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CHEMICAL VAPOR DEPOSITION OF ATOMICALLY-THIN MOLYBDENUM DISULFIDE (MoS_2)

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March 2015

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Munitions Engineering Technology Center

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14. ABSTRACT

A method of synthesizing monolayers of molybdenum disulfide (MoS_2) via chemical vapor deposition is described. In this process a tube furnace is used to evaporate MoS_2 over silicon/silicon dioxide substrates. Sulfur is then evaporated and flown over the substrates via a stream of inert gas. Optical and scanning electron microscopy and Raman spectroscopy are utilized to characterize the growth of the MoS_2 monolayers. Density-functional theory simulations are used to compare theoretical predictions to the observed photoluminescence.

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CONTENTS

	Page
Introduction	1
Experimental Procedure	1
Results and Discussion	3
Conclusions	5
Bibliography	7
Distribution List	9

FIGURES

1	Top and side views of molybdenum disulfide (MoS_2) (2H-polytype)	1
2	Schematic of the experimental setup	2
3	Temperature profile of the furnace during the CVD of MoS_2	2
4	OM (top) and SEM (bottom) images of as-grown MoS_2. The triangular crystals vary in size from 10 to 50 µm	3
5	Raman spectra data	4
6	The band structure of 2H-MoS_2	4

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INTRODUCTION

Recently, an explosion of interest in low-dimensional materials has arisen across a vast array of disciplines including physics, materials science, chemistry and engineering on account of their exotic properties. Graphene is a unique example of a two-dimensional (2D) material exhibiting high electron mobility, the lowest resistivity of any known material, high mechanical strength and excellent thermal conductivity. Naturally, the research in graphene served as the impetus to study different 2D materials such as transition metal oxides including titania and perovskite-based oxides, graphene analogues such as boron nitride and atomically-thin transition metal dichalcogenides (TMDs). Of these materials, the TMDs show a wide a range of electronic, optical, mechanical, chemical, and thermal properties that are complementary and in some cases superior to that of graphene. For example, while pristine graphene lacks a bandgap, several TMDs possess bandgaps of the order of 1-2 eV thereby showing promise for novel field effect transistors and optoelectronic devices. Since many 2D materials, in their bulk form exist as lamellar structures, they can be exfoliated into individual, atomically-thin layers. While the exfoliated 2D materials serve as the medium for demonstrating some of the exotic properties of the 2D materials, concomitantly significant progress has been made in wafer-scale synthesis methods such as chemical vapor deposition (CVD) for large scale production.

The TMDs are a class of compounds having the chemical formula MX_2 where M is a group 4 (e.g., Ti, Zr), group 5 (e.g., V, Nb, Ta), or group 6 (e.g., Mo, W) transition metal, and X is a chalcogen from group 16 (e.g., S, Se, Te). The TMDs form a hexagonal lattice in the xy-plane with two monolayers of chalcogen atoms bonded, from above and below, to an atomically-thin layer of transition metal atoms in the form X-M-X (fig. 1.)

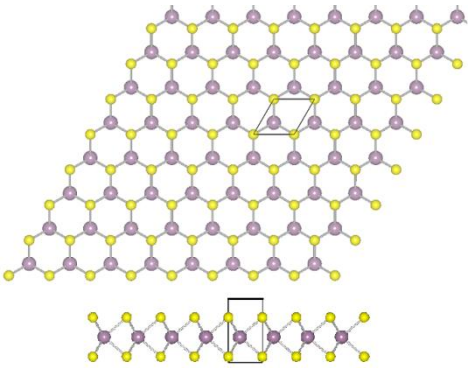


Figure 1
Top and side views of molybdenum disulfide (MoS_2) (2H-polytype)

The procedure for the successful synthesis of large, high quality, crystalline MoS_2 by chemical vapor deposition will be discussed in this report. The material shall be characterized by optical microscopy (OM), scanning electron microscopy (SEM), and Raman spectroscopy (RS). The photoluminescence (PL) peak in the Raman data shall be compared to band structure data from *ab-initio* simulations of the 2H-polytype of MoS_2.

EXPERIMENTAL PROCEDURE

The experimental setup is demonstrated in figure 2. As shown in the figure, a combustion boat with 10 mg of MoO_3 powder spread along the bottom is placed in the center of a tube furnace. An identical boat containing 1 g of sulfur is placed at a position upstream at the opening of the furnace such that the maximum temperature at that position is 250°C while heating. During the entire

experiment, ultra-high purity argon gas flows at a rate of 50 standard cubic centimeters per minute. The P-doped silicon substrates with a layer of thermal oxide 300 nanometers (nm) thick are placed face-up on the boat containing the MoO_3 powder. After the tube is sealed, the argon is allowed to flow at room temperature for 10 min in order to purge any remaining oxygen. The furnace is then heated to 715°C over a period of 25 min at which point the temperature is held constant for an additional 15 min. The furnace is then allowed to cool back to room temperature naturally. This process is illustrated schematically in figure 3.

