Effects of Ozone Plasma Treatment and X-Ray Irradiation on Optical Properties of Atomically Thin Molybdenum Disulfide

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BRIEF. This study examines the optical properties of MoS_2 and how they can be modulated via thermal annealing and ozone and X-ray exposure.

ABSTRACT. Atomically thin molybdenum disulfide (MoS_2) is a transition metal dichalcogenide (i.e., of the form MX_2 where M is a transition metal and X is S, Se etc.) compound with unique electrical properties. Although an indirect band gap semiconductor in bulk form, it is a direct band gap material as a monolayer, and is considered a semiconducting analogue of graphene. Extremely sensitive and efficient photodetectors and other optoelectronic devices could be constructed using monolayer MoS_2 because of this direct band gap property and its unique high-surface area structure. In this study, mechanical peeling of bulk MoS_2 was utilized to isolate few layer and monolayer flakes of MoS_2. Bright-field optical microscopy and Raman and photoluminescence (PL) spectra were used as characterization methods for identifying monolayer flakes. Additionally, we demonstrate that the PL intensity and Raman response of monolayer molybdenum disulfide can be enhanced by X-ray irradiation and ozone plasma exposure. This result could allow for more efficient optolectronic devices, such as sensors and LEDs, based on atomically thin MoS_2. We also find that the thermal annealing process significantly increases PL intensity and makes PL and Raman signals of single-layer MoS_2 sensitive to the adsorption of ambient O_2 and other oxygen species. This may indicate that the annealing process induces sulfide vacancies, which can interact with ambient molecules. Moreover, the Raman spectra, used as a unique identifier for layer number, presents a distinct change after the X-ray or ozone exposure. Here, adsorbed oxygen may slightly perturb the atomic structure and induce a change in the Raman spectra that is unique and not observed in as-prepared samples. These experimental results could aid in understanding how the material's properties are altered in space or radioactive environments, and lead to further studies that aim to tailor optical properties of two-dimensional (2-D) monolayer materials through surface modification and defect engineering.

INTRODUCTION.

Semiconductor materials, such as silicon, have become ubiquitous over the past 30 years. They are widely used in the development of microelectronic transistors, which have possible made many innovations in computer technology and electronic devices. Semiconductors can be split into two classes: indirect and direct band gap materials. The core difference in these two classes is that direct band gap semiconductors are useful in applications that involve electronic and optical interactions or energy transfer. Thus, semiconductors with direct band gaps are more aptly suited for use in sensitive photodetectors or other optoelectronic devices. For instance, LEDs, which can be used as light sources or in thin-film flat panel displays, are almost exclusively made out of direct semiconductors, as indirect materials will not emit light when used in the same diode circuit.

Molybdenum disulfide (MoS_2) is a semiconducting transition metal compound that has recently attracted much research attention. MoS_2 is a layered material, similar to graphite, and its layers can be isolated from one another by mechanical exfoliation (repeated peeling of the material) or chemical modification via surface functionalization [1]. In monolayer form, MoS_2 has a direct band gap and exhibits strong photoluminescence (light emission stimulated by incident photons) unlike the bulk material, which is an indirect band gap semiconductor [2]. Monolayer MoS_2 is a three-atom thick, two-dimensional (2-D) material, which is considered a semiconducting analogue to the popular 2-D material graphene. This structure lends to a high carrier mobility, or rapid flow of electrons, which is useful for enhancing the performance capabilities of ultra-fast electrical and optoelectronic devices.

The research question in this study has two main elements: first, a thorough characterization of atomically thin samples of MoS_2 must be established as a standard record for the material in its unaltered state. We examine the optical properties of the material, namely the Raman and photoluminescence (PL) spectra, for varying thicknesses. The second part of the research question addresses whether exposure to a chemical or X-ray treatment has an effect on the optical appearance and characteristics of the material as recorded under normal conditions. These fundamental studies help test the viability of using this material in electrical, optical and optoelectronic devices that are exposed to harsh environments, and to understand which properties can be modulated by irradiation and plasma treatments [3, 4]. Knowledge of how a material's properties hold up under such conditions opens the possibility of usage in devices made for space or other radioactive environments[5], as well as engineering material properties through chemical and X-ray treatments.

MATERIALS AND METHODS.

Sample Preparation.

