Impact of radiation on the electronic structure of MoS_2

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Electrons in a semiconductor occupy states within certain energy ranges, called energy bands. The position of the Fermi level with respect to these energy bands determines the charge carrier type of the semiconductor. Molybdenum disulfide (MoS_2) is a two-dimensional, *n*-type semiconductor with potential applications in flexible electronics, transparent electronics, and optoelectronics. Electronic devices containing MoS_2 could be used in environments where radiation affects device performance. Thus, it is important to determine the impact of radiation on MoS_2. A one-molecule-thick layer of MoS_2 (monolayer) and a two-molecule-thick layer of MoS_2 (bilayer) were placed onto different areas of a gold (Au) substrate containing 1.2-µm-deep holes. The MoS_2 was suspended over these holes but supported by the Au elsewhere on the substrate. This sample configuration was used to determine the

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effect of He^+ radiation on the electronic properties of the suspended MoS_2 and the Au-supported MoS_2. The MoS_2 was irradiated by He^+ ions in two stages. The energy bands of the MoS_2 were measured with respect to the Fermi level via photoelectron emission microscopy before irradiation and after each irradiation stage. From each measurement, the charge carrier type of the MoS_2 after the corresponding irradiation stage was determined. The Fermi levels of the suspended monolayer and bilayer decreased by ≈0.15 eV with respect to the bands during the first irradiation stage During the second irradiation stage, however, the Fermi levels didn't change significantly. This lack of change supports the existence of a radiation threshold, above which the electronic properties of suspended MoS_2 remain the same. The Fermi levels of the supported monolayer and bilayer increased over the cumulative irradiation and didn't show evidence of a threshold. Thus, suspended MoS_2 becomes less *n*-type as it is irradiated. Supported MoS_2, however, becomes more *n*-type as it is irradiated. These results could inform the development of radiation tolerance standards for MoS_2, and thus, radiation-tolerant MoS_2-based electronics.

INTRODUCTION

Electrons in a material may exist in only certain quantum states. The energy values of these states are grouped into ranges. These energy ranges are called energy bands [1]. As shown in Figure 1, electrons will occupy the lowest-energy states in the bands, filling the bands in increasing order of energy. The bands in different materials exist in different ranges of energies; that is, the band structure of each material is different.

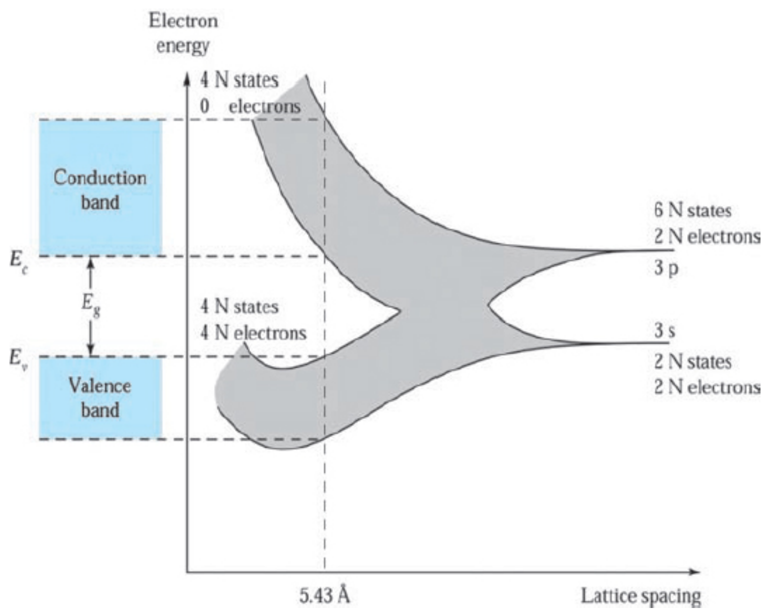

Figure 1: Diagram of electron energy states in silicon (Si) atoms as a function of the spacing between the Si atoms. The conduction and valence bands form as the Si atoms are brought closer together. From Reference [2].

