo(i);
    else
        tempMoAS(i)=tempMoAS(i-1)+tempshiftASMo(i);
        tempMoS(i)=tempMoS(i-1)+tempshiftSMo(i);
    end
end

%%
figure (105)
plot(power1, tempAlgMo,'-xb', power1, tempMoAS,'--or',power1, tempMoS,'*--r',... 
     'LineWidth',2)
title('Temperature Calc From Intensity and Peak Shift Mo','FontSize', 20)
xlabel('Input Power (\muW)','FontSize', 20)
ylabel('Temperature (K)', 'FontSize', 20)
legend({'Alg Intensity Calc', 'Peak Shift Calc AS', 'Peak Shift Calc S'}, 'FontSize', 18, 'location', 'southeast')
axis([0 1100 200 700])

set(gca, 'FontSize', 18)
print('temp 3 ways Mo', '-dtiffn')
saveas(gcf, 'temp 3 way Mo')

%% Peak Shift with Temperature Shift W
Tr=295;
x=.013; % in cm^-1/K Alg linear temperature coefficient taken from paper

peakshiftASW = diff(ASpW);
tempshiftASW = [0 peakshiftASW/xt];

peakshiftSW = diff(SpW);
tempshiftSW = [0 peakshiftSW/xt];

l = length(power1);
tempWAS = [Tr zeros(1, l-1)];
tempWS = [Tr zeros(1, l-1)];

for i = 1:length(power1)
    if i == 1
        tempWAS(i) = tempWAS(i) + tempshiftASW(i);
        tempWS(i) = tempWS(i) + tempshiftSW(i);
    else
        tempWAS(i) = tempWAS(i-1) + tempshiftASW(i);
        tempWS(i) = tempWS(i-1) + tempshiftSW(i);
    end
end

%%
figure (107)
plot(power1, tempA1gW, '-xb', power1, tempWAS, '--ok', power1, tempWS, '*--r', ...
     'LineWidth', 2)
title('Temperature Calc From Intensity and Peak Shift W', 'FontSize', 20)
xlabel('Input Power (\mu W)', 'FontSize', 20)
ylabel('Temperature (K)', 'FontSize', 20)
legend({'Alg Intensity Calc', 'Peak Shift Calc AS', 'Peak Shift Calc S'}, 'FontSize', 18, 'location', 'southeast')
axis([0 1100 250 700])

set(gca, 'FontSize', 18)
print('temp 3 ways W', '-dtiffn')
saveas(gcf, 'temp 3 way W')
figure
subplot(1,2,1)
plot(xAS8,yAS8,'--b',xAS4,yAS4,:k',...  \
'LineWidth',2)
ylabel('Intensity (counts)','FontSize', 20)
axis([-430 -325 0 300])
title('Evolution of Raman Spectrum with Power','Anti-Stokes','FontSize', 20)
xlabel('Raman Shift (cm^-1)','FontSize', 20)
legend({'1mW','200 \muW'},'FontSize', 18,'location','northeast')
set(gca,'fontsize',16)
subplot(1,2,2)
plot(xS8,yS8,'--b',xS4,yS4,:k',...  \
'LineWidth',2)
title('Stokes','FontSize', 20)
axis([325 430 0 900])
set(gca,'fontsize',16)
print('SAS Raman with power','-dtiffn')
saveas(gcf,'SAS Raman with power Difference')


%%
diffMol=SpMo-SpMoE2g;
diffWl=SpW-SpWE2g;

figure (108)
plot(power1, diffMol,'-ob', power1, diffWl,'-^k',...  \
'LineWidth',2)
title('A1g E2g Difference','FontSize', 20)
xlabel('Input Power (\muW)','FontSize', 20)
ylabel('Frequency Diff cm^-1','FontSize', 20)
legend({'Mo','W'},'location','northeast','FontSize', 12)
axis([0 1100 26 27])
set(gca,'fontsize',18)
print('A1g E2g Difference','-dtiffn')
saveas(gcf,'A1g E2g Difference')