First, optical lithography and wet etching, techniques common in the semiconductor industry for fabricating microelectronic circuits, were used to pattern alphanumeric arrays (on the order of 7 μm) onto a silicon dioxide (SiO_2) substrate, to be used as markers for identifying suitable flakes. The substrate was then cut into square centimeter pieces using a diamond tip pen and cleaned using an oxygen plasma cleaner and/or washed with acetone, isopropanol, and deionized (DI) water successively. Mechanical exfoliation, a method pioneered for the isolation of graphene that involves repeated peeling of the material by use of adhesive tape, was used to thin MoS_2 flakes [1]. The scarcely visible remaining MoS_2 was transferred directly from the tape to a clean substrate. The optical microscope was then utilized to observe color contrast of thin flakes to identify the thickness of samples. This preparation process was repeated with only slight variation to make over 50 samples. The process was systematically varied in order to try and optimize the procedure, based on the results obtained from sample to sample, but was generally difficult to regulate, thus yielding slightly different numbers of atomically thin (3-20 atoms) samples with each attempt. Some samples had as many as five such flakes while others had none at all, but generally each sample had at least one flake that warranted further characterization.

Optical Characterization.

An optical microscope was used to search the samples, and the patterned marks were used as a guide for locating viable MoS_2 flakes. Flakes were judged on their color contrast and surface area. According to previous literature, MoS_2 that appears from dark blue to translucent purple under the optical microscope is from approximately 10 to 1 layers thick, respectively [6, 7, 8]. A light purple flake with a surface area of 40 square microns, for example, was noted as a suitable flake for use in further characterization and experimentation. Image-J (NIH, Bethesda, MA) was used to measure the lengths and widths of sizeable flakes, and thus used to estimate the surface area of those flakes. When an optimal flake was located, its alpha-numeric coordinates were recorded, and an image was captured for reference.

A Raman microscope (Thermo Scientific™ DXR) was used to characterize the

thickness of selected MoS_2 flakes. Because Raman scattering of a given material is dependent on that material's phonon structure, it yields distinct spectra for different layer numbers of the same two-dimensional material. Ensemble averaging of the Raman spectra was incorporated to enhance the signal-to-noise ratio. In MoS_2, it has been previously shown that the distance between the two characteristic Raman peaks, the E_{2g} and A_{1g} peaks, decreases as the thickness of the flake decreases, and vice versa [7, 8]. Thus, the Raman spectra of MoS_2 can be used in comparison with visual observations in order to make more accurate assumptions about the thickness of the samples.

The same instrument was also used to analyze the PL spectra of selected MoS_2 flakes. For atomically thin samples, a rapid intensity increase occurs in the PL peak at ~665 nm of MoS_2 as the layer number is decreased, owing to the gradual transition from indirect to direct band gap semiconductor that occurs as MoS_2 thickness approaches the monolayer [9]. Combined with visual and Raman spectra characterization, PL spectra help to verify the precise layer thickness of a flake.

Chemical Treatment/Surface Modification.

In order to observe modulations in the three previously mentioned characterization techniques, ozone plasma was used to chemically treat samples. Samples were exposed to ozone plasma in one-minute intervals and optical, Raman, and PL characterizations were taken in between each treatment. This process was repeated until the flake was completely damaged or no longer present on the sample. Sometimes, the flake was not extensively damaged, in which case the treatments were stopped after there appeared to be no further effect, or degradation in optical quality, based on the modulation of the spectra.

Additionally, different samples were irradiated with 10 keV X-rays, in varying total ionizing doses (TID). Raman and PL spectra were taken between each dose of radiation. Some samples were vacuum annealed before X-ray or ozone exposure, as this sensitized the MoS_2 to the treatments, by inducing sulfide vacancies [3]. Samples were annealed at 450°C for 45 minutes in a tube furnace under vacuum (approximately 10 mTorr). We compared the PL and Raman signals of monolayer MoS_2 before and after the annealing process.

RESULTS.

The first procedure involved in this study was the fabrication of atomically thin MoS_2 on the SiO_2 substrate. The typical substrate chip contained about three samples of interest for further testing after examination under the optical microscope. One of these samples is shown in Figure 1A. Of over 50 prepared substrate chips (each approximately 1 cm^2), around half contained flakes with the proper surface area and thinness for further characterization.

We found that a sample that was perceived to be monolayer had a Raman shift separation of about 18-19 cm^{-1} as depicted in Figure 1B, which was consistent with previous results [7, 8]. A prominent PL spike at ~665 nm, demonstrated in Figure 1C, was observed in all spectra collected from samples that were deemed monolayer from visual analysis as well as from consistent peak separation on the Raman spectra. Thus, a large PL intensity could be considered a third line of verification of the thickness of a monolayer MoS_2 flake.

As shown in Figures 2b and 3c, the Raman peaks of a single-layer flake separated gradually over consecutive periods of ozone exposure or X-ray irradiation. After a certain number of exposure periods, the PL intensity increased dramatically (Figs. 2a, 3a, and 3b). After further exposure, the PL intensity decreased from the maximum value reached, likely due to nanoscopic etching of the material. The results of ozone plasma were very similar to those seen in the X-ray treatment graphs. The same patterns of modulation arose as a result of both experiment types. In both cases, it was found that annealing the sample before treatments could generally enhance the trends seen in non-annealed samples.

