

Use of micromechanical exfoliation of bulk graphite and MoS₂ to establish a graphene/MoS₂ junction

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Abstract

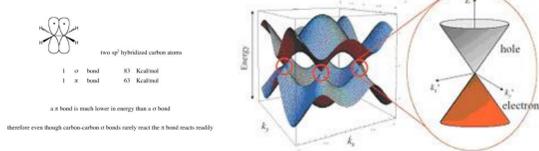
The goal of this study is to explore the properties of a graphene/MoS₂ junction using photoconductivity measurements. To begin, micromechanical exfoliation via the scotch-tape method has been used to obtain monolayer and few layer thick flakes of graphene and MoS₂. Optical and Raman microscopes have been used to determine whether the flakes are one atomic layer thick. Using the same cleavage process as for cleaving bulk graphite and MoS₂, graphene and MoS₂ will be cleaved separately and then a single-layer graphene will be placed on the top of a single layer MoS₂ through a microposition alignment setup to create a junction between the two single-layer flakes. This mixture will be deposited onto the SiO₂/Si substrate. This will form a Schottky barrier between the graphene, a semimetal and MoS₂, a p-type doped semiconductor. Electrodes will then be deposited connecting to both materials on the silicon wafer. Analysis of the electronic transport properties and photon-electron conversion of the graphene/MoS₂ junction will allow for further research into the potential usage of such a device in photovoltaics, transistors, and optoelectronic devices.

Background and Introduction

2-D atomic materials have been studied extensively in recent years for their potential usage in microelectronic processing and the semiconductor industry [1]. Two such promising 2-D materials are graphene and molybdenum disulfide (MoS₂). Graphene is classified as a semimetal having high mobility, conductivity, and mechanical stiffness and strength [2]. MoS₂ is a semiconductor, which is thin and optically transparent in its single layer form [1].

Band Structure of Graphene

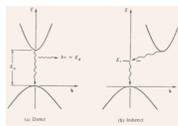
- Graphene contains two carbon atoms per unit cell. Two carbon atoms bonded together in graphene forms the sp² hybridization from one s and two p-orbitals [3].



- Graphene is composed of non-interacting π and π^* states. The π states form the valence band while the π^* states form the conduction band [4].
- The bands of graphene touch at six points, called Dirac points. These points are reduced to two points, K and K', due to symmetry. It is because the bands touch at this Dirac point that graphene is called a zero-bandgap semiconductor. Due to symmetry about the Dirac point, electrons and holes in pure, free-standing graphene should exhibit the same properties [4].

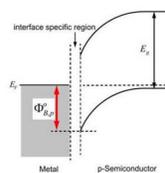
Band Structure of MoS₂

- Single layer MoS₂ is a direct bandgap semiconductor with a bandgap of 1.8 eV [1]. In direct bandgap semiconductors, the minimum of the conduction band and the maximum of the valence band occur at the same value of wave number, k ($k=2\pi/\lambda$). This means that the electron and hole can combine with no loss or gain of momentum and give off a photon with $E_g = h\nu$ [5].



Graphene/ MoS₂ Junction Properties

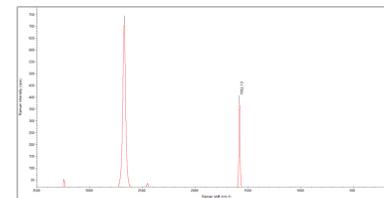
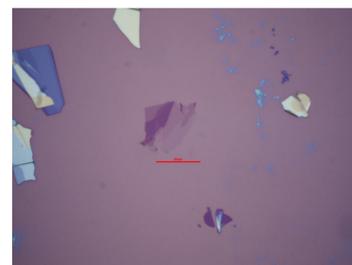
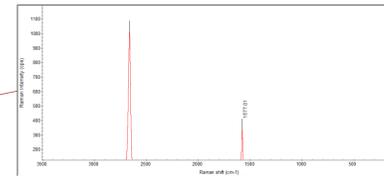
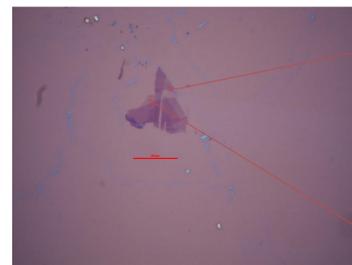
- Graphene acts as a metal while MoS₂ acts as a p-type semiconductor in a junction formed between the two materials. In this junction, the valence and conduction bands will bend upward (negative curvature) due to mismatch in Fermi energies of the metal and the p-type semiconductor [6].
- The potential difference across the junction establishes an electric field between the two materials.
- In a p-type semiconductor, the depletion region contains negative immobile charges. There is no obstruction for electron motion from metal to p-type semiconductor or vice versa, but there is a Schottky barrier for hole motion.



