Synthesis and Investigation of Multiple Application for Two-Dimensional MoS_2 via Chemical Vapor Deposition

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***Abstract*—**Molybdenum disulfide with a direct band gap has been synthesized in atmospheric pressure by chemical vapor deposition (CVD). MoS_2 atomic sheets are synthesized on SiO_2 substrates by using MoO_3 and S powders as the reactants. The process was based on the alteration of MoO_3 to MoO_2 by sulfurization. Successful fabrication and characterization of MoS_2 domains have been completed. Two applications have been chosen firstly we transferred MoS_2 layer to the carbon electrode. Electrochemical hydrogen evolution reaction (HER) test for continuous MoS_2 monolayers on carbon electrodes has been investigated. In another application a field-effect transistor of MoS_2 monolayer has been investigated.

***Index Terms*—** MoS_2, SiO_2, MoO_3 .

I. Introduction

Transition metal dichalcogenides (TMDCs) which can be considered as semiconductors, that is highly practical for fields of catalysis, hydrogen storage, nanotribology, lithium batteries, microelectronics, medical and optoelectronics. Transition metal dichalcogenides (TMDCs) with the structure of MX_2 , in which (M) is a transition metal atom (Mo, W, etc.) that sandwiched between two layers of X chalcogen atoms (S, Se or Te). This material due to ability to get highly thick layers have been attracted enormous interest. More than 1173 two-dimensional (2D) materials identified and the number still growing. Amongst these 2D materials, MoS_2 has attracted many scientists research aims because of abundant and exceptional possessions, some of Interesting properties of MoS_2 like containing relatively high carrier mobility (~10 cm^{-2} $V^{-1}s^{-1}$), moderate band gap in the range of 1.30 to1.8 eV. This property has given us a very good chance to fabricate a new thin device like field-effect transistors (FETs),[1-2] photodetectors,[3] light- emitting diodes (LEDs),[4] sensors,[5] photovoltaic, and hydrogen evolution reaction[6].

In order to synthesis 2D materials, there are a variety of method like mechanical exfoliation, chemical exfoliation and molecular beam epitaxy (MBE). In recent times, chemical vapor deposition (CVD) has been one of the highly promising methods of producing large areas and high quality MoS_2 thin films. For this aim some precursors have been used, such as MoO_3, and $MoCl_5$ as a source for molybdenum [7]. As we can see from different results a variety of MoS_2 domain shapes have been synthesized such as triangles, hexagons, truncated triangles, three-point stars, and six-point stars [8] .Chemical vapor deposition is typical bottom-up and vapor-phase growth method that is currently accepted as one of the best techniques capable of forming large and uniform 2D films or flakes with the desired electrical or optical properties [9].

On the one hand, the organized study of the growth parameters of MoS_2 is still under improvement and the parameters related to amount of MoO_3 is still challenging [10]. On the other hand, the controllable growth of TMDCs is also challengeable as many of parameters should be tuned in the same direction in order to synthesis a high quality 2D material [11]. Thus, This report the shape evolution of monolayer growth of MoS_2 and progress to achieve centimeter scale of MoS_2 as a continuous layer by implementing MoO_3 as Mo source material [12]. The results show the growth of monolayer MoS_2 could be efficient from the precise control of the applying sulfur and the S/Mo ratio. The size of MoS_2 flakes are highly depended to a number of precursors [13]. These studies demonstrate a better understanding of the growth and application of MoS_2 and similar 2D materials [14].