The electronic properties of a material depend on how full the most-energetic electron-containing band, called the valence band, is. The valence band in a metal, which is a good conductor, is only partially full. The valence band in an insulator is completely full, and electrons are unable to be thermally excited to a higher band because a large energy gap exists above the valence band. This energy gap, called a band gap, is small enough in semiconductors to enable valence-band electrons to be thermally excited to the next band, called the conduction band. Thus, the valence band in a semiconductor is partially empty, and the conduction band is partially full [1]. This partial filling enables electric current to pass through a semiconductor.

A semiconductor can be *n*-type or *p*-type. Most of the current passed through *n*-type semiconductors is carried by negatively charged electrons, while most of the current passed through *p*-type semiconductors is carried by positively charged “holes” [2]. Much like how bubbles are gaps in water, holes are gaps in the electronic states of a material—where an electron should be but isn’t. Thus, a hole has the same magnitude of charge as an electron. The distinction between *n*-type and *p*-type semiconductors is important, as electronic devices function differently depending on the arrangement of each type of semiconductor [2].

The charge carrier type of a semiconductor depends on the position of the Fermi level with respect to the semiconductor's energy bands [2]. An electron in a material has a 50% probability of occupying a state with an energy equal to the Fermi level, if such a state exists, when the material is in thermodynamic equilibrium. States with energies lower than the Fermi level are more likely to be occupied by electrons than unoccupied, and states with energies higher than the Fermi level are more likely to be unoccupied than occupied. Electrons in a material with a Fermi level close to its conduction band can be excited to the conduction band (and thus carry current) more easily than holes can be "excited" to the valence band. Thus, electrons will be the main charge carrier, and the semiconductor will be *n*-type. Similarly, holes can be excited more easily than electrons in a semiconductor with a Fermi level just above the valence band, a *p*-type semiconductor [2]. The band structures of *n*-type and *p*-type semiconductors are shown in Figure 2. Thus, the position of the Fermi level determines the semiconductor's charge carrier type.

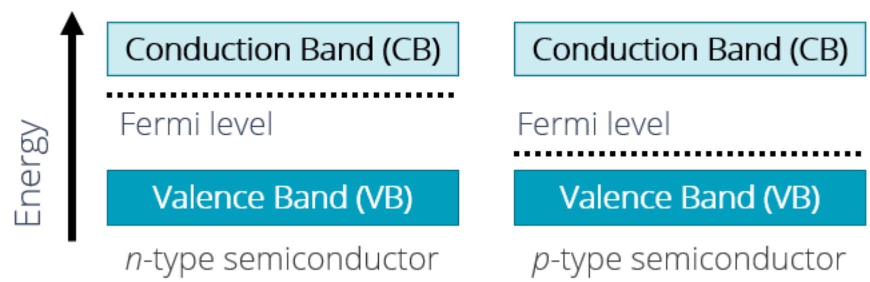

Figure 2: Band structures of an n-type and a p-type semiconductor. The Fermi level in the n-type semiconductor is close to the conduction band, while the Fermi level in the p-type semiconductor is close to the valence band.

Molybdenum disulfide (MoS_2) is a two-dimensional (2D), *n*-type semiconductor. Molybdenum disulfide crystals form in layers that are one molecule thick, as shown in Figure 3. Covalent bonds connect each S atom to two Mo atoms and each Mo atom to four S atoms (two above and two below). Multiple layers of MoS_2 are held together by the van der Waals force. As the distance across one layer of MoS_2 (including the gap between layers) is 0.67 nm, MoS_2 is a 2D material.

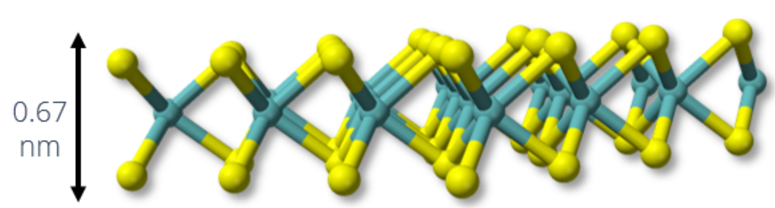

Figure 3: Ball-and-stick model of a MoS_2 monolayer. Covalent bonds connect the Mo atoms (teal) to the S atoms (yellow). In bulk MoS_2, each layer occupies a space that is 0.67 nm thick. Credit: Adapted from Ben Mills, wikipedia.org

Two-dimensional layers of MoS_2 have many potential applications in electronic devices [3]. Molybdenum disulfide could be used as a semiconductor in flexible electronics, transparent electronics, and optoelectronics [4]. Most relevant to this manuscript, however, is MoS_2's potential to be used in radiation-hard electronics. Particles of radiation in the environment could hinder the performance of electronic devices containing MoS_2. Thus, it is important to determine the impact of radiation on the electronic properties of MoS_2.

