

Monolayer Semiconductors

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Abstract

Silicon may be unable to continue serving as the backbone for future technologies. The search for silicon replacements has led to the investigation of thin 2-D materials. Some of these materials are single layers of group VI transition metal dichalcogenides. Through mechanical exfoliation, these materials can be isolated and used to construct monolayer field effect transistors. A transfer process can be used to control the placement of monolayers and exfoliated samples. Investigation of the photoluminescence of these materials has shown that they possess strong electrical tunability in the form of electrostatic doping, and that quantum coherence may be generated between the states associated with the 2-D hexagonal Brillouin zone corners. It is suggested that an improved transferring process be sought after in order to further investigate the properties of these materials.

1 Introduction

Advancements in computing technology have been made at an exponentially rapid rate over the past century. This is due to the ability of manufacturers to continue miniaturizing and improving silicon-based transistors on integrated circuits and microchips. However, it is believed that the limit of miniaturization for silicon will be met sometime in the near future. Because of this looming obstacle, a search for new materials and methods has begun in order to have future technologies built around them.

Some materials being considered are 2-D materials, which consist of a single layer of atoms or molecules and have thicknesses on the order of nanometers.

One of the first of these materials to be successfully and reliably isolated is graphene, which has received a lot of attention due to the fact that it is relatively easy to fabricate. However, pristine graphene does not have a band gap, which is an important property of semiconductors that allows for the control of the conductivity of a device. Recently discovered semiconducting 2-D materials are group VI transition metal dichalcogenides, which possess a direct band gap in the visible frequency range. Figure 1 shows the 2-D hexagonal lattice structure that these materials possess, which is similar to the lattice structure of graphene. Layers of this material stack in such a way that causes inversion symmetry in bulk form. They are loosely

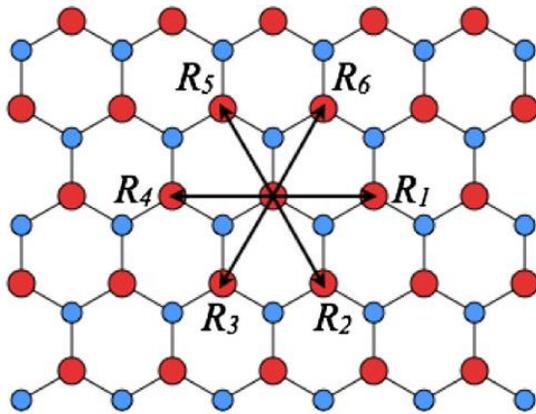


Figure 1: Top view of a monolayer of a MoSe_2 monolayer. Red circles represent Mo atoms, and blue circles represent Se atoms. [1]

bound together by Van der Waals interactions, which allows for mechanical exfoliation of these materials. However, as shown in Figure 2, the layers of these materials break inversion symmetry, which differentiates it from graphene.

The conduction and valence band edges of these materials are located at the K points of the Brillouin zone, which are inequivalent valleys that may be used as a binary index for charge carriers, and are coupled to photon polarization. The valley physics of these materials differs from graphene in that the dichalcogenides also possess strong spin orbit coupling that causes spin splitting at the top of the valence bands [1]. By fabricating field effect transistors with these materials and investigating their photoluminescence, the electrical tunability and valley physics of these materials can be observed.

2 Monolayer Transistors

2.1 Exfoliation

Due to the weak Van der Waals interactions between layers of these

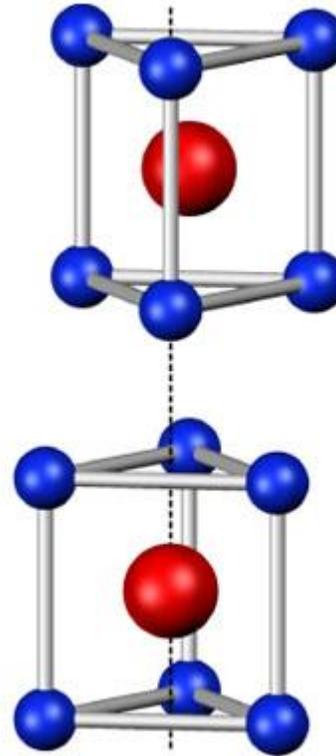


Figure 2: The stacking structure of layers of MoSe_2 where Mo atoms are represented by red spheres and Se atoms are represented by blue spheres. [1]

materials, mechanical exfoliation can be used to begin fabricating devices with monolayers of these dichalcogenides. Mechanical exfoliation is carried out by sticking flakes of bulk samples onto a tape, and then sticking this tape onto some kind of Silicon wafer. When the tape is peeled off, single layers of the dichalcogenides may peel and stick onto the wafer.