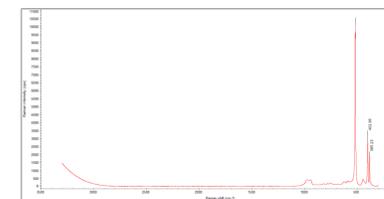
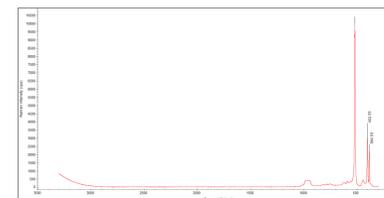
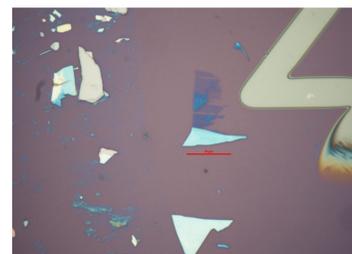
Results and Discussion

Graphite flakes were obtained from Asbury Carbons, Inc. A small MoS₂ crystal was obtained from SPI Supplies. Patterned SiO₂/Si wafers were prepared using photolithography techniques. This allowed for easier location of areas containing graphene and MoS₂ under an optical microscope. Micromechanical exfoliation was used to obtain single layers of MoS₂ and graphene. In this method, flakes of bulk graphite (or MoS₂) are deposited onto a piece of scotch tape. The scotch tape was folded together several times, separating individual layers of bulk material and then placed face down onto an SiO₂/Si wafer. After that, the graphene (or MoS₂) was "scratched" onto the SiO₂/Si wafer using a plastic tool for about two minutes. The tape was peeled from the wafer very slowly, for about one minute. A Nikon optical microscope was then used to identify the locations on the wafer containing graphene (or MoS₂) single layers. A DXR Raman microscope was used to verify the thickness of the graphene and MoS₂ layers.

Obtaining Graphene

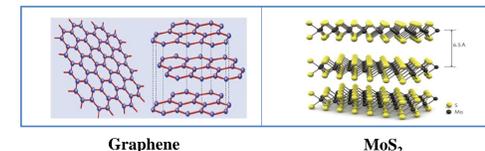


Obtaining Single Layer MoS₂



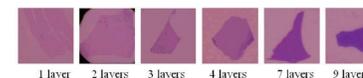
Differences in cleaving graphene and MoS₂

- Single layer graphene appears lighter on the microscope compared to single layer MoS₂ because of larger layer thickness of MoS₂ to graphene [1, 10].
- Graphene cleaves more easily via scotch tape method than MoS₂, yielding larger and a greater density of flakes on a given substrate.



Trends in Raman Spectroscopy for graphene

- The Raman spectra of graphene includes a G peak at ~1580 cm⁻¹ and a so-called G' band at ~2700 cm⁻¹ [7].
- The G peak decreases in intensity (height) as the number of layers decreases.
- The G' peak becomes sharper (narrower) and increases in intensity as the number of layers decreases.
- Characterizing the intensity and sharpness of the G' band is a more reliable method of determining whether a flake is single-layer than by viewing the G peak.



Change in contrast under an optical microscope with increasing number of graphene layers [8].

Trends in Raman Spectroscopy for MoS₂

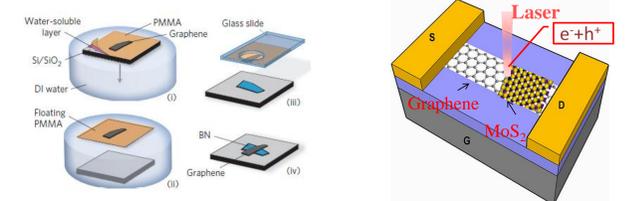
- The two primary peaks for molybdenum disulfide are located at 383 and 408 cm⁻¹ [9].
- The peak for silicon should be at ~521 cm⁻¹.
- The peak at 408 cm⁻¹ shifts to 403 cm⁻¹ for single layer MoS₂ [9].
- The intensity of the peaks decreases (peaks get shorter) as the number of layers decreases.
- This is noted by lighter relative contrast of a flake on SiO₂/Si substrate.

Conclusions

Micromechanical exfoliation (cleavage) is a successful method for obtaining single and few layer thick flakes of graphene and MoS₂. An optical microscope enables the user to clearly decipher the relative thicknesses of different graphene and MoS₂ flakes deposited onto the SiO₂/Si substrate. Trends noted in the Raman spectrum for graphene and MoS₂ are accurate for confirming the thickness of the flake being viewed under the Raman microscope. Using these analytical tools, similar procedures can be carried out to obtain and successfully identify single layer flakes of graphene and MoS₂. Knowledge of the Raman spectrum and successful identification and fabrication techniques is critical to enable these two materials to be incorporated into future microelectronic devices.

Future Work

- Micromechanical exfoliation has been a method proposed to form a junction between graphene and MoS₂. In this method, two pieces of scotch tape are prepared. The materials are cleaved separately until they were ready for deposition onto the SiO₂/Si substrate. Instead of depositing flakes onto separate wafers, the two pieces of scotch tape are rubbed together, mixing the graphene and MoS₂ flakes. One of these tapes is used to "scratch" the mixture onto a SiO₂/Si substrate. This method sounds plausible, however, the probability of obtaining a single layer of both graphene and MoS₂ that are crossing- forming a junction- and could have electrodes attached to either side of the flake is very low.
- An alternative method for forming a junction between the two materials has been identified and could be modified to fit the requirements of this study [11]. This method is shown schematically below. The only difference in this study is that BN will be replaced with MoS₂ on the SiO₂/Si substrate.
- E-beam lithography will be used to deposit electrodes and form the device.
- Photoconductivity measurements will be made on the device.



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Acknowledgements

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