Hydrogen is a very important energy source for future generations as a clean energy, in addition sustainable producing hydrogen and oxygen from water has attracted scientists to find a new and cost-effective methods [16]. Pt group metals are extremely useful HER electrocatalysts. Many investigations have proven that MoS_2 is a favorable 2D material to electrocatalyst for HER. Here, firstly we report the synthesis of MoS_2 on SiO_2 and demonstrating the high HER electro catalytic activity, and then we will give a report and study about mobility of MoS_2 and how to fabricate a transistor as a field-effect transistor [16]

II. Thesis objectives

The objective of this thesis is to study multiple applications for Two-Dimensional MoS_2

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Monolayer layer growth via CVD process. To achieve this goal, the following stages are to be implemented over the course of the thesis:

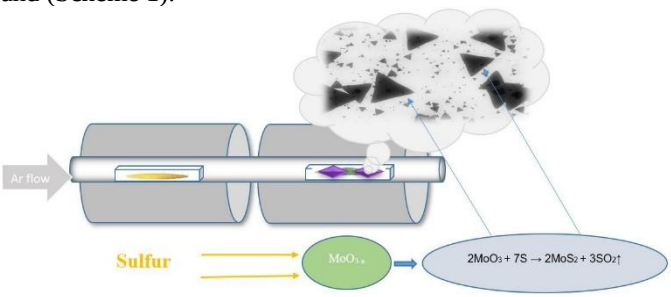
* Synthesis of two-dimensional MoS_2 monolayer in the two shapes, monolayer triangular with the flake size in the range of 35 to 45μm, and continuous layer in the range of 1 cm2.
* characterization of two-dimensional MoS2 monolayer
* Application of MoS_2 monolayer as effective hydrogen evolution reaction (HER) catalyst.
* Finally, fabrication of MoS_2 field effect transistor.

III. Experimental Methods

A. *Experimental method for synthesis of MoS_2*

The initial step is tube preparation as a cleaning and drying. After cutting the SiO2/Si substrate into squares of 2 cm × 2 cm, they were immersed in acetone and sonicating for 15 min to make clean the Si oxide following by washing with copious amount of deionized water and subsequently rinsing with isopropanol alcohol (IPA).We applied a droplet of 3,4,9,10-perylene- tetracarboxylic-dianhydride (PTCDA) solution as a seeding promoters on the SiO2/Si substrate, it was spun on the substrate surface followed by drying at 50 °C. Afterwards, 0.4 gr of Sulfur, and 0.05 gr of MoO3 were placed in two separated ceramic boats. We placed substrate faced down and mounted on the top of boat with containing MoO3. A separate ceramic boat with sulfur powder (0.4 g) was placed next to the MoO3 powder with 45 cm apart from each other in the quartz tube (Fig1). Then, substrate was then placed inside the 120 cm long quartz tube. One side of the quartz tube is connected to ultra-high purity Ar and carrier gas while the other side is attached to the vacuum pumps.

The quartz tube was first kept in a flowing protective atmosphere of high purity Ar gas, the flow rate was 50 sccm (standard cubic centimeters per minute). For the first furnace which contains sulfur we have settled on 220˚C on the program furnace of 11˚C/min, respectively, during the synthesis of MoS2 sheets, the reaction chamber was heated to 700 ˚C in Ar environment with introducing 50 sccm of Ar to the system. When the furnace temperature reached 700 ˚C (~ 30 min), the Ar flow rate was increased from 50 sccm to 220 sccm to the growth chamber. After 5 min, substrates were cooled down rapidly (10 min) under the flow 400 sccm of Ar. Cooling can be quickly done by using electric fans. (Table1) and (Scheme 1).



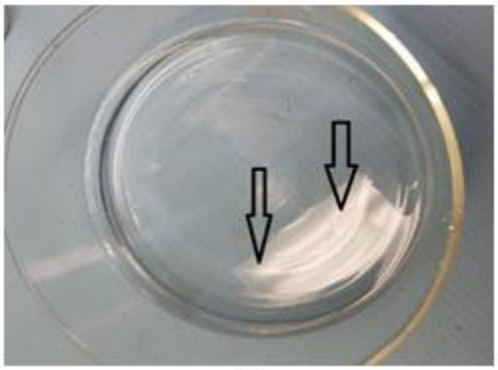
Scheme 1 (a) Experimental setup of the CVD system, and schematic representation of the vapor−solid growth process of triangular shaped MoS_2