Once a tape has been peeled off of a wafer, the wafer is then placed under an optical microscope. These monolayers are visible under an optical microscope, which is a useful property when searching for them. The surface of the chip is visually scanned under 20x magnification, and monolayers that are found have their location marked and mapped out for future retrieval.

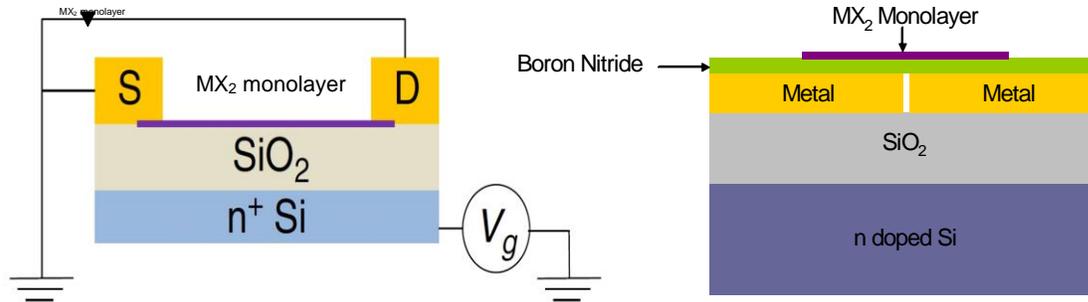


Figure 3: Two different field effect transistor designs. The first one on the left is a monolayer on top of approximately 300 nm of Silicon Dioxide, which is an insulating material [2]. The second design on the right is a monolayer on top of approximately 10 nm of Boron Nitride – an insulating material – placed on top of prepared gates. This design requires that samples be transferred to their desired location from separate wafers.

2.2 Designs

Two designs of field effect transistors that are currently being used to investigate the properties of these dichalcogenides can be seen in Figure 3. Both designs incorporate an insulating material that serves as a gate dielectric that avoids shorting out the monolayer sample to the bottom gate. Metal contacts were then fabricated using electron beam lithography. These contacts are connected to the monolayer, and then grounded.

Applying a voltage across the drain and gate causes an electric field to form between them. This field effect can be used to electrically control the monolayer in the form of electrostatic doping. The distance between the gate and monolayer is also inversely proportional to the strength of the electric field that is generated, so the design with the thinner gate dielectric of Boron Nitride can generate a stronger field effect and may allow stronger electrostatic doping to be achieved.

2.3 Transfer Process

Exfoliated samples of Boron Nitride and dichalcogenide monolayers can be

placed more selectively through a transfer process. The process begins by preparing a Silicon wafer with a layer of polyvinyl alcohol spun on top of it, followed by a layer of polymethyl methacrylate. This wafer can then be exfoliated onto and visually scanned very similarly to any other mechanical exfoliation. Samples that are found on this wafer have a square cut around them, approximately a square centimeter in area. The square can then be placed in water where it will float.

The polyvinyl alcohol is water soluble, causing the middle layer of polymers to dissolve. The polymethyl methacrylate is not water soluble, so it will remain floating with the exfoliated samples on top of it while the Silicon wafer sinks to the bottom of the water. The floating membrane can then be scooped with a loop device to hold it. This loop can then be placed in a manipulating device that allows for placement of samples to be controlled in windows of space with dimensions on the order of micrometers. This transfer process allows for levels of control over the placement of samples to the point where the construction of devices such as the second design shown in Figure 3 are possible, even if the monolayer,

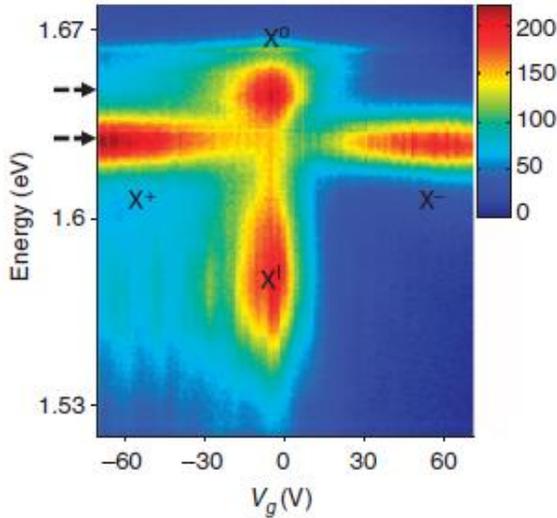


Figure 4: The photoluminescence of a Molybdenum Diselenide monolayer excited by a 1.73 eV laser at temperature of 30 K. The vertical axis is the energy of the emission detected. The horizontal axis is the voltage applied across the gate. The intensity of the detected emission is indicated by the color scale on the right [2].