%%
\[ T = \text{table}(\text{power1}', \ \text{tempA1gMo}', (\text{tempMoAS}+50)', (\text{tempMoS}+50)', \text{tempA1gW}', (\text{tempWAS}+50)', (\text{tempWS}+50)') \]

**Raman Fitter**

```matlab
function [TA1gW,TA1gMo,TE2gMo,TE2gW,coefAS,coefS] = ramanfitter(x,y,fitparamsAS,fitparamsS)

%% split the vector
% split up the stoke and antistokes peaks

xAS=x(200:350,1);
yAS=y(200:350,1);
xS=x(1000:1200,1);
yS=y(1000:1200,1);

%% Fit: 'lorentzfitAS'.
[xData, yData] = prepareCurveData(xAS, yAS);

% Set up fittype and options.
ft = fittype( '(a1/((x-b1)^2+c1))+(a2/((x-b2)^2+c2))+(a3/((x-b3)^2+c3))+(a4/((x-b4)^2+c4))'+d', 'independent', 'x', 'dependent', 'y' );
excludedPoints = excludedata(xData, yData, 'Indices', fitparamsAS.Indices);
opts = fitoptions('Method', 'NonlinearLeastSquares');
opts.Display = 'Off';
opts.Lower = fitparamsAS.Lower;
opts.MaxFunEvals = 8000;
opts.MaxIter = 5000;
opts.Robust = 'Bisquare';
opts.StartPoint = fitparamsAS.StartPoint;
opts.Exclude = excludedPoints;
opts.Upper = fitparamsAS.Upper;

% Fit model to data.
[fitresultAS, gofAS] = fit(xData, yData, ft, opts);

% Plot fit with data.
figure('Name', 'Anti Stokes Fit');
h = plot(fitresultAS, xData, yData, excludedPoints);
```
legend( h, 'yAS vs. xAS', 'Excluded yAS vs. xAS', 'Antistokes Fit', 'Location', 'NorthEast');

% Label axes
xlabel('Raman Shift (cm^-1)')
ylabel('Counts')
gridd on

coefAS=coeffvalues(fitresultAS)';
a1=coefAS(1);
a2=coefAS(2);
a3=coefAS(3);
a4=coefAS(4);
b1=coefAS(5);
b2=coefAS(6);
b3=coefAS(7);
b4=coefAS(8);
c1=coefAS(9);
c2=coefAS(10);
c3=coefAS(11);
c4=coefAS(12);

fun1=@(x) (a1./((x-b1).^2+c1));
IAS1=integral(fun1,-500,-300);
fun2=@(x) (a2./((x-b2).^2+c2));
IAS2=integral(fun2,-500,-300);
fun3=@(x) (a3./((x-b3).^2+c3));
IAS3=integral(fun3,-500,-300);
fun4=@(x) (a4./((x-b4).^2+c4));
IAS4=integral(fun4,-500,-300);

%% Fit: 'lorentzfitS'.
[xData, yData] = prepareCurveData( xS, yS );

% Set up fittype and options.
ft = fittype( '(a1/((x-b1)^2+c1))+(a2/((x-b2)^2+c2))+(a3/((x-b3)^2+c3))+(a4/((x-b4)^2+c4))+d', 'independent', 'x', 'dependent', 'y' );
excludedPoints = excludedata( xData, yData, 'Indices', fitparamsS.Indices );
opts = fitoptions( 'Method', 'NonlinearLeastSquares' );
opts.Display = 'Off';
opts.Lower = fitparamsS.Lower;
opts.MaxFunEvals = 8000;
opts.MaxIter = 5000;
opts.Robust = 'Bisquare';
opts.StartPoint = fitparamsS.StartPoint;
opts.Exclude = excludedPoints;
opts.Upper = fitparamsS.Upper;

