Chemical Treatment Effects on the Optical Properties of Single to Few-Layer Molybdenum Disulfide

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Abstract

This study focuses on the optical properties of single and few-layer molybdenum disulfide to chemically treated with ozone plasma. In particular, the changes the photoluminescence and Raman spectra of the MoS_2 were studied throughout treatment. The cumulative length of exposure to ozone plasma, the number of layers of MoS_2 in each sample, and whether a given sample was annealed prior to treatment were all criteria in comparative study. To also compare exfoliated versus synthesized MoS_2, we attempted vapor-solid synthesis of MoS_2 monolayers but were unsuccessful. We determined that single-layer MoS_2 annealed prior to treatment exhibited the greatest response in photoluminescence, perhaps due to adsorption of oxygen species, but prolonged exposure would reduce photoluminescence, likely due to MoS_2 etching and defect formation.

Background

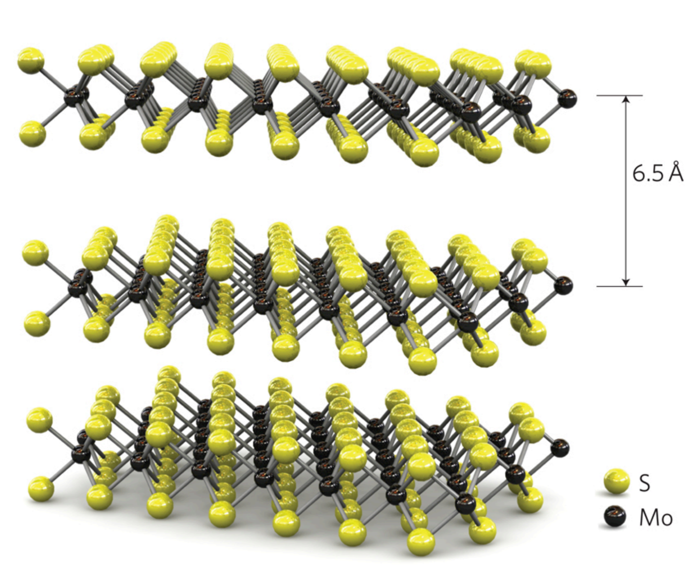

Figure 1: Structure of molybdenum disulfide layers[5]

Molybdenum disulfide, in its monolayer form:

- Acts as a direct bandgap material with a bandgap of about 1.8eV, unlike bulk MoS_2, which is an indirect bandgap material
- Has a photoluminescence demonstrated to be much higher than thicker MoS_2
- Is often compared to graphene, another two-dimensional material known for its applicability in electronics; graphene has been found to exhibit a higher photoluminescence after oxygen plasma treatments[1], though ozone plasma and x-ray treatments can introduce defects into the material and hinder its electronic performance.[2] This comparison suggests that it is important to attempt similar treatments on MoS_2 in order to expand our understanding of the material.

Materials and Methods

Mechanical Exfoliation: MoS_2 flakes were taken from bulk MoS_2 using Scotch tape. The tape was used to peel back layers from the bulk MoS_2; then the tape was folded in order to spread and separate flakes. The flakes were then transferred from the tape to a silicon dioxide-coated wafer. The flakes were characterized by optical microscopy and Raman spectroscopy.

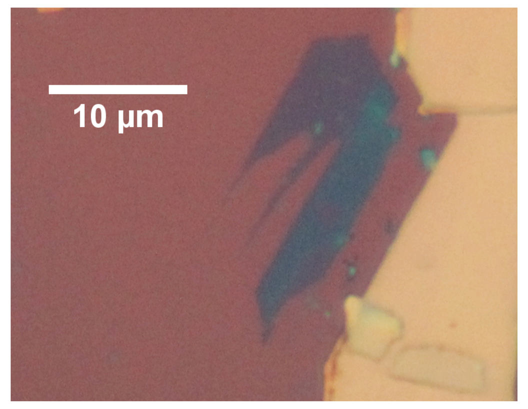

Figure 2: Optical image of mechanically exfoliated molybdenum disulfide bilayer flake

Vapor-Solid Synthesis: MoS_2 powder was used as a source and a SiO2-coated wafer as a substrate. The source was placed in a boat within a quartz tube and heated to ~900°C in a furnace. As a carrier gas, argon flowed through the tube to bring the MoS_2 vapor to a colder portion of the furnace where the substrate was located. The cooling MoS_2 would then form monolayer films on the substrate.[4] This process was attempted but unsuccessful, as no monolayer films and only extremely small crystals were observed.

