Study of Exfoliated Molybdenum Disulfide (MoS_2)

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In this study, We demonstrate mono and few layers MoS_2 samples on the $SiO_2(270nm)/Si$ substrate from bulk MoS_2 crystal by micromechanical exfoliation technique. We also report that the Raman and PL intensity can be thermally modulated by annealing $1L, 2L$ and $7L MoS_2$ in a vacuum or air. We have systematically studied Atomic Force Microscopy, Raman and PL properties of mono and few layer MoS_2 on the $SiO_2(270nm)/Si$ substrate. First, we find that the number of layer values dependent the Raman and PL emission. First, Raman intensity area ratio of the MoS_2 $E_2^1 g, A_g^1$ and $2LA$ modes to that area of the Si substrate increased linear with increasing number of layers MoS_2. Second, Normalized PL intensity area of the (A) peak decreased linear with increasing number of layers MoS_2. The value of those graphs is a method to understand the number of layers the exfoliated MoS_2. Third we found that some effects of the few layers MoS_2 after thermal annealed (vacuum and air 300^0C for 40 min).

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I. INTRODUCTION

In the last decade, single atomic layer of graphite[1], great interest has grown on two dimensional materials. Two dimensional materials are attractive for use in next-generation nanoelectronic devices because, compared to one-dimensional materials, it is relatively easy to fabricate complex structures from them. MoS_2 is one of two dimensional materials and MoS_2 layers are bound together by weak van der Waals interactions and laminated 0.7 nm one to another.

Differently from graphene, MoS_2 is semiconductor with an indirect band gap of 1.2 eV[2] in bulk to direct band gap 1.8 eV for a monolayer MoS_2[3–7], make MoS_2 attractive for a variety of electronic and optoelectronic devices. MoS_2 layers are bound together by weak van der Waals interactions and stacked 0.7 nm one to another. This feature enables easy exfoliation of the bulk molybdenite, similar to graphite, and suggests the possibility to fabricate monolayer MoS_2 following similar methods to the ones performed to obtain graphene[1, 11]. Micromechanical exfoliation technique[4, 5, 9, 10] (like for graphene) is the simplest and cheapest way to obtain exfoliated molybdenite with planar dimensions of the order of μm. Atomically thin MoS_2 layers can be peeled from molybdenite bulk and, once deposited on a substrate, identified by optical microscopy. The possibility to estimate the numbers of layers of the exfoliated molybdenite on 270 nm SiO_2 substrate[8] has been demonstrated. As in the case of graphene, MoS_2 has a wide range of applications. Due to the MoS_2 flexibility, future applications will be focused on Two-dimensional MoS_2 may be used in sensors[10, 12, 13] and memory[14] and photovoltaic devices[15] and Monolayer MoS_2 has also been used to fabricate a solar cell (with TiO_2 nanoparticles and poly (3-hexylthiophene)) with photo conversion energy of 1.3% [16]. Direct band gap in monolayer MoS_2 makes this material attractive for optoelectronics[17–19] potential applications in short-channel transistors[9, 22–24] and gas sensing[20, 21].

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II. EXPERIMENTS

A. Sample Fabrication and Optical Characterization Setup

Mono and few layer MoS_2 samples were prepared on the $SiO_2(270nm)/Si$ substrate from bulk MoS_2 crystal (SPI Supplies, CAS 1317-33-5) by micromechanical exfoliation technique. Heavily n-doped silicon substrate (resistivity 0.01 Ωcm) has been cleaned by the usual process with acetone, isopropyl alcohol, de-ionized water, in ultrasonic bath (15 minutes for each step). MoS_2 crystal has been exfoliated using a scotch tape, to fabricate mono and few layers MoS_2 flakes. The flakes have been deposited on the silicon substrate and, to remove glue and other contaminants, cleaned in acetone and isopropyl alcohol (10 minutes for each step). The quantitative optical characterization of the MoS_2 flakes is carried out with an Olympus BH-2 microscopy equipped with a LEICA EC3 3.1 Mpixel digital camera. Then height of one of these flakes have been analyzed by Atomic Force Microscopy (AFM Digital D5000, Veeco, conductive AFM tip, cantilever resistivity 0.01-0.025 Ωcm, antimony n-doped silicon, tip radius 10 nm, nominal resonant frequency 320 kHz, tapping mode