METHODS

Crystals of 2D MoS_2 were created and deposited onto a gold (Au) substrate. A one-molecule-thick layer of MoS_2 (monolayer) and a two-molecule-thick layer of MoS_2 (bilayer) were created via exfoliation. The monolayer and bilayer were deposited onto different parts of an Au substrate containing 1.2-µm-deep holes. The MoS_2 was suspended over these holes but supported by the Au elsewhere on the substrate. This sample configuration was used to determine the effect of the Au substrate on the band structure of the MoS_2 and the interaction between the radiation and the MoS_2. Specifically, the holes were used to determine whether radiation that penetrates through the MoS_2, bounces off the Au, and interacts with the MoS_2 again from the underside affects the band structure of the MoS_2. After the sample was prepared, it was irradiated.

The MoS_2 sample was irradiated in two stages. In the first stage, the sample was exposed to 1×10^{14} He^+ ions/cm^2. In the second stage, the sample was exposed to 1×10^{15} He^+ ions/cm^2, for a total radiation exposure of 1.1×10^{15} He^+ ions/cm^2. The energy bands of the MoS_2 were measured before irradiation and after each irradiation stage.

The energy bands of the MoS_2 were measured with respect to the Fermi level via photoelectron emission microscopy (PEEM). In a PEEM system, laser light at a set wavelength is directed into a sample. Photons from the laser excite electrons in the sample, causing the electrons to be emitted via the photoelectric effect. The emitted electrons are steered to a detector by electric and magnetic fields [5]. Using the electrons, the detector produces a magnified image of the sample [6]. A schematic diagram of a PEEM system is shown in Figure 4. Wavelengths that excite more electrons correspond to energies with more states—energies inside the valence band. To determine the Fermi level, PEEM data were taken of an area of the substrate that was not covered by MoS_2. By comparing the Fermi level to the valence band energies, the charge carrier type of MoS_2 was determined for each irradiation stage.

RESULTS

During irradiation, the Fermi levels of the suspended MoS_2 monolayer and bilayer decreased up to a threshold. During the first irradiation stage, the Fermi levels of the suspended monolayer and bilayer decreased by 0.13 eV and 0.17 eV, respectively, with respect

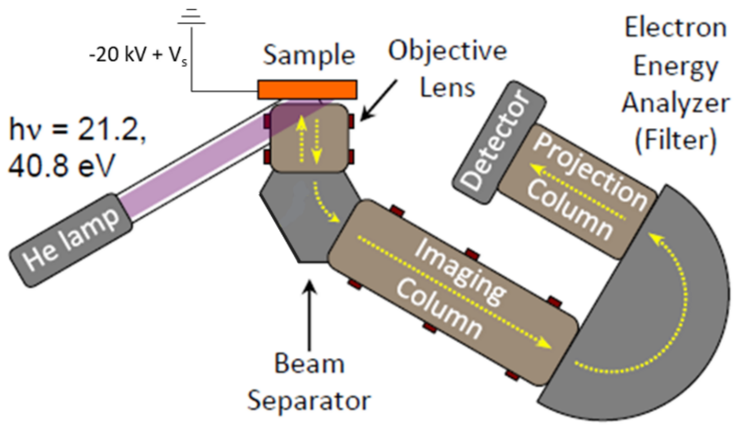

Figure 4: Schematic diagram of a PEEM system. Photons from the He lamp excite electrons in the sample. These electrons are focused into a beam that hits a detector. The detector detects the energy of each electron. Credit: Adapted from Morgann Berg

to the valence band maxima. During the second irradiation stage, however, the Fermi levels of the suspended monolayer and bilayer increased by 0.02 eV and 0.03 eV, respectively. Since this increase is negligible compared to the earlier decrease, the data support the idea of a radiation threshold. As suspended MoS_2 is irradiated up to this threshold, the Fermi level decreases. Above this threshold, however, the electronic properties of the irradiated MoS_2 don't change. The band diagrams for the suspended monolayer and bilayer are shown in Figure 6 and Figure 5, respectively.