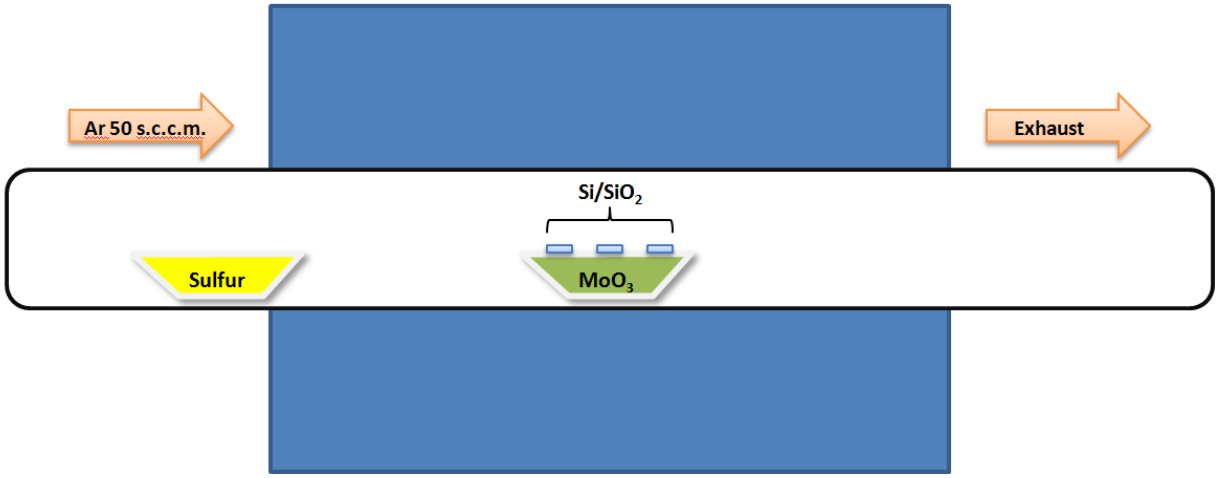


Figure 2
Schematic of the experimental setup

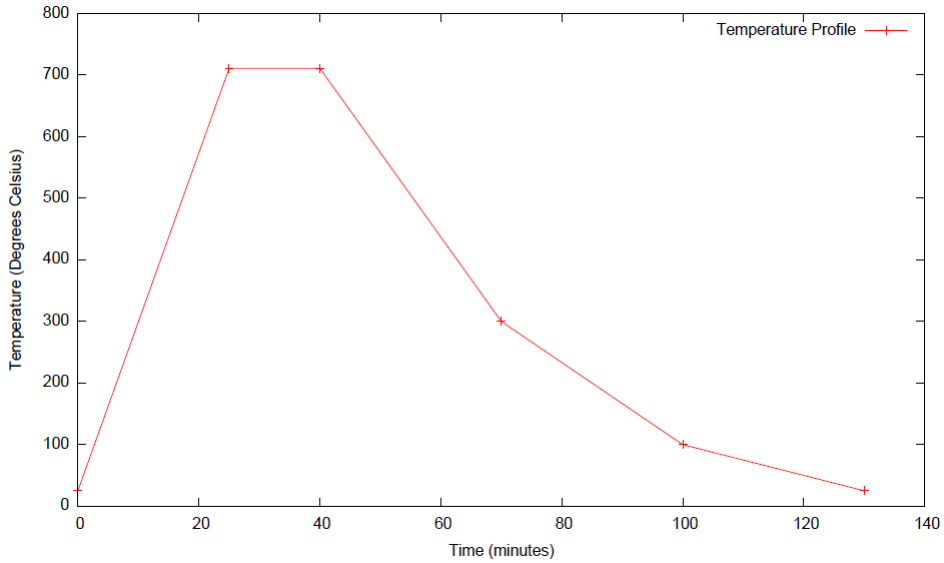


Figure 3
Temperature profile of the furnace during the CVD of MoS_2

RESULTS AND DISCUSSION

In order to verify the growth of atomically-thin MoS_2 crystals, we have characterized the materials via OM, SEM, and RS. Figure 4 shows OM and SEM images of triangular crystals of MoS_2. As displayed in the figure, the material grows in triangular crystals of variable size. Typical sizes range from 10 to 50 µm. Furthermore, it was found that crystal growth is most favorable near the corners of the substrates where both the largest single crystals and highest density of triangles can be found. As shown in the figure, single crystals also tend to merge into more complex shapes, possibly forming bilayer to multilayered materials.

