Two Dimensional Maps of Photoluminescence and Second Harmonic Generation

Tara Boland

University of North Dakota

University of Washington INT REU, 2014

Advisor: Xiaodong Xu

(Dated: August 31, 2014)

Abstract

Technology today demands smaller devices and thus there is a need for smaller components to these future devices. With semiconductors being the backbone of modern technology, there is a need for smaller and smaller semiconducting materials. After the discovery of graphene, other research into monolayer semiconducting materials began. Group IV transition metal dichalcogenides, or MX_2, became the interest of research groups because of its properties. The direct band gap in the monolayer limit, along with its two dimensional nature, make these materials interesting to study for future optoelectronic devices.

Introduction

The recent increase in better and smaller technology is due to the ever shrinking devices that recent science has made use of. What happens when we finally cannot get today's common technological circuits any smaller? There is some limit at which certain materials just cannot get any smaller and function property. Modern technology can only get so much smaller and information can only be processed so fast. What if there was a faster and safer way to compute and send information? Valleytronics could be that next generation of technology.

Valleytronics use the local minimum and maximum of the conduction and valence bands of special types of semiconducting materials to control the valley degree of freedom [1]. Materials which have shown to have promising physics, optically and electrically, are known as group IVB transition metal dichalcogenides. As a bulk, these materials have an indirect band gap and the 2D hexagonal MX_2 layers are loosely bound together by Van der Waals interactions, shown in Figure 1. This makes them easy candidates for mechanical exfoliation.

The bulk material has inversion symmetry; thus the physics of interest is only predicted to exist in thin films with odd number of layers where inversion symmetry is broken[2]. Monolayer MX_2 has a broken inversion symmetry which gives rise to interesting physics-like second order nonlinear optics, such as: second harmonic generation, strong light interactions, electrically controllable, novel spin physics and the valley hall effect.

The monolayer MX_2 specifically of interest in this paper are M = Mo, W, and X = Se, S. These materials form 2D hexagonal layers with trigonal prismatic molecular geometry, shown in Figure 2. Due

to the 2 dimensional nature of these monolayers, when electrons are excited into the conduction band leaving a hole in the valence band, the electron hole pair experiences a strong attractive Coulomb force forming a strongly bound exciton caused by the monolayers confining the excitons to three atomic layers.

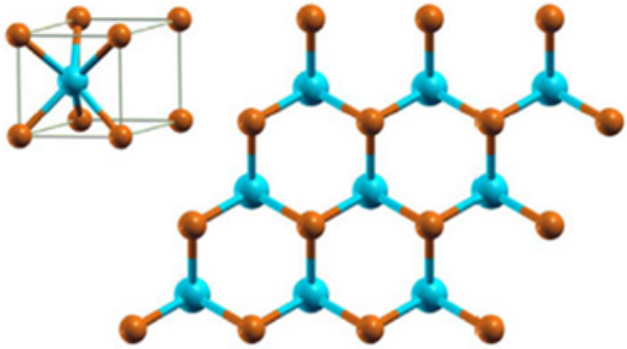


Figure 2- Crystal structure of MX_2 where the blue sphere is the metal atom and the orange sphere is the chalcogenide atom. Top left diagram is the trigonal prismatic molecular geometry. The right figure is the hexagonal lattice structure that MX_2's forms.

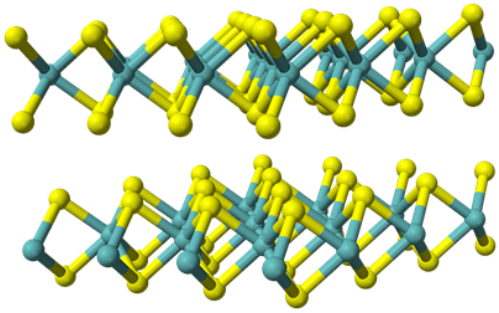


Figure 1- Crystal lattice structure of bulk MX_2's weakly bonded by Van der Waals forces between layers but strongly covalently bonded between atoms.