The idea of a radiation threshold is supported by the literature. As shown in Figure 7, Bussolotti, et al. found that the Fermi level of a graphite-supported MoS_2 monolayer decreased by 0.95 eV as the concentration of sulfur vacancies (S-vacancies, c_v^{exp}) increased to 7%. Sulfur vacancies were created as the MoS_2 was irradiated by Ar^+ ions. As the concentration of S-vacancies increased from 7% to 25%, however, the Fermi level was found to decrease by only 0.07 eV [4]. Thus, the radiation threshold for the graphite-supported MoS_2 monolayer would be at an S-vacancy concentration $c_v^{exp} \leq 7\%$.

The Fermi level decrease may be caused by the presence of energy states in the band gap [7]. As the MoS_2 is irradiated, He^+ ions (or Ar^+ ions, in the case of the graphite-supported MoS_2 monolayer) knock S atoms out of the MoS_2, creating S-vacancies [4]. These vacancies are filled by oxygen (O) atoms from the air. Since O is more electronegative than S, O defects in the MoS_2 will create energy states in the band gap slightly below the conduction band. These gap states will make the irradiated MoS_2 less *n*-type.

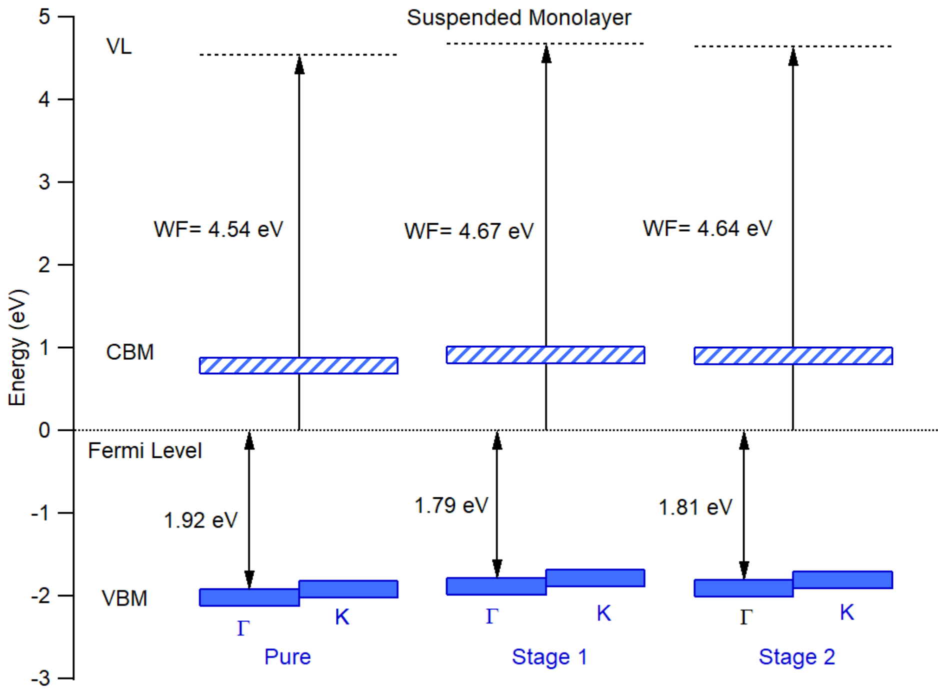

Figure 6: Band diagrams of a suspended MoS_2 monolayer. As it is irradiated to irradiation stage 2 ($1.1{\times}10^{15}$ He^+/cm^2), the Fermi level increases by 0.11 eV. The valence band maxima (VBM) at the Γ and K points are shown. Also shown are the conduction band minima (CBM), vacuum levels (VL), and work functions (WF).

