Optical Characterization of Spins and Defects in Thin Films and Heterostructures

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ABSTRACT

This research focused on using optical techniques to characterize of thin film materials, specifically Quantum Point Defect emitters and spin in heterostructures. These are important in the field of spintronics, with possible application in other fields such as quantum information. This research focused on three materials, hexagonal Boron Nitride (hBN), Tungsten Diselenide (WSe_2), and graphene. hBN is used in heterostructures, where defects in the lattice are problematic [1]. However, defects in hexagonal Boron Nitride in previous research has been found to be single photon sources [2]. This research focused on learning more about defects in the hBN lattice by making and characterizing defects in hBN. Tungsten Diselenide is a semi-conductor that is also used in heterostructures due to its interesting band structure that allows for spin/valley polarization and long spin/valley lifetimes [3]. Graphene, on the other hand, has a short spin/valley lifetime but can transport spins and charge carriers well [4]. These two materials were studied in heterostructures to learn more about the spin movement and interaction between materials.

Photoluminescence was taken on both hBN and heterostructures samples. Time-resolved Kerr rotation was used to investigate the spin/valley lifetimes of graphene-WSe_2 heterostructures. In hBN, annealing and depositing an atomic layer of Chromium resulted in single photon source peak being found. In the graphene-WSe_2 heterostructures, there was a decrease in excitation decay in the graphene overlap region versus the original Tungsten Diselenide flakes, suggesting the movement of spins and electrons from one material into the other.

I. Introduction

Spintronics is a field of solid-state physics with interest of manipulating and moving spins for application in spintronic devices. A research topic in this field is Van der Waals heterostructures – thin film materials stacked on one another and held together by Van der Waal forces [1]. These structures allow the thin films to interact and couple. Numerous material has been researched for use in heterostructures, but the ones this research will study is Tungsten Diselenide (WSe_2) and graphene.

WSe_2 is a Transition Metal Dichalcogenide (TMD), which is a lattice made up of a transition metal with two chalcogenides in the form of MX_2 (Fig 1a). TMDs are of interest due to the unique band structure they have, allowing the light to selectively excite spin depending on the helicity of the excitation beam (Fig. 1d) [5]. When the electron recombines, it emits the same polarization, making optical measurements a favored method for characterizing spin/valley interaction in TMDs [3]. However, a direct band-gap is only seen in two-dimensional

TMDs rather than the indirect band-gap observed in bulk structures, making single layer preferred in optical research [6]. Another interest in TMDs is their long spin/valley lifetimes [7]. Having long spin/valley lifetimes and the ability to transport spins would be exceptionally useful for spintronic devices. However, transporting spin is difficult is difficult in TMDs. In comparison, graphene has a long spin-transport length [4]. Graphene is a 2D conductor with a hexagonal lattice consisting of carbon atoms (Fig 1c) [4]. Although useful in moving spins and electrons, graphene has a short spin/valley lifetime. Therefore, the purpose of this research with heterostructures was to study overlapping WSe_2 flakes with graphene to attempt to achieve these wanted characteristics of graphene and Tungsten Diselenide. These heterostructures were optically characterized using different techniques.

Another material of interest is hexagonal Boron Nitride (hBN). hBN is a 2D honeycomb lattice with alternating nitrogen and boron atoms. hBN has a wide band-gap, making it an insulator. Often hBN is used in heterostructures for such purpose, however, defects in the hBN lattice cause complications in that application. Although still applicable in heterostructures, defects in hBN have been found to be single photon sources – which can have many applications [2].

A possible application of single photon sources is quantum photonics, and more specifically quantum information. Quantum information is a field that uses quantum systems to carry information rather than a binary coded system. One of the goals of quantum information is faster and more secure computing than seen in modern-day computers. Single photon emitters would be pertinent to quantum information as it allows carrying binary information with helicity and increases security as information emitted cannot be attained without obstructing signal.

Other materials have been researched for this purpose, examples being nitrogen vacancies in diamonds as well as Gallium Arsenide [8]. However, these materials only emit at a specific wavelength or short range of wavelengths; rather, hexagonal Boron Nitride (hBN), an insulating material with a large bandgap, has recently been found to luminess over a wider range of over 200 nm in wavelength [2]. Also, hBN can emit at room temperature, whereas some other quantum emitters emit at low Kelvin temperatures [9]. This makes hBN a good candidate for possible single photon source application, and hence the purpose of this research on hBN is making and optically characterizing defects in the lattice structure.