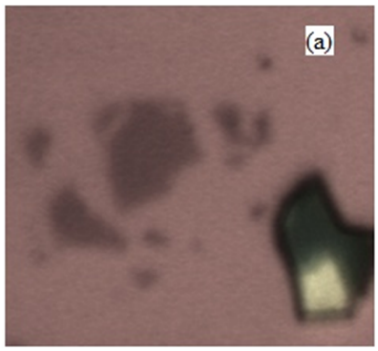
n layer numbers of the MoS_2	Height of the layers (nm)	Different Raman modes $\Delta\nu$ (cm^{-1})	Raman ratio of Intensity area $(E^1_{2g} + A_{1g} + 2LA)$ to Si	Normalized PL Intensity area (arb. units)
1L	0.87	20.77	0.2335	1.0778
2L	1.35	22.14	0.2865	0.8686
3L	2.0	22.99	0.3447	0.8327
4L	2.6	23.11	0.5526	0.7195
5L	3.2	23.36	0.7605	0.6503
7L	4.0	23.51	1.0282	0.3636
10L	5.7	23.79	1.4859	0.1820
bulk	51	26.25	7.5585	-

TABLE I: Atomic force microscopy (AFM), Raman and Photoluminescence spectroscopy data

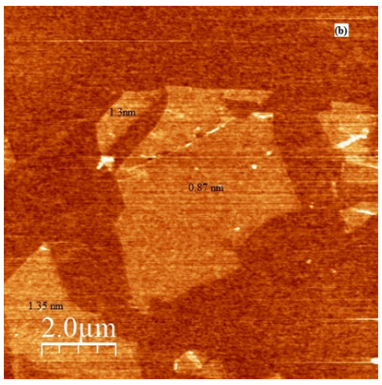
microscopy).

B. Raman and Photoluminescence Spectroscopy Setup

Raman and photoluminescence (PL) spectra are recorded simultaneously in a micro-Raman spectrometer (Renishaw in via) in backscattering configuration excited with an Ar laser ($\lambda = 632.8$ nm). The laser beam was focused on the MoS_2 sample by 100x objective. The scattered light was collected and collimated by the same lens. The scattered signal was dispersed by a spectrometer working at 1800 grooves/mm in the Raman and at 300 grooves/mm in the Photoluminescence and were detected by a thermoelectrically cooled CCD (charge-coupled device) detector at 60^0C. Typical integration times are in the order of 240 s in the Raman and in the order of 10 s Photoluminescence. All of the Raman and Photoluminescence were recorded for the same integration time, laser power, and focus status. The size of focused beam was about 1 μm and only flakes larger than 2 μm were used.



(a)



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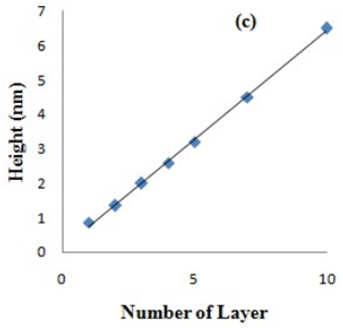


(c)

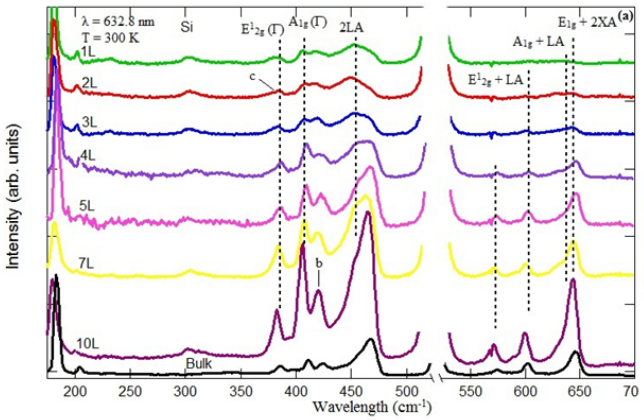
FIG. 1: (a) Optical image and (b) AFM image of the exfoliated Monolayer MoS_2. (c) Measured height (H) number of layer. Squares are experimental data, and the line is linear fit.

C. Annealing Process

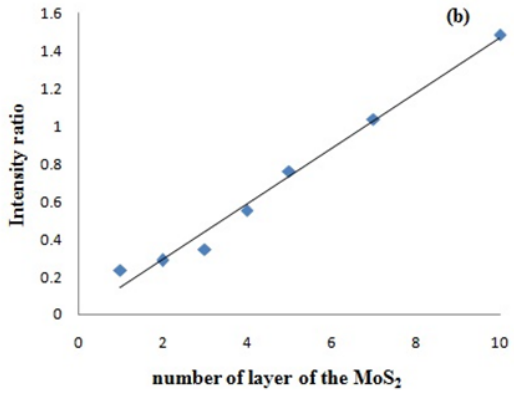
To modify the Raman and PL characteristics, some samples were annealed in the UHV chamber (pressure 10-9 torr) and in air at 300^0C for 40 min.