DISCUSSION.

Although the results from the sample preparation procedure were difficult to regulate, in terms of few-layer and monolayer yield, it is still the best known process for isolating pristine, atomically thin flakes of two-dimensional materials like graphene and MoS_2, as well as being the least time-consuming of available

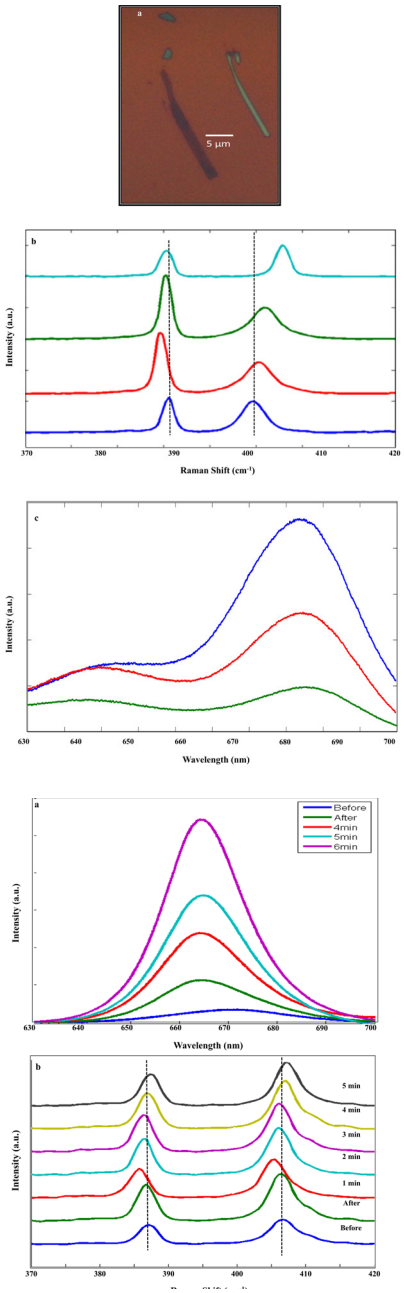

Figure 1. (a) A MoS_2 flake with varying thicknesses, where the translucent purple indicates a monolayer region. (b) Raman and (c) PL spectra of MoS_2 flakes of varying thicknesses. The spectra show monolayer (blue), bilayer (red), tri-layer (green) and bulk (cyan).

Figure 2. (a) PL and (b) Raman spectra of MoS_2 exposed to ozone plasma for various time points.

options. The separation of Raman peaks as thickness increases was confirmed in this work as a viable tool for identifying the thickness of a MoS_2 flake, as shown in previous reports [7, 8]. Also, it was found to be a higher throughput method of thickness identification, as compared to atomic force or transmission electron microscopy. A definite correspondence arose between perceived thickness under the optical microscope and difference of Raman shift between the E_{2g} and A_{1g} peaks of a given sample. We found that a separation of 19 cm^{-1} was indicative of monolayer, 22 cm^{-1} of bilayer, and 25 cm^{-1} of few-layer and bulk samples.

The gradual decrease in PL intensity as thickness increased indicated that there was a gradual transition between direct band gap at the monolayer, and indirect band gap at bulk thickness [2, 8]. Given that the samples were pristine and mechanically exfoliated, it could be assumed that the PL intensity change was directly dependent on layer number. This indicates that because thin MoS_2 exhibits PL, a bilayer or even few-layer sample of MoS_2 has properties closer to that of a direct semiconductor than an indirect semiconductor, as shown in previous reports[1][3].

Previous literature has indicated that thermal annealing induces sulfide vacancies in the material [3]. It has also shown that the PL intensity increases