Two of the important properties of these materials are the degenerate direct band gaps that form at the corners or ±K points of the hexagonal Brillouin zone and have a band gap present in the visible range which are important for future detectors and optoelectronic devices. The degeneracy in these materials has shown that valley polarization of the K points can selectively absorb and emit right or left circularly polarized light. Since MX_2 has degenerate band gaps, there is an opportunity to use this property of these 2D materials as a way to manipulate the valley index using optical means and thus providing a new form of technology which uses polarized light[2].

1.1 Monolayer MX_2

Recent interest in monolayer semiconductors came about after the discovery of graphene. The appeal of monolayer MX_2 is that they have interesting and different physics than their bulk, many layered, counterparts. There is potential for applications in new optoelectronic devices because of their wide range of interesting optoelectronic properties in monolayer limit, like strong interactions with light, electrical controllability and novel spin physics. These properties could be applicable in LEDs, solar cells, nano-lasers or quantum information processing.

The 2-dimensional nature of these semiconductors leads to a tendency to form strongly bound excitons because the electron hole pair is confined to the monolayer. Excitons are created when a photon is absorbed by an electron in a semiconductor and it is excited into the conduction band. This leaves a positive hole in the valence band and a negative charge in the conduction band, which are attracted by the Coulomb force. Excitons are strongly polarizable which gives an optical means of control. MX_2's can also be attached to a gate voltage, which allows electrical control over the formation of the types of exciton species that form. MX_2's can be optically controlled using left or right circularly polarized light to control the valley polarization.

One of the most important properties of these monolayers is the broken inversion symmetry that occurs in odd number thin layers. This directly leads to second order nonlinear optical effects like second harmonic generation (SHG). The strongest second order nonlinear optical effects occur in the monolayers. Though it is possible to stack monolayers in such a way as to not restore inversion symmetry and thus creating a means to effectively double the second order nonlinear optical effect. Without the broken inversion symmetry in the MX_2's, second order nonlinear optics like SHG would not be possible in these materials.

1.2 Second Harmonic Generation

There are three types of frequency generation: sum frequency generation, difference frequency generation and second harmonic generation[3]. Second harmonic generation is created by a second order nonlinear optical effect known as frequency doubling and is a special case of sum frequency generation[4]. SHG has a few conditions that must be met in order to occur. The material must be non-centrosymmetric or lack inversion symmetry. Two photons of the same frequency interacting with a nonlinear medium of this type will effectively combine to create new photons with twice the energy, twice the original frequency, and thus half the wavelength [4]. Creating second harmonic generation requires a high energy laser because the atomic response scales quadratically with the applied optical field. Thus the intensity of light generated at the second harmonic frequency tends to increase as the square of the intensity of the applied laser light[3].

Second harmonic generation is useful for producing new frequencies of coherent radiation, a purely optical probe that gives an inherent surface sensitivity comparable to the best electron spectroscopies or scanning tunneling microscopy. Some uses for SHG in MX_2's are its ability to be an optical probe for determining the polarization axis within crystals, the stacking order of crystals, the quality of chemically grown samples, defects and layer thickness. One of the uses for this is stacking heterostructures and multilayers to investigate the effects that the stacking order has on the optoelectronic properties. SHG is a useful and fast way to determine many properties of a sample and can greatly assist in research with growths and creating heterostructures.

1.3 Photoluminescence

There are many forms of luminescence from matter. Photoluminescence (PL) comes from a process in which a material absorbs photons and then re-radiates photons at a different wavelength. Photoluminescence is light emission from any form of matter. Quantum mechanically, this can be described as a jump to a higher energy state followed by a transition to a lower energy state by the emission of a photon.

MX_2 are amazing in the fact that even though they are only three atomic layers, they absorb about 10% of light and strongly emit photons. Photoluminescence is useful for quickly determining the purity and crystalline quality of materials [6]. Photoluminescence can also be used to determine if samples are mono-, bi-, or tri-layers, because photoluminescence from monolayers is stronger than photoluminescence from bi- or tri-layers. As you can see in Figure 3.