Boron Nitride, and gate are all on three separate wafers.

3 Electrical Control and Optical Generation

3.1 Excitons and Trions

Electrons that are excited into the conduction band of a monolayer dichalcogenide leave a hole with a positive charge in the valence band. These two particles can bind together to form a neutral exciton. If the monolayer has free electrons or holes in it, then an extra particle may bind with the exciton to form a charged trion. By optically exciting a monolayer sample in a field effect transistor and allowing excitons and trions to form and then recombine and emit light, the electrical tunability of monolayer dichalcogenides can be investigated.

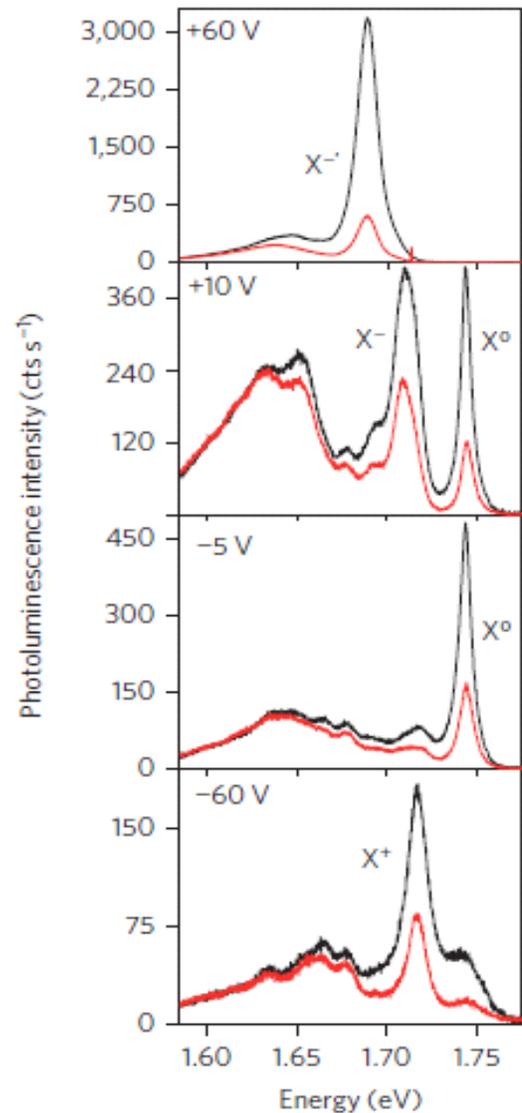


Figure 5: Polarization resolved photoluminescence of a monolayer of Tungsten Diselenide at various gate voltages. Samples were excited with right circularly polarized light at energy of 1.88 eV at a temperature of 30 K. The black curves are the detected right circularly polarized light, and the red curves are the detected left circularly polarized light [3].

The tunability of these materials is illustrated in Figure 4. Applying a negative gate voltage to a monolayer field effect transistor will cause a gas of free holes to form, and allows for the

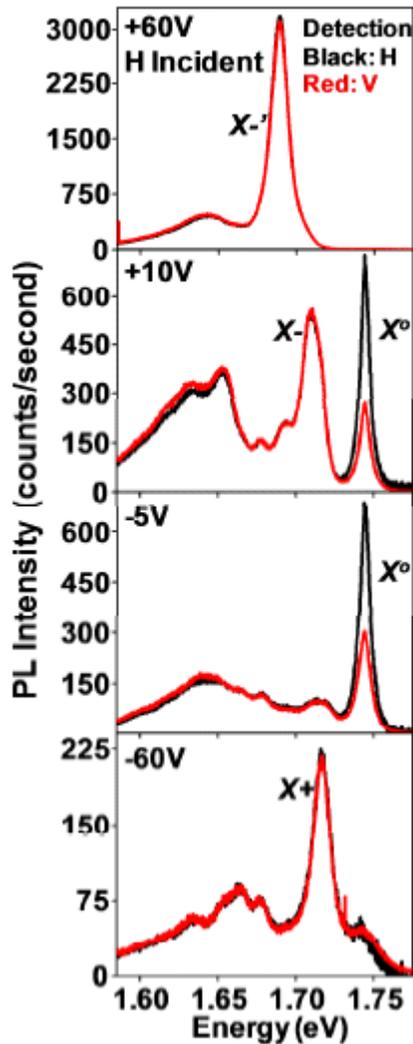


Figure 6: Polarization resolved photoluminescence of Tungsten Diselenide at various gate voltages. Samples were excited under linearly polarized light with an angle of polarization horizontal to some arbitrary axis. The black curves are the detected horizontal linearly polarized photoluminescence, while the red curves are the detected light with an angle of polarization vertical to the arbitrary axis. These curves show that only the exciton has highly linearly polarized photoluminescence [3].