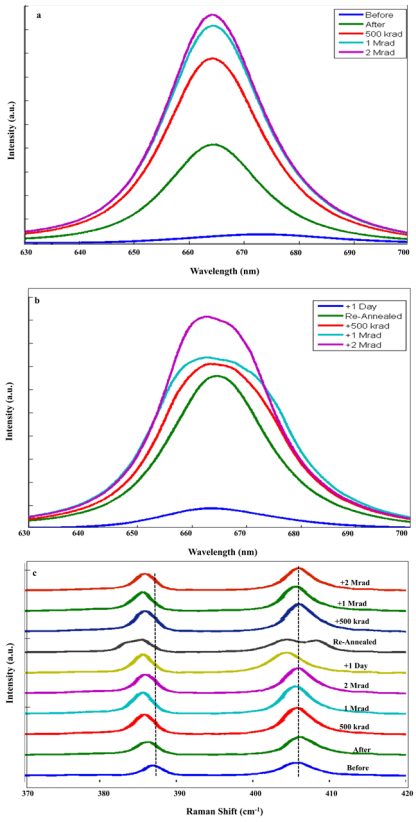

Figure 3. PL and Raman spectra of MoS_2 irradiated with X-rays, over two sets of exposures. PL spectra of (a) the first set and (b) the second set. (c) Raman of both sets of exposures. Each set consisted of taking the as-is (or for second set, 'rested') flake, vacuum annealing the sample, and then exposing it to increasing dosages of radiation.

whenever oxygen is adsorbed on the sample. We thus investigated how thermal annealing would enhance PL in conjunction with ozone plasma exposure and X-ray irradiation. The core results of these experiments are the effects of the ozone plasma and X-ray treatments on the optical properties of MoS_2. Both types of treatments yielded similar patterns of results. Ozone treatments resulted in both a slight separation between Raman peaks (Figure 2b) and a large increase in the PL intensity (Fig. 2a) that eventually subsided. In the ozone treatments, these results were likely due to adsorption of oxygen on the surface of the samples [3], which decreased exciton (electron-hole pair) screening and caused a dramatic increase in the radiative recombination rate, allowing a large PL intensity. The subsequent decrease in the PL intensity that followed (not shown) can likely be attributed to the formation of spatial defects that hinder oxygen adsorption to that local region, resulting in an overall decrease of PL intensity. This hypothesis is supported by the fact that samples developed some regions with lower PL than others as further ozone plasma treatments were performed.

Distinct samples were irradiated with 10 keV X-rays. Varying doses were used throughout the experiments, and doses presented here are the total absorbed doses. Figure 3a details the first set of annealing and exposures, while Figure 3b shows the same experiment repeated after one day of letting the material rest in ambient environment. The fact that the PL intensity goes down during this period suggests that the enhancement is also dependent on the surrounding environment. It is interesting to note that high PL intensity can be recovered with subsequent re-annealing and X-ray exposure. This suggests that molecular adsorption of oxygen species is responsible for the drastic enhancement via charge depletion in the material, as it reduces charge screening and allows more excitons to recombine radiatively[4]. Moreover, annealing of the crystal led to a much higher increase in the PL intensity overall in this process. This may indicate that the annealing process can create vacancies in the materials, making the materials more sensitive to the binding of oxygen species during exposure and leading to more efficient enhancement in PL signals. We also observe small increases in the signal and frequency shift difference of the two characteristic Raman peaks (Fig. 3c). This may indicate that adsorbed O_2 perturbs the phonon (atomic vibrational) structure and causes a monolayer sample to have an increased frequency difference (20 – 20.5 cm^{-1}), which is closer to that of a bilayer sample. It was seen that the two peaks gradually separated further after both ozone plasma and X-ray treatment, even though the sample was still monolayer. Additionally, the material was shown to be robust to X-ray radiation, withstanding doses of up to 6 Mrad TID without any noticeable degradation of the material or its optical properties. This shows that the material is radiation-hard, as generally devices that can withstand 1 Mrad TID are considered space-grade.

In this study, we demonstrate that the PL intensity of monolayer MoS_2 can be enhanced when exposed to X-ray or ozone plasma, owing to the molecular absorption on sulfide vacancies induced during a pre-annealing process. In the future, we are interested in modulating optical and optoelectronic properties of MoS_2 or other 2-D materials using controllable surface modification. Additionally, our results show promise for molecular-sensors or molecular 'gating' devices utilizing these 2-D materials with desirable surface decoration and controlled defect engineering.

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REFERENCES.

1. Oriol Lopez-Sanchez *et al.*, *Nature Nanotechnology*. 8, 497 (2013).
2. B. Radisavljevic *et al.*, *Nature Nanotechnology*. 6, 147 (2011).
3. Sefaattin Tongay *et al.*, *Nano Letters*. 13, 2831 (2013).
4. T. Gokus *et al.*, *ACS Nano*. 3 (12), 3963 (2009).
5. En Xia Zhang *et al.*, *IEE Transactions on Nuclear Science*. 58(6) (2011).
6. Changgu Lee *et al.*, *ACS Nano*. 4(5), 2695 (2010).
7. Hong Li *et al.*, *Advanced Functional Materials*. 22, 1385 (2012).
8. R. S. Sundaram *et al.*, *Nano Letters*. 13, 1416 (2013).
9. Andrea Splendiani *et al.*, *Nano Letters*. 10(4), 1721 (2010).

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