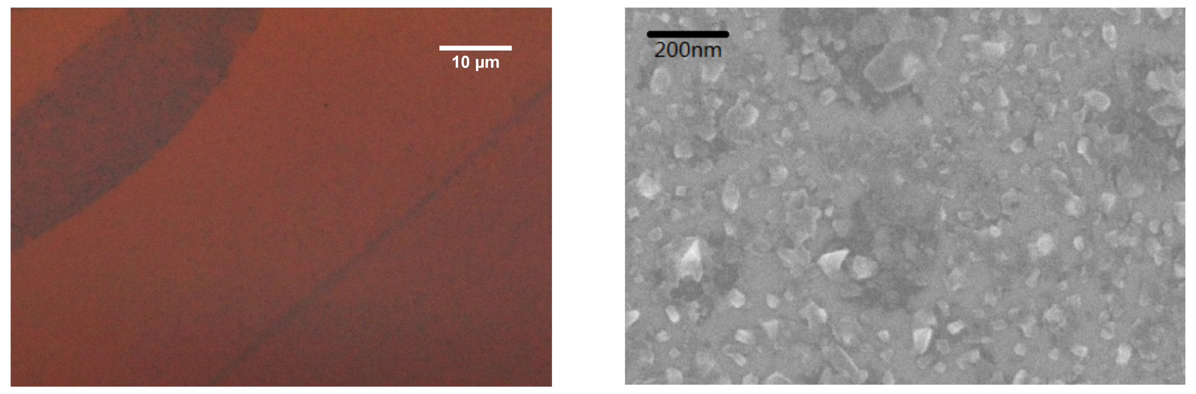

Figure 3: (left) Optical image of MoS2 deposited on SiO2 substrate; (right) SEM image of the area of deposition

Annealing: The samples to be annealed were placed in a quartz tube inside a furnace. The system was pumped down to a vacuum of about 10 milliTorr, and the samples were heated for 40 minutes at 450°C.

Ozone Plasma Treatment: Single and few-layer flakes of MoS_2 were tested for their Raman and photoluminescence spectra, then either annealed with a subsequent measurement of the spectra or kept as-exfoliated. The samples were then placed in a UV Ozone cleaner and exposed to ozone plasma for various intervals. The photoluminescence and Raman spectra were measured for each sample after each interval.

Raman Spectroscopy:

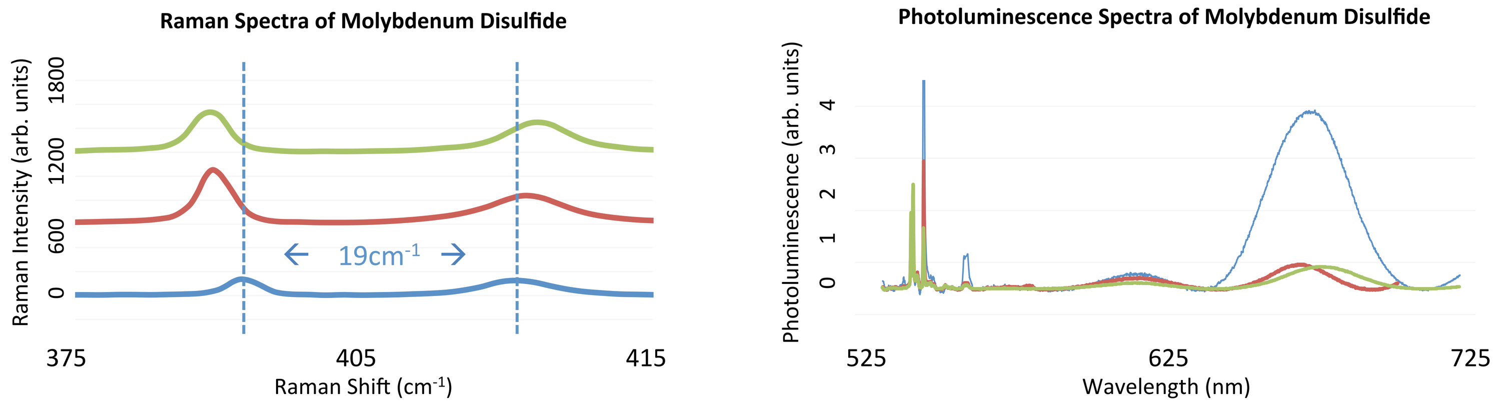

Figure 4: Characteristic Raman Spectra (left) and photoluminescence spectra (right) for monolayer (blue), bilayer (red), and few-layer (green) molybdenum disulfide