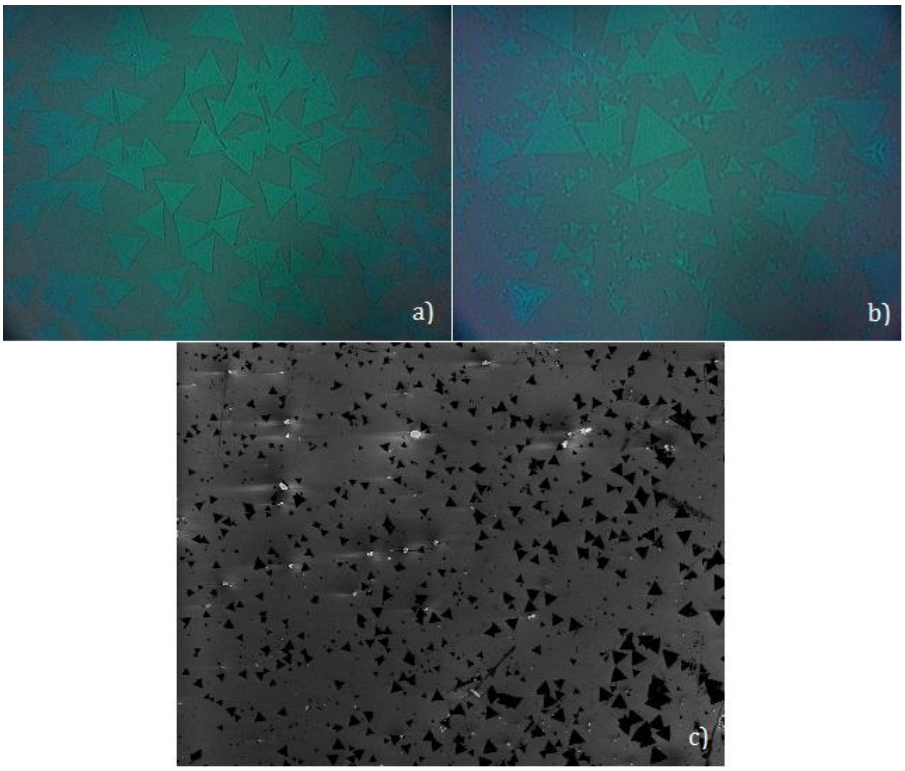
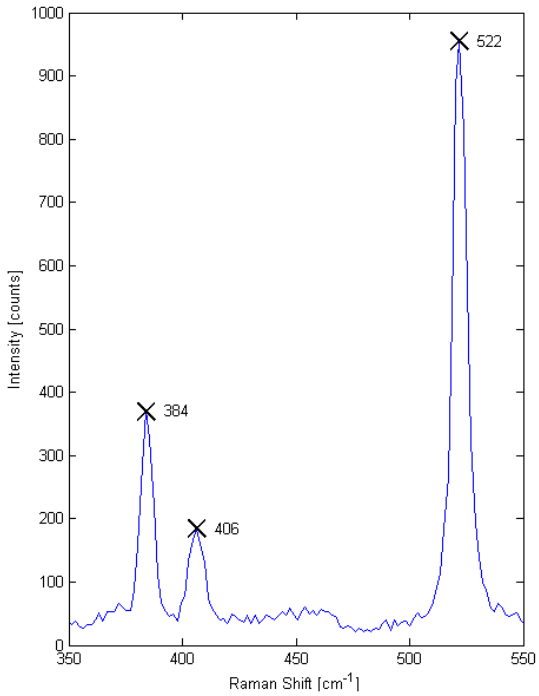
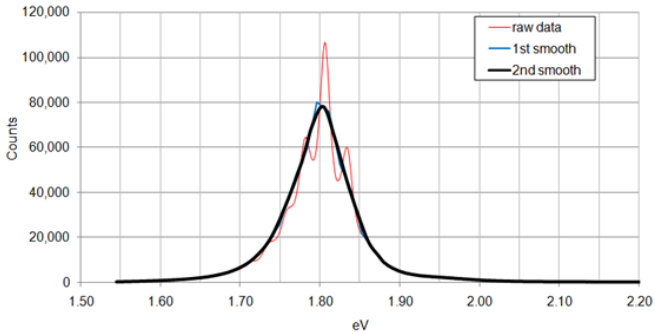


Figure 4
OM (top) and SEM (bottom) images of as-grown MoS_2. The triangular crystals vary in size from 10 to 50 µm.

Figure 5 shows the Raman spectrum obtained for a representative sample of atomically-thin MoS_2; all data were taken using a 514 nm excitation wavelength. Figure 5 (a) clearly shows the MoS_2 Raman peaks at 384 and 406 cm^{-1}. Figure 5 (b) shows the PL peak corresponding to the direct bandgap transition in atomically-thin MoS_2. Since the PL originates from a monolayer of MoS_2 on a thick substrate, the observed PL curve exhibits interference like oscillations. A smoothing routine was used to obtain the PL lineshape, and the peak was found to correspond to an energy of 1.80 eV in good agreement with the results of *ab-initio* simulations that yielded an energy gap of 1.83 eV. The band structure of 2H-MoS_2 derived from the *ab-initio* simulations is presented in figure 6, in which the direct bandgap at the K-point of the Brillouin Zone can be seen.