% Fit model to data.
[fitresultS, gofS] = fit( xData, yData, ft, opts );
% Plot fit with data.
figure( 'Name', 'Stokes Fit' );
h = plot( fitresultS, xData, yData, excludedPoints );
legend( h, 'YS vs. XS', 'Excluded yS vs. xS', 'lorentzfitS', 'Location', 'NorthEast' );
% Label axes
xlabel ( 'Raman Shift (cm^-1)' )
ylabel Counts
grid on

coeffS=coeffvalues(fitresultS)';
a1=coeffS(1);
a2=coeffS(2);
a3=coeffS(3);
a4=coeffS(4);
b1=coeffS(5);
b2=coeffS(6);
b3=coeffS(7);
b4=coeffS(8);
c1=coeffS(9);
c2=coeffS(10);
c3=coeffS(11);
c4=coeffS(12);

fun1=@(x) (a1./((x-b1).^2+c1));
IS1=integral(fun1,300,500);
fun2=@(x) (a2./((x-b2).^2+c2));
IS2=integral(fun2,300,500);
fun3=@(x) (a3./((x-b3).^2+c3));
IS3=integral(fun3,300,500);
fun4=@(x) (a4./((x-b4).^2+c4));
IS4=integral(fun4,300,500);

%% Temp Calculation

hbar=1.05457180013e-34; %J s
kb=1.3806485279e-23;  %J K^-1
ace=299792458;        %m/s
Tr=295;               %room temp K

omegaA1gW=2*pi*c*((b4+18800)*100);  %18800 is 531.9nm in wavenumbers
omegaA1gMo=2*pi*c*((b3+18800)*100); %add back to use absolute wavenumbers
omegaE2gMo=2*pi*c*((b2+18800)*100);
omegaE2gW=2*pi*c*((b1+18800)*100);

omegaL=2*pi*c*(531.9e-7^-1);
CW=((omegaL-omegaA1gW)/(omegaL+omegaA1gW))^4;
CMo=((omegaL-omegaA1gMo)/(omegaL+omegaA1gMo))^4;
CWE=((omegaL-omegaE2gW)/(omegaL+omegaE2gW))^4;
CMoE = ((\omega_L - \omega_{E2gMo})/(\omega_L + \omega_{E2gMo}))^4;

\omega_{A1gW} = 2\pi c \times ((b4) \times 100);
\omega_{A1gMo} = 2\pi c \times ((b3) \times 100);
\omega_{E2gMo} = 2\pi c \times ((b2) \times 100);
\omega_{E2gW} = 2\pi c \times ((b1) \times 100);

TA_{1gW} = \hbar \omega_{A1gW} / (k_b \log(IS4/(IAS1\times CW)));
TA_{1gMo} = \hbar \omega_{A1gMo} / (k_b \log(IS3/(IAS2\times CMo)));

TE_{2gMo} = \hbar \omega_{E2gMo} / (k_b \log(IS2/(IAS3\times CMoE)));
TE_{2gW} = \hbar \omega_{E2gW} / (k_b \log(IS1/(IAS4\times CW)));

end

Raman Plotter

function ramanplotter
(x,y,hcrit,wcrit,figname,titl,xaxis,yaxis,axisbounds)

%peaking finding that accepts x and y data with height and width
%selection criteria. it returns the peak positions and a label string to be used in
%plotting.
% also rounds the peak position to 5 significant figures

% cntrwve=532*10^{-7}; % can convert to wavenumbers if needed
% cntrwve=x(342);
% x=(1/cntrwve)-(1./x);

[pks,locs,w,p] = findpeaks(y);
loc=[];
pk=[];

for i=1:length(locs)
    if p(i)>hcrit && w(i)>wcrit
        pk(i)=pks(i);
        loc(i)=x(locs(i));
        disp(loc(i))
        disp(pk(i))
        disp(w(i))
        disp(p(i))
    end
end
labels=cellstr(num2str(round(loc',5,'significant')));

figure('Name',figname)
plot(x,y,'-k',...
    loc,pk,'or',...
    'LineWidth',2)
    % 'MarkerSize',10,...
    % 'MarkerEdgeColor','b',...
    % 'MarkerFaceColor',[0.5,0.5,0.5])
    text(loc,pk,labels,'VerticalAlignment','bottom')
title(titl,'FontSize', 18)
xlabel(xaxis,'FontSize', 18)
ylabel(yaxis,'FontSize', 18)
axis(axisbounds)
    % %findpeaks(y,x,'MinPeakProminence',4,'Annotate','extents')
end