TABLE.1. SUMMARY OF SOURCE MATERIALS AND THEIR LOADS IN CVD GROWTH OF 2D-MOS_2 ATOMIC LAYERS VIA CVD

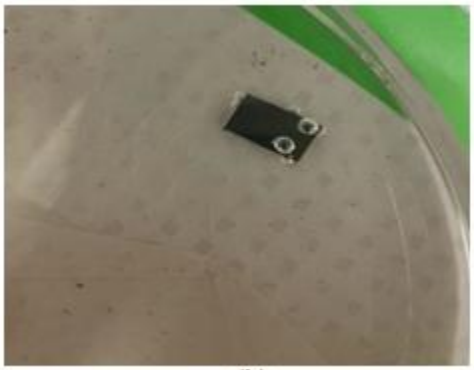
Sulfur source	MoO3 source	CVD Program Sulfur	CVD Program MoO3	Temp MoO3	Temp Sulfur	Gas Ar Flow rate	Gas flow for growing	Cooling	ubstrate/ Set-up
0.4	0.135	11 ˚ C/min	35 ˚ C/min	775 ˚ C	180 ˚ C	100 sccm	250 sccm	After 580 ˚ C	Face-down

B. *Experimental method for transferring Monolayer MoS_2*

Transferring MoS_2 from SiO_2 to Carbon can be achieved by a utilizing poly (methyl methacrylate) (PMMA) handle. The surface of MoS^2 monolayer on SiO_2 has been spin coated by PMMA. The sample was next baked at 100 ºC for 1 minute to harden the PMMA. Then, we have prepared 0.1 M NaOH in order to plunge substrates for about 4 days, (Fig. 1a). After completely transferring the MoS_2 layer, the MoS_2 layer covered by PMMA was softly transferred to a carbon, so as to remove PMMA we used two techniques ,first we applied acetone and then in order to be sure that all the PMMA have been removed, we put the sample in CVD in 300 ˚C for about 3 hours,at the end we have measured MoS_2 Raman spectra, Raman has shown that we have pure MoS_2



(a)



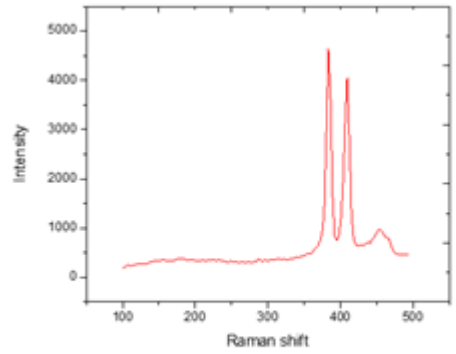
(b)

c)

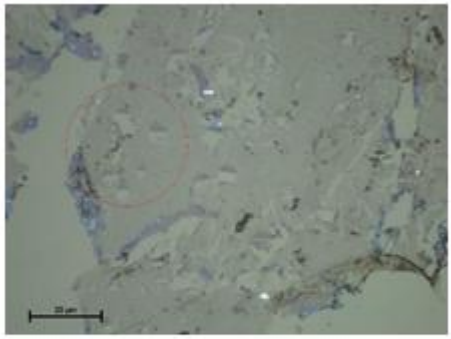
Fig. 1 .(a,b) plunge substrates in 0.1 M NaOH, and (c) transferring MoS_2 monolayer from SiO_2 to Carbon.

C. Experimental method for scanning electrochemical cell microscope

Linear sweep voltammetry measurements by means of the scanning electrochemical cell microscope enabled microdroplet cell measurements atop a glassy carbon electrode previously modified with a MoS_2 continuous monolayer sheet. A 5x5 point matrix was sampled with a 10 µm quartz micropipette probe as the quasi Ag/AgCl reference-counter electrode, on the modified glassy carbon working electrode. The probe reservoir solution was 0.5 M H2SO4 and the potential scanning range was from +1 V to -1.2 V (vs Ag/AgCl). The same conditions provided reference measurements on the plain glassy carbon electrode, except for a larger potential scanning range being from +1 to -1.8 V (vs Ag/AgCl).



(a)



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