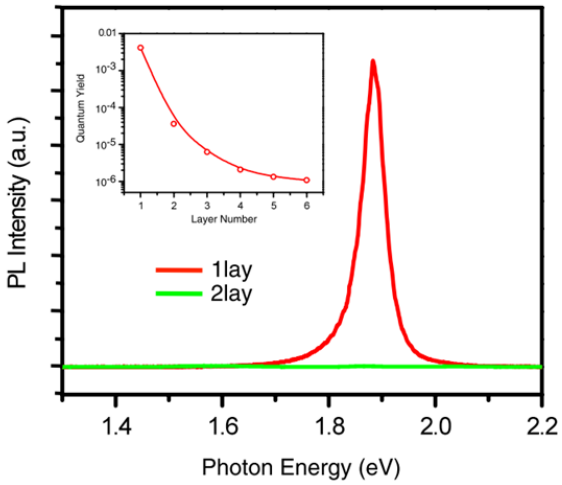


Figure 3- A photoluminescence spectra with PL Intensity vs Photon Energy (eV). The red line represents a monolayer of WSe_2 and the green line represents a bilayer of WSe_2.

This makes photoluminescence a tool useful for investigating defects in growths. It is also a nondestructive technique to investigate properties of materials like MX_2's.

2.1 Two Dimensional Scanning Photoluminescence and Second Harmonic Set-up

My goal for the summer was to design a setup, using some basic optical theories, such as how lenses bend light, focal planes and focal lengths, that was capable of scanning over a two dimensional area. The only moving part of the entire setup was to be a scanning mirror which consisted of 2 silver mirrors, one horizontal and the other vertical, controlled by an input voltage which would cause the scanning over an area.

The theory behind the scanning mirror and lenses is easily shown in Diagram 1.

Diagram 1- Take the beams origin to be the scan mirrors and the plane at which the light is reflected back through the beam path to be the MX_2 sample.

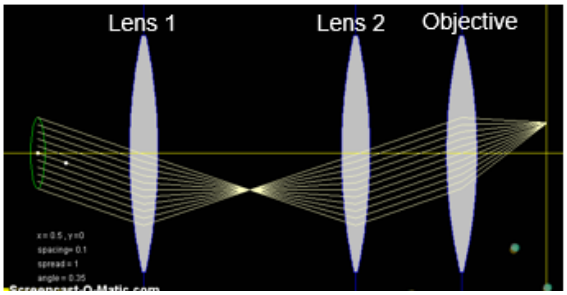
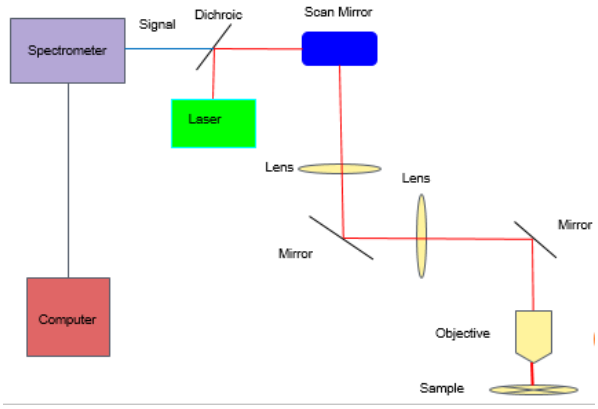


Diagram 2- Schematic for the PL/SHG setup



As the mirrors on the scanning mirror move, the laser beam is displaced. The laser beam hits lens 1 and is focused down to a point on the focal plane. Lens 2 is placed a distance equal to it's focal length away from the focal plane of lens 1; thus collimating the light and creating a focal plane that never moves on the back of the objective lense. This allows the laser beam to scan over the sample while being fixed on the back of the objective lens. After the signal was de-scanned by the scanning mirrors, it was passed by a dichroic mirror and sent to the spectrometer to be analyzed. The schematic of my set up is shown in Diagram 2. The scan mirror voltage is controlled by a LabView program which also sent out an external sync pulse to the CCD that controlled the spectrometer. Another program collected the spectra from the spectrometer which was then exported and analyzed in MATLAB to create the 2-dimensional images. The spectra collected, similar to those shown in Figure 5, are made into a 2-dimensional map of the sample.