III. RESULTS AND DISCUSSION

Figure 1a and 1b shows the optical and AFM images of the mono layer exfoliated MoS_2 flakes are reported. The lateral size and height distributions of the flakes determined by Optical microscopy and AFM analyses. This image shows that the heights of the flakes are about (1.2 – 1.8) nm (tapping mode microscopy) and (0.87 – 1.35) nm (contact mode microscopy) and lateral size of the image 5x5 μm. Mono layer height was 0.8 nm. AFM height of the flakes are depend tip and microscopy mode. Figure 1c measured height (H) number of layer. Figure 2a shows the Raman resonance of different layer MoS_2 flakes recorded using 632.8 nm laser line. Ra-

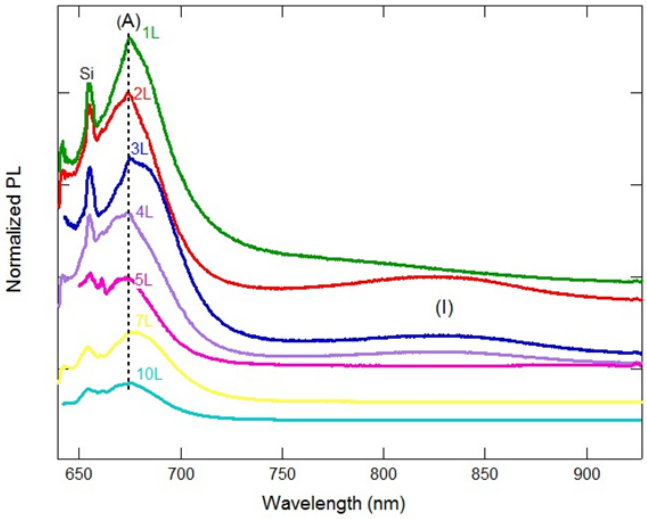


(a)

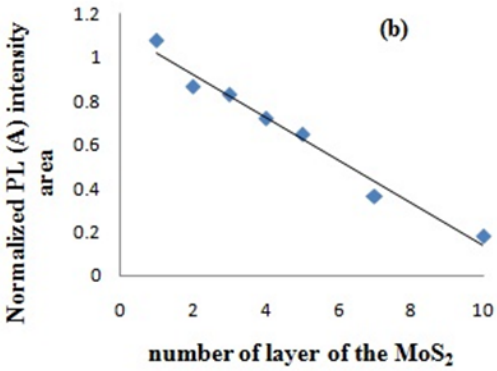


(b)

FIG. 2: (a) Resonant Raman spectra of different layers of MoS_2 using 632.8 nm laser line at the 300 k. (b) Calibration curve of the intensity area ratio of the MoS_2 E^1_{2g}, A^1_g and 2LA Raman modes to that area of the Si substrate. Squares are experimental data, and the line is linear fit.



(a)



(b)

FIG. 3: (a) Normalized PL spectra of different layers of MoS_2. (b) Calibration curve of the normalized PL intensity area I(A). Squares are experimental data, and the line is linear fit.

man spectroscopy has already been established as a reliable tool to investigate the layer number of MoS_2 samples. We identified mono, bi, tri, four, five, or seven layer MoS_2 images. This result Raman E^1_{2g} and A^1_g modes each layer number different other results. We calculated number of layers MoS_2 dependence, Raman intensity area ratio figure 2b Calibration curve of the intensity area ratio of the MoS_2 E^1_{2g}, A^1_g and 2LA Raman modes to that area of the Si substrate. Squares are our experimental data, and the line is the linear fit. Figure 3a shows Photoluminescence spectra of different layers MoS_2 flakes. We have demonstrated mono, bi, tri, four, five, or seven layer MoS_2 images. We also calculated number of layers MoS_2 dependence, normalized PL intensity area figure 3b Calibration curve of the normalized PL intensity area I(A). Squares are our experimen-

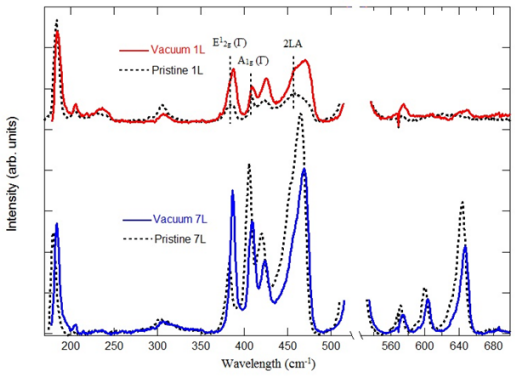


FIG. 4: The Raman spectra before and after annealing in a vacuum (300^0C for 40 min).