formation of positive trions and a p-type doping to occur in the material. The more negative the voltage is, the

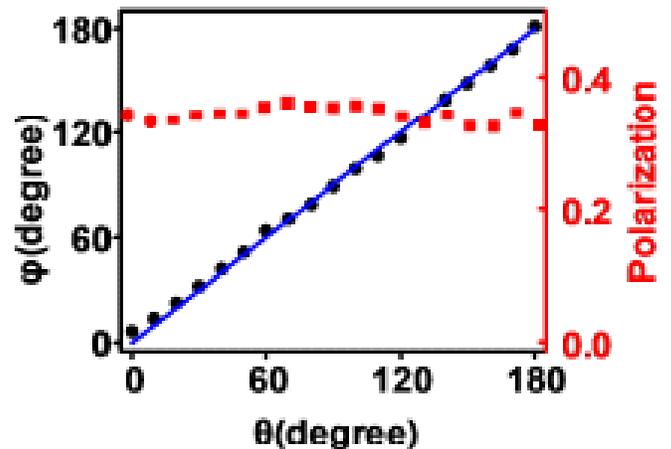


Figure 7: The black dots and blue line plot the angle of polarization for the detected photoluminescence versus the angle of polarization of the incident light used for excitation of a Tungsten Diselenide monolayer. This illustrates the isotropy that these materials possess. The red dots are the degree of polarization versus the angle of polarization of the incident light [3].

stronger the positive trion emission peaks become. A similar situation occurs when applying a positive gate voltage, favoring more negative trions as a more positive voltage is applied. The emission of the neutral exciton is strongest near a gate voltage of zero volts.

The difference in energy of the emission peaks of the trions and exciton are similar, implying that the both trions have similar binding energy and effective mass. All peaks are also at nearly identical intensities, implying that there is a conservation of the total number of excitons and trions in the system. Using this data, it may be concluded that these 2-D semiconducting possess strong electrical tunability in the form of electrostatic doping.

3.2 Polarized Photoluminescence

The valleys that form in the band structure of these materials at the corners of the 2-D hexagonal Brillouin zone are coupled to photon polarization for photo excitation. As shown in Figure 5, the photoluminescence detected from monolayers of dichalcogenides is also highly circularly polarized. When right circularly polarized light is incident upon the sample, more right circularly polarized light is detected from emissions of both trions and the exciton than left circularly polarized light.

Another interesting observation comes from the use of linearly polarized light for excitation. As shown in Figure 6, only the exciton exhibits strong linear polarization, while both trions do not. Linear polarized light is a superposition of right and left circularly polarized light, so it is possible that this linearly polarized emission is caused by the superposition of coupled right and left circularly polarized light generated in the two valleys of the band structure.

As shown in Figure 7, the angle of polarization emitted by the exciton is equal to the angle of polarization of incident light for all angles, and the degree of polarization is also equal for all angles of polarization. Similar properties have been observed in other crystals before, but have always required some kind of anisotropy in their structure and depended on wave propagation direction. In the monolayer, it is believed that these properties are isotropic which is believed to be unique amongst all known solid state systems.

3.3 Future Work

Because the transfer process allows for fairly well controlled placement of monolayers and other samples, further investigation of other heterojunctions may be sought. These heterojunctions may be different monolayers of different dichalcogenides stacked on top of one other. Another kind of heterojunction that may be constructed may involve

placing Boron Nitride on top of the monolayer field effect transistors in Figure 4. This top layer of Boron Nitride may act as a gate dielectric material for a top gate that could allow for stronger electrostatic doping of the monolayers.

Along with the increased control of sample placement, this transfer process also introduces more residue to devices. Therefore, an improved transfer process may be sought. Improvements may not only include fixing the residue problems; they could include making the transfer process simpler and more reliable.

4 Conclusions

The weak Van der Waals interactions between layers of these group VI transition metal dichalcogenides allow them to be mechanically exfoliated for the purpose of finding monolayers. This is a relatively easy method for isolation and fabrication of 2-D materials which has led graphene to receive a lot of attention in the past. However, these dichalcogenide monolayers also have properties that differentiate them from graphene and may be useful in future technological applications.

The direct band gap and strong electrical tunability that these materials possess makes them good candidates for future optoelectronics. The valley physics inherent to these materials may also be exploited for future quantum logic devices.

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