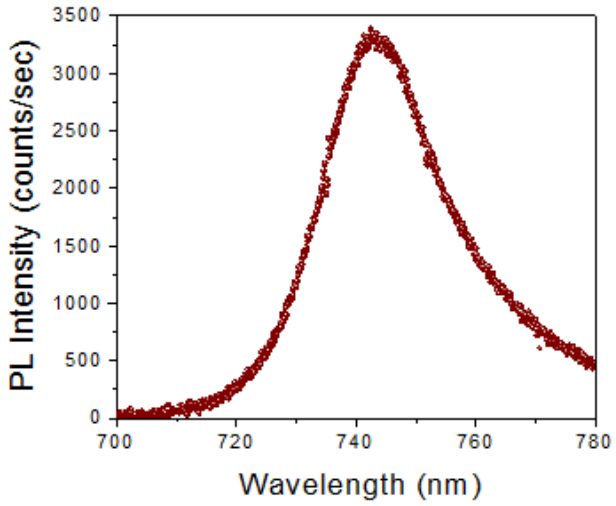


Figure 4- A photoluminescence spectra taken of WSe_2.

2.2 Results

The SHG scans are capable of resolving defects approximately one to two microns in diameter. Looking at the microscope image in Figure 6, we can see cracks in the crystal structure along with the stacking of the single crystals. One property that is of interest to investigate in the crystal is how the stacking order affects certain properties like exciton binding energy. Second harmonic generation, as stated earlier, can detect stacking order within crystals from the intensity of the second harmonic generation. Here, one can see that inversion symmetry is not restored where the crystals overlap and thus the crystal's order is AA stacking, which results in an increase in intensity and a brighter region. Figure 7 shows this more intense region where the AA stacking occurs. The SHG image also shows defects in the crystal structure that may not be visible under a microscope.

Since SHG can be used to examine defects in crystal structure, below in Figure 6 is a microscope image of WSe_2 coined "The Hanging Bat" for its similarity to a bat. In the microscope image of this sample, seems to have a uniform thickness with cracks along the wing of the bat. While this may look uniform, the SHG scan appears to show a thinner, less intense SHG signal indicating possible crystal defects and layer thickness.

Figure 6- Microscope image of WSe_2 "The Hanging Bat" "The Hanging Bat"

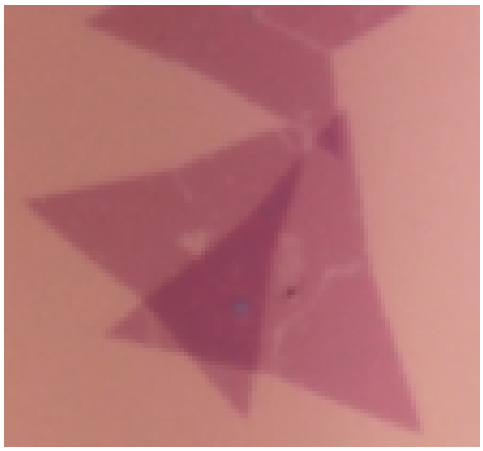
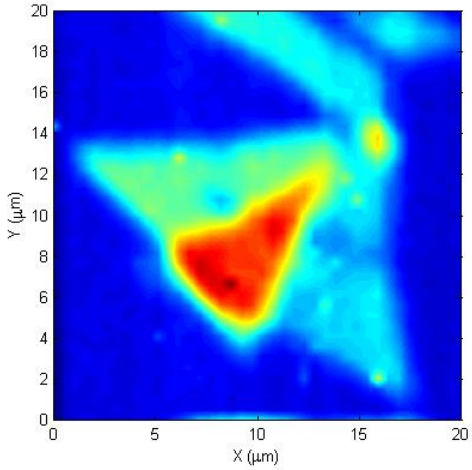


Figure 7-Second Harmonic Generation from WSe_2



The major limiting factor in the resolution of the SHG image is the diffraction limit, but it is not the only factor in obtaining a well defined image. Pixel density is also important. Figure 8 is a microscope image of a single crystal stacked on top of a snowflake-like crystal which is composed of single crystals rotated 60 degrees between each point. Figure 9 and Figure 10 show the difference between 2 pixels per micron from 4 pixels per micron, respectively.