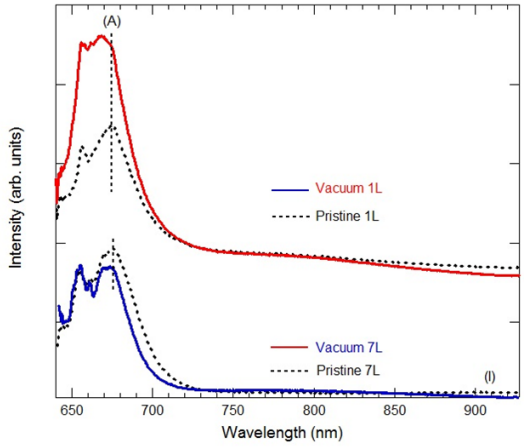


FIG. 5: PL spectra before and after annealing in a vacuum (300^0C for 40 min).

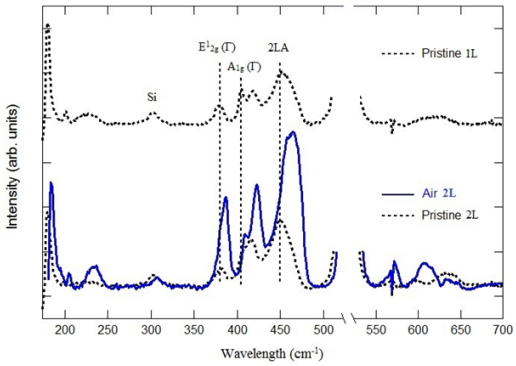


FIG. 6: The Raman spectra before and after annealing in the air (300^0C for 40 min).

tal data, and the line is linear fit. Table I: Atomic force microscopy (AFM), Raman and Photoluminescence spectroscopy data Figure 4, 6 shows effects of the thermal treatment on Raman spectra of 1L and 7L MoS_2, respectively for a vacuum and in air. We demonstrated that the Ultra-high vacuum and air annealing increased the Raman modes area. Figure 5, 7 Shows the PL spectra in vacuum annealing mono layer MoS_2 increased the PL intensity (IA) and peak energy (EA), respectively for 60% and 13.3 meV. (300^0C for 40 min) We also surprising finding in this work, the indirect gap of the few layers MoS_2 were changed after thermal annealing (vacuum and air).

IV. CONCLUSION

In conclusion, we have systematically studied the Raman and PL properties of mono and few layer

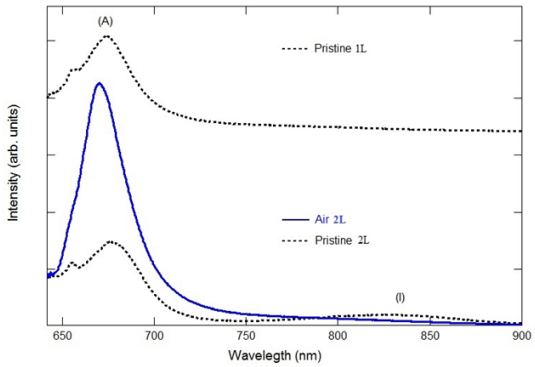


FIG. 7: PL spectra before and after annealing in the air (300^0C for 40 min).

MoS_2 on the SiO_2 (270nm)/Si substrate. We calculated that the number of layer dependent quantitative the Raman and PL emission. First, Raman intensity area ratio of the MoS_2 E^1_{2g}, A^1_g and 2LA modes to that area of the Si substrate increased linear with increasing number of layers MoS_2. Second, Normalized PL intensity area of the (A) peak decreased linear with increasing number of layers MoS_2. The value of those graphs is a method to understand the number of layers the exfoliated MoS_2. Third we found that some effects of the few layers MoS2 after thermal annealed (vacuum and air 300^0C for 40 min). Our results are combined characterization by quantitative optical microscopy, Atomic force microscopy (AFM), Raman and Photoluminescence spectroscopy are presented in Fig 1, 2, 3. Our results are compared with the available experimental results. Same results are presented in table I.

V. ACKNOWLEDGMENT

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