Results and Conclusions

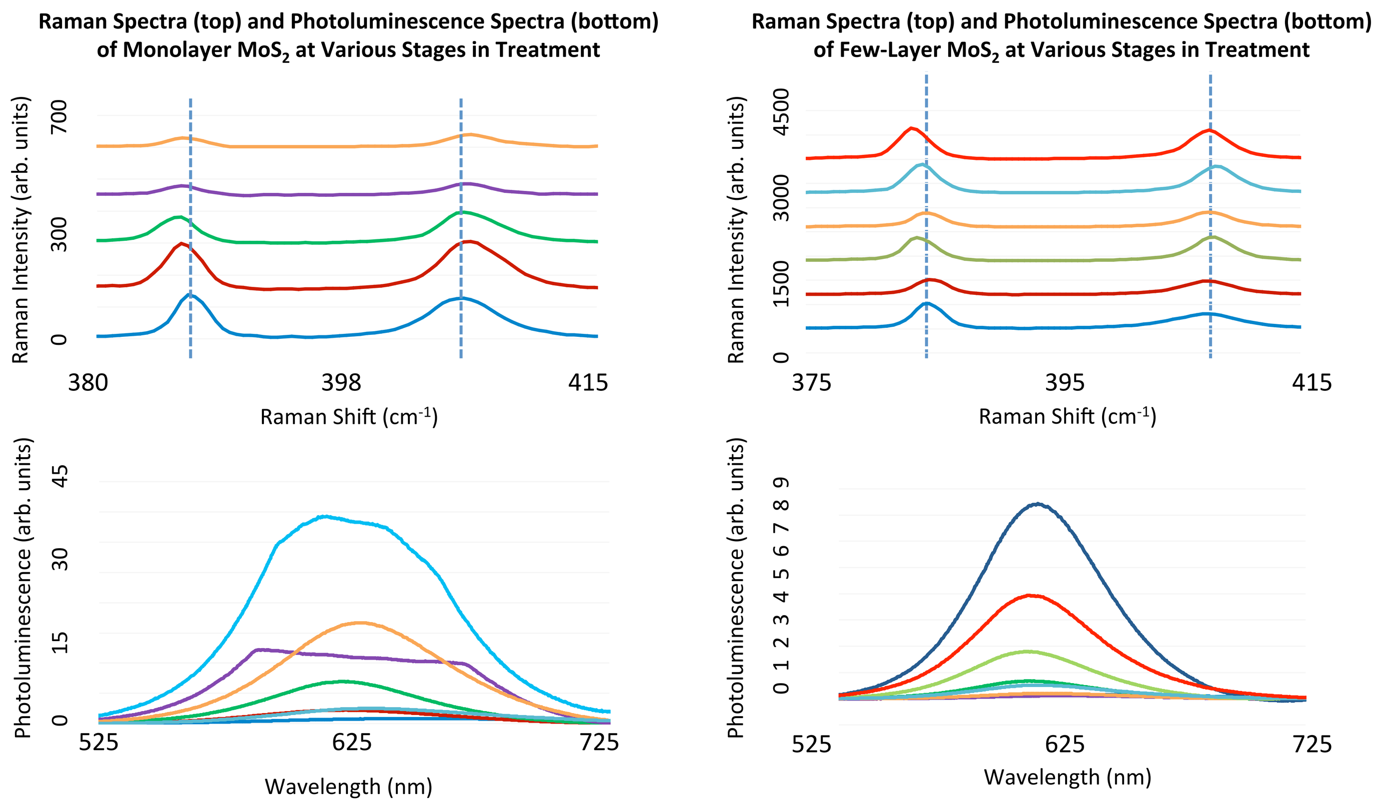

Figure 5: MoS2 Raman and photoluminescence spectra during treatment at various times: before annealing (blue); annealed, 0 min. (dark red); 1 min (green); 2 min. (purple); 3 min. (light blue); 4 min. (light green); 5 min. (orange); 6 min. (dark blue); 8.5 min. (aqua); 10 min. (red)

Comparing the photoluminescence response across annealed and non-annealed samples of varying thicknesses over the course of several intervals of plasma treatment, we found that single-layer molybdenum disulfide samples that had been annealed exhibited a significantly greater response to the ozone plasma treatment. We hypothesize that these responses are the result of the adsorption of oxygen by the MoS_2 during treatment, as oxygen adsorption has been shown to enhance photoluminescence in MoS_2.[3] The Raman spectra show slight separation variations and left-shifting, but the data does not support a definite conclusion.

Future Research

Future research stemming from this project will involve:

- Continuing study of the etching and photoluminescence enhancement effects
- Repetitions of this experiment using other treatments such as oxygen plasma or x-rays in order to better establish the mechanism of photoluminescence enhancement
- Study the effects of chemical treatments on the electronic properties of MoS_2
- Re-evaluation and improvement of vapor-solid synthesis methods

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