Figure 8- Microscope image

Figure 9- SHG map with 2 pixels per micron

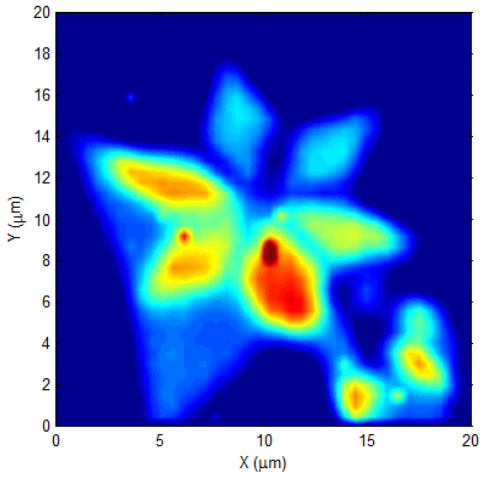
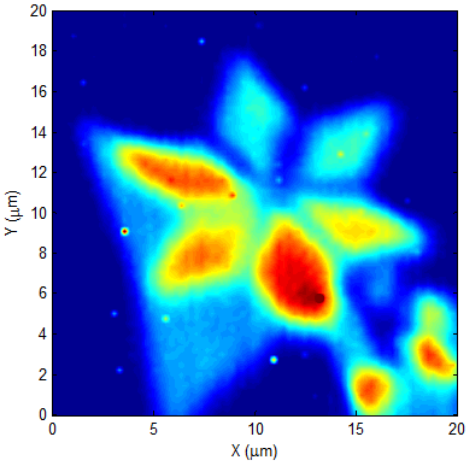


Figure 10- SHG map with 4 pixels per micron



2.3 Future Work

The 2D maps of SHG and PL can effectively resolve defects and cracks in the crystal structure that are on the order of a few microns. To better improve the resolution of the image, certain techniques can be employed, such as lowering the diffraction limit and thus decreasing the beam spot to resolve defects in the crystal structure on the order of a micron or less. This can be done by either increasing the index of refraction or decreasing the wavelength of the excitation beam. Another hope for the SHG

setup is to be able to do polarization-resolved SHG to be able to determine the polarization axis of the samples. This would be useful for investigating the effects that the polarization axis would have on exciton formation in heterostructures.

4 Conclusion

The unique properties of group IV transition metal dichalcogenides, like their broken inversion symmetry and strong interactions with light in the monolayer limit, has given a new way to investigate the effects that polarization has on excitons. SHG also allows for a new way of investigating the polarization axis of these monolayers with interest of stacking monolayers to observe the effects it has on exciton formation. Being able to construct a 2-dimensional map of the polarization axis would give invaluable information for stacking heterostructures.

5 Acknowledgements

I would like to thank Xiaodong Xu for letting me work with his group this summer. I obtained a lot of invaluable experience. I would also like to thank Deep Gupta, Alejandro Garcia, Janine Nemerever and Linda Vilett for organizing the REU program, and the NSF for funding.

Citations

[1] "Valleytronics." *Wikipedia*. Wikimedia Foundation, 6 June 2014. Web. 12 Aug. 2014. <http://en.wikipedia.org/wiki/Valleytronics>.

[2] Jones,, Aaron, and Hongyi Nirmal J. Ghimire, Sanfeng Wu, Grant Aivazian, Jason S. Ross, Bo Zhao, Jiaqiang Yan, David G. Mandrus, Di Xiao, Wang Yao & Xiaodong Xu Yu. "Optical Generation of Excitonic Valley Coherence in Monolayer WSe_2." *Nature Technology* 8.9 (2013): 634–638. *Nature Nanotechnology*. Web. 14 Aug. 2014. <http://www.nature.com/nnano/journal/v8/n9/full/nnano.2013.151.html>.

[3]Boyd, Robert W. "The Nonlinear Optical Susceptibility." *Nonlinear Optics*. 3rd ed. Amsterdam: Academic, 2008. 1-58. Print.

[4]"Second-harmonic Generation." *Wikipedia*. Wikimedia Foundation, 13 Aug. 2014. Wegb. 27 Aug. 2014.

[5]http://depts.washington.edu/xulab/wordpress/wp-content/uploads/2012/03/Coupled-Spin-Valley-Physics-Xu.pdf

[6] "Photoluminescence." *Wikipedia*. Wikimedia Foundation, 24 Aug. 2014. Web. 27 Aug. 2014.