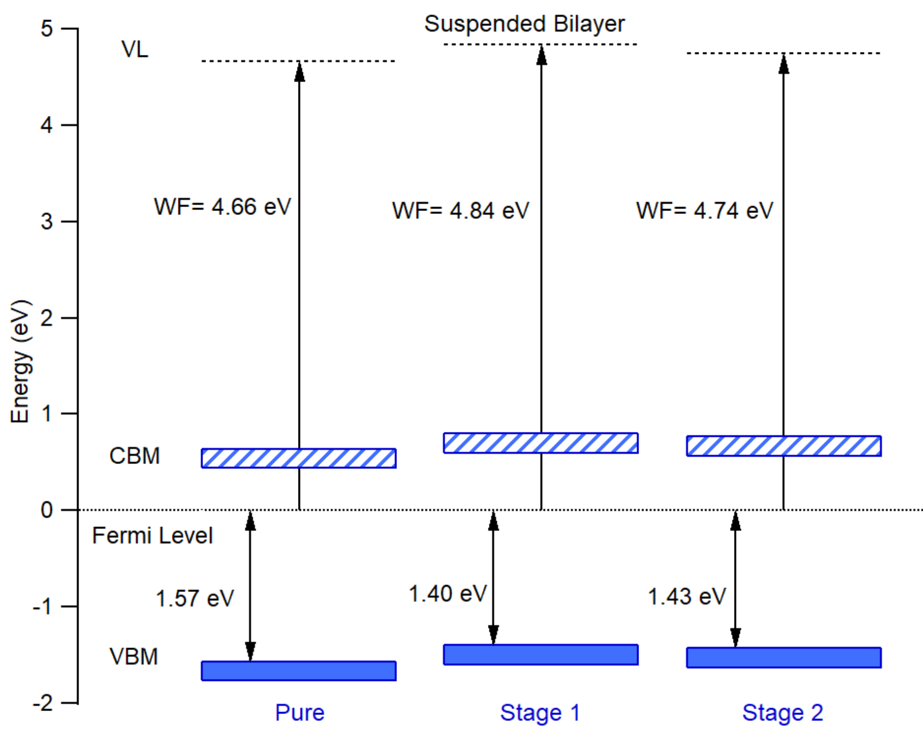

Figure 5: Band diagrams of a suspended MoS_2 bilayer. As it is irradiated to irradiation stage 2 ($1.1{\times}10^{15}$ He^+/cm^2), the Fermi level increases by 0.14 eV. Also shown are the valence band maxima (VBM), conduction band minima (CBM), vacuum levels (VL) and the and work functions (WF).

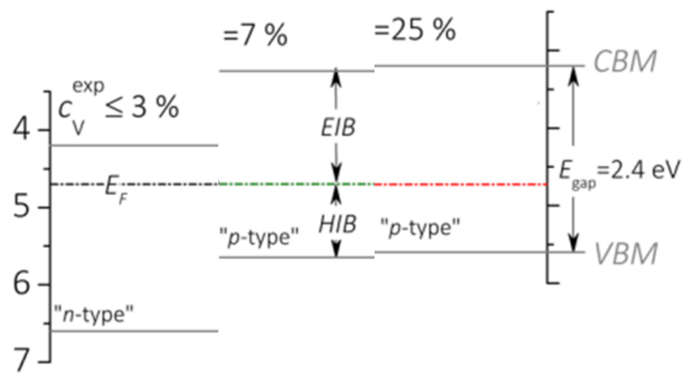

Figure 7: Band diagrams of a graphite-supported MoS_2 monolayer at different stages of irradiation. The concentration of sulfur vacancies is given by c_v^{exp}. Adapted from Reference [4].

During irradiation, the Fermi level of the supported MoS_2 monolayer increased, as shown in Figure 8. The Fermi level of the supported monolayer had a negligible increase, by 0.02 eV, during the first irradiation stage. During the second stage, however, the Fermi level increased by 0.09 eV. This larger increase suggests that the Fermi level of the supported monolayer may increase monotonically with irradiation. Additionally, the impact of the radiation on the Fermi level may have been amplified by the substrate, as He^+ ions could penetrate the monolayer, ricochet off the Au, and interact with the MoS_2 a second time. Further study is needed to elucidate the effect of the gold on the electronic properties of the MoS_2.

The effect of irradiation on the Fermi level of the supported MoS_2 bilayer is undetermined. As shown in Figure 8, the Fermi level of the supported MoS_2 bilayer decreased by 0.08 eV during the first irradiation stage but increased by 0.12 eV during the second irradiation stage. Therefore, the Fermi level of the supported MoS_2 bilayer doesn't change monotonically with irradiation. Further study is needed to verify the effect of radiation on Au-supported MoS_2 bilayers.