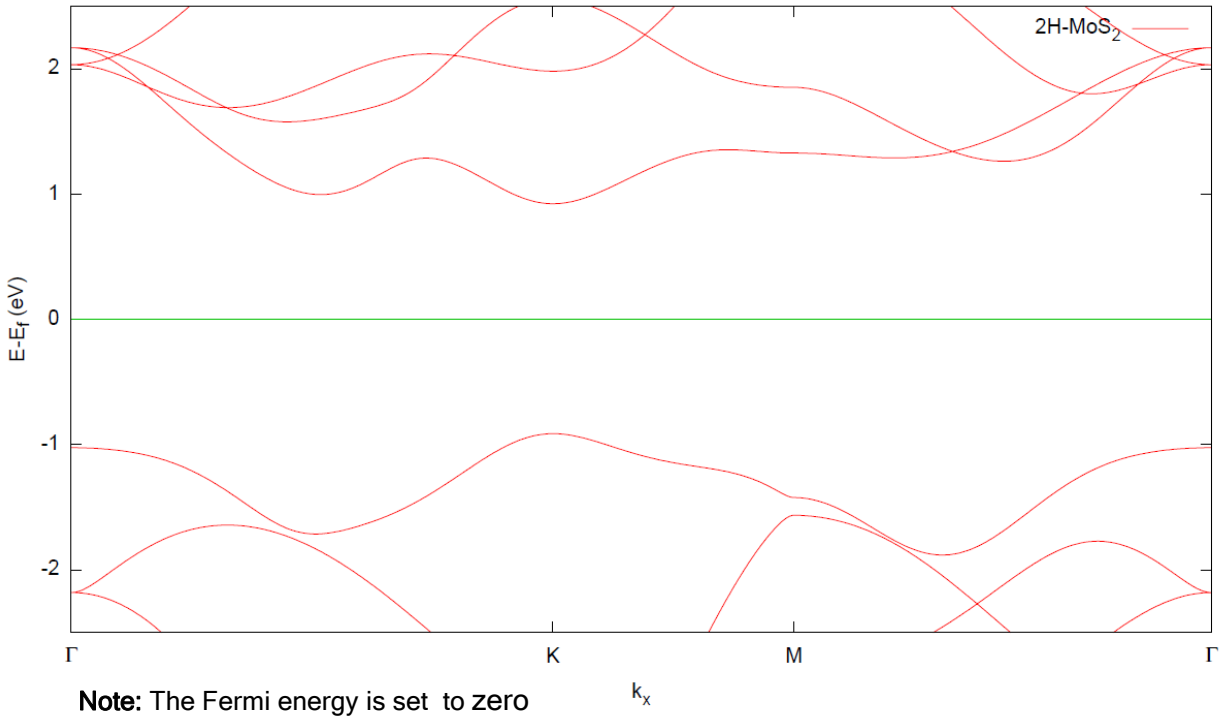


(a) Raman peaks at 384 and 406 cm^{-1}, Silicon peak at 522 cm^{-1}



(b) PL signal with a corresponding peak centered at 1.80 eV

Figure 5
Raman spectral data



Note: The Fermi energy is set to zero

Figure 6
The band structure of 2H-MoS_2

The *ab-initio* simulations were performed utilizing the local density approximation along with norm-conserving pseudopotentials and split-valence double-zeta basis sets with polarization functions and a plane wave cutoff of 300 Ry. A uniform k-grid consisting of 400 points (20 by 20 by 1) for Brillouin zone integration was sufficient to converge the total energy to less than 0.1 meV. The 40 Å of vacuum spacing was used in order to eliminate all spurious interactions between repeating images of the system. All pseudopotentials were tested and resulted in calculated parameters that were in good agreement with previous results. The structure was allowed to relax until forces were less than 0.01 eV/Å. Electronic convergence was accelerated by Pulay mixing of the density matrix without loss of accuracy in the calculated energies.

CONCLUSIONS

Atomically-thin molybdenum disulfide (MoS_2) can be grown, via chemical vapor deposition, according to the method described in this report. Raman and photoluminescence data corroborate the finding that 10 to 50 µm – sized triangular crystals are composed of monolayers of MoS_2. *Ab-Initio* density-functional theory calculations are shown as a method to accurately compute the bandgap of two-dimensional (2D), semiconducting transition metal dichalcogenides with regards to experimental methodologies. Further efforts are needed in the uniform growth of 2D materials over a large area in order to take full advantage of the electronics applications offered by this material.

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