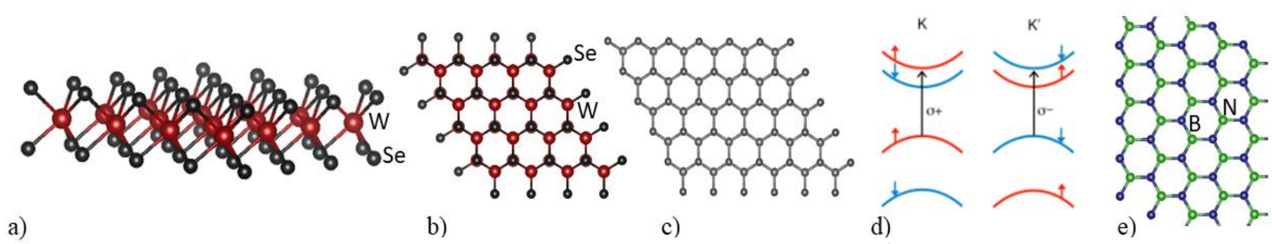

Figure 1. Introduction to researched materials. a) Tungsten Diselenide as seen from the side. Black atoms are Se, and red are W. This is monolayer WSe_2. b) WSe_2 as seen from top. c) Graphene as seen from top. Grey atoms are carbon. d) Band-gap for WSe_2. As shown, polarization selects which valley is populated. e) Hexagonal Boron Nitride, as seen from top. Blue atoms are boron, green atoms are nitrogen.
All atomic structure imaged using VESTA [10].

II. Methods

Hexagonal Boron Nitride flakes were drop-casted onto a Silicon/Silicon dioxide wafer using isopropyl alcohol. These were then visually characterized using a microscope (Fig. 2a). The sample was then annealed in vacuum to 850˚C for 30 minutes. An atomic layer of Chromium was deposited using Molecular Beam Epitaxy (MBE) while heating the sample to 400˚C to increase the energy of the system, trying to assist the formation of Chromium defects into the hBN lattice. Photoluminescence (PL) of the sample was taken with a continuous 532 nm 100mW diode laser to characterize the defect emission *in situ*.

For studying spin in heterostructures, graphene was partially overlapped with two WSe_2 flakes. These monolayer TMD flakes were grown using chemical vapor deposition (CVD) onto Silicon/Silicon dioxide substrate. The device had gold electrical contacts for applying a gate to the sample (Fig. 2b). The device was first characterized using PL with a 532 nm 100 mW diode continuous laser, with the beam being focused down to 1 micron with a power of 100 µW hitting the sample. Then the spin/valley lifetimes were investigated using time-resolved Kerr rotation (TRKR) with a linear probe and circular pump beam line from the same 150 fs pulsed laser (Fig. 1d). The pump would selectively populate valleys (K or K') depending on the rotation of the circularly polarized light, giving a local magnetic field for the sample. The linear probe pulses are then used to observe the Kerr rotation in the linear polarization axis. The linear probe is also sent through a delay line that physically changes the path length, changing the time between pump versus probe hitting the sample. This allows observation of the exciton decay.

During TRKR measurements, a gate of -30 V was applied to the sample to get p-type WSe_2, which has a longer spin/valley lifetime [11]. A Coherent mode-locked Pump Ti-Sapphire 18-watt laser was used

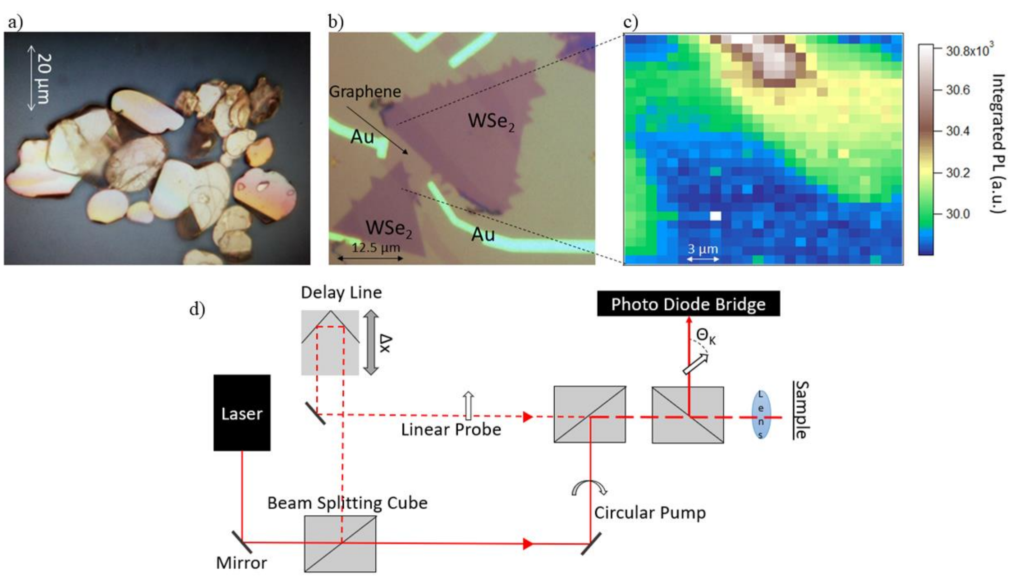

Figure 2. Compilation of methods. a) hBN flakes from drop-casting. Flakes are approximately 20 microns across, and 20 nm thick. b) Device made from CVD monolayer WSe_2 flakes, graphene, and gold contacts. c) A PL map to see the area of investigation on the device. Each box is 1 micron. d) TRKR set-up. Beam splitting cube splits the beam into pump and probe. Probe goes through a delay line and rejoins pump beam at sample with beam splitting cube.

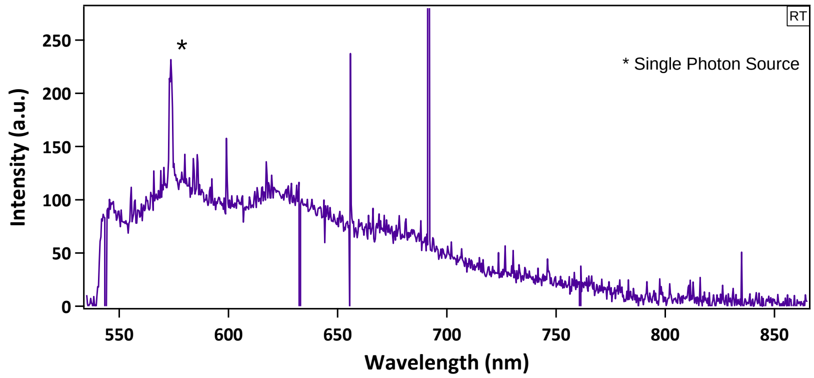

Figure 3. Photoluminescence of hBN defect. Point at 575 nm is thought to be a single photon source from previous literature and is labelled [2]. Peaks at 660 and 700 nm are noise from the spectrometer.

with a wavelength of 730 nm. The laser is focused down on the sample to 1 micron with a pulse power of 65 µW. Noise analysis was done with cascading lock-in measurement with a photodiode bridge.

III. Results and Discussion

PL was taken of the hBN to characterize defects in vacuum, which means the sample did not interact with air after annealing in the MBE chamber (Fig. 3). The PL from the post-annealed Cr deposited hBN showed a wide peak approximately around 550 nm to 750 nm. This is a defect, as the hBN lattice itself emits in the UV range. A large emission peak was found in 575 nm, which matched previous research's peak of a single photon source [2]. This suggests this peak is from a single photon emitter.

The polarization of the excitation beam's effect on the emission of the sample was also investigated. This was done by placing a ½ wave plate into the beam line, rotating the linearly polarized laser. The PL graphs were compared, and no correlation was found. Changes in the wave-plate affected the intensity of the

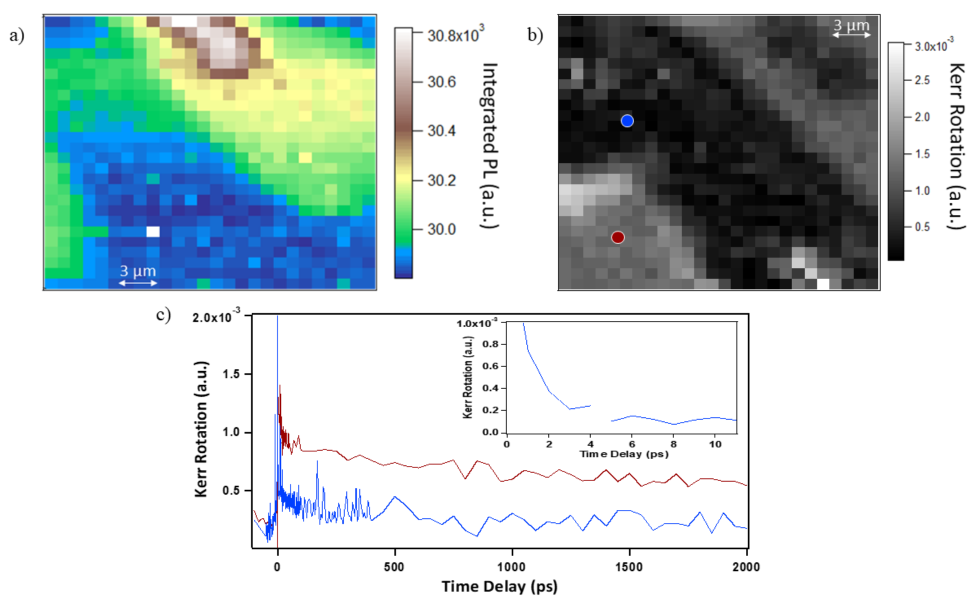

Figure 4. Graphene-WSe_2 heterostructures data. a) PL map taken between the two TMD flakes (Fig. 2). b) TRKR map run at 1 ps time delay. Bright spots correspond to longer lifetimes. Red dot is on the TMD flake, blue dot is on the graphene-WSe_2 overlap region. c) Time delay TRKR scans of the two spots shown on b (color-coded). The red line takes a couple of ns to decay, the blue takes less than 10 ps, as seen in inset graph.

incoming beam rather, and the results were not repeatable, suggesting that the polarization of the beam did not affect the emission of the sample.

For the heterostructures, a PL map (a map plotting the PL data of each spot in the region) was taken on the graphene-TMD overlap (Fig. 4a). It was found that the emission from the TMD was quenched where the graphene overlapped. To investigate this, TRKR was used to study the spin/valley lifetimes of the materials and the overlap. A TRKR map was taken at 1 ps delay to compare the exciton decay at different points on the device (Fig 4b). On the WSe_2 flake, the spin/valley lifetime was long: around or more than a couple of nanoseconds. However, on the graphene-TMD overlap the lifetime was significantly smaller: less than 10 picoseconds. The decrease in spin/valley lifetimes on the graphene-TMD overlap suggests that spins and charge carriers are moving from the WSe_2 into the graphene.

IV. Conclusions

Annealing and post-anneal Cr deposit causes hBN to have a single photon source at 575 nm. Further investigation could include comparison of different dopants deposited post-annealed with the same procedure. Further research could also include studying the polarization of the emission from the defects.

For the heterostructures, the spin/valley lifetimes were found to decrease on graphene/WSe_2 overlap compared to the TMD flake alone. This suggests movement of spins and charge carriers from the TMD flake into the graphene. This movement of spin and spin/valley polarization is important for device fabrication.

These two projects studied materials important in the field of spintronics with application in others. Single photon sources and heterostructures have potential application in device making, as well as understanding spins and defects in materials.

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VI. References

[1] A. Geim and I. Grigorieva. (2013). “Van der Waals heterostructures”. Nature (London) **499**: 419–425.

[2] T. Tran, et al. (2016). “Robust Multicolor Single Photon Emission from Point Defects in Hexagonal Boron Nitride”. ACS Nano **10**: 7331−7338.

[3] E. McCormick, et al. (2018). “Imaging spin dynamics in monolayer WS_2 by time-resolved Kerr rotation microscopy”. 2D Mater. **5**: 011010.

[4] K. Novoselov, et al. (2012). “A roadmap for graphene”. Nature, **490**: 192–200.

[5] T. Cao, et al. (2012). “Valley-selective circular dichroism of monolayer molybdenum disulphide”. Nat. Commun., **3**: 887.

[6] K. Mak, et al. (2010). Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. **105**: 136805.

[7] F. Volmer, et al. (2017). “Intervalley dark trion states with spin lifetimes of 150 ns in WSe_2”. Physical review B **95**: 235408.

[8] R. Marina, V. Jelena. (2018). “Quantum Photonics Incorporating Color Centers in Silicon Carbide and Diamond.” Archive.

[9] B. Zuerbig, et al. (2012). “Single-photon emission from single InGaAs/GaAs quantum dots grown by droplet epitaxy at high substrate temperature”. Nanoscale Research Letters, **7**:493.

[10] K. Momma, F. Izumi. (2011). "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data." J. Appl. Crystallogr., **44**: 1272-1276.

[11] P. Dey, et al. (2017). “Gate controlled spin-valley locking of resident carriers in WSe_2 monolayers”. Phys. Rev. Lett. **119**: 137401.