CONCLUSIONS

Suspended MoS_2 becomes less *n*-type as it is irradiated, but only up to a threshold. As suspended MoS_2 is irradiated up to 1×10^{14} He^+ ions/cm^2, the Fermi levels decrease by ≈0.15 eV with respect to the energy bands. As the MoS_2 is further irradiated to 1.1×10^{15} He^+ ions/cm^2, the Fermi levels decrease by <0.04 eV. Thus, the Fermi levels exhibit major change as the MoS_2 is irradiated up to 1×10^{14} He^+ ions/cm^2. Beyond that level, the Fermi levels do not change significantly. As it is irradiated, suspended MoS_2 remains *n*-type, but the density of charge carriers is reduced.

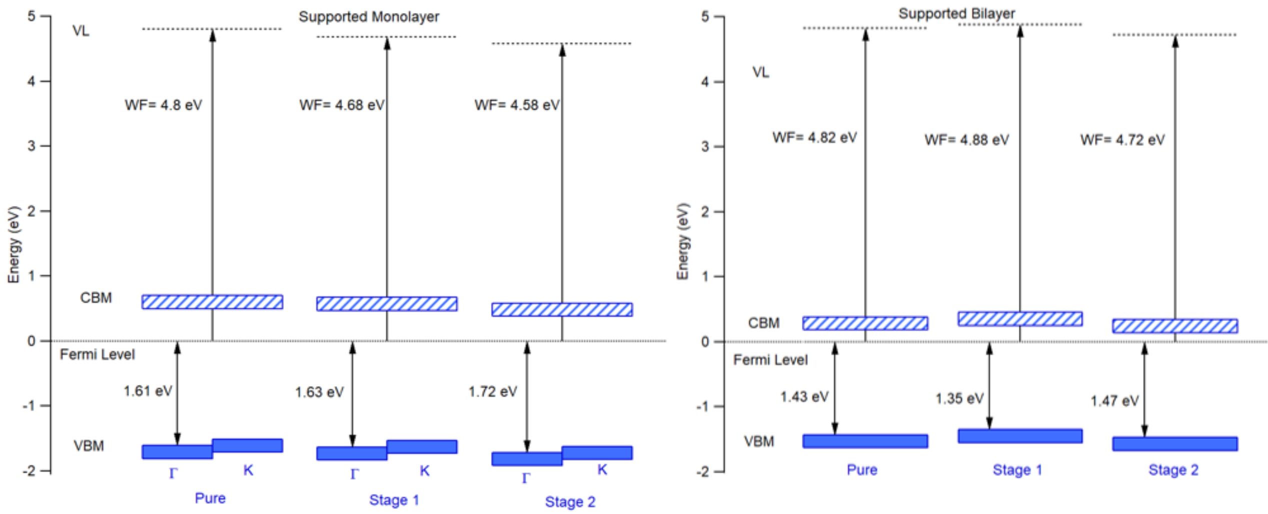

Figure 8: Band diagrams for the Au-supported MoS_2 monolayer and bilayer. During irradiation, the Fermi level of the monolayer increases with respect to the band energies. The impact of radiation on the bilayer, however, is undetermined.

Further research is needed to learn more about the effect of radiation on suspended MoS_2. More research could elucidate the level of radiation at which the threshold lies, and whether this level depends on the number of layers of MoS_2. Furthermore, the Fermi levels of the suspended MoS_2 continue to decrease beyond the threshold. This continued decrease may cause MoS_2 to become a *p*-type semiconductor after a larger dose of radiation than was studied in this manuscript. This research would further knowledge about the impact of radiation on MoS_2.

Supported MoS_2 becomes more *n*-type as it is irradiated, but further research is needed to determine a more specific relationship between the radiation dose and the Fermi level position. Additionally, more research could determine if more irradiation causes the Fermi level to increase to the conduction band minimum, thus changing the MoS_2 from a semiconductor to a conductor.

The results described in this manuscript contribute to an understanding of the effect of particle radiation on 2D MoS_2. This understanding could be used to develop radiation-tolerance standards for MoS_2. These standards would inform the development of radiation-tolerant electronic devices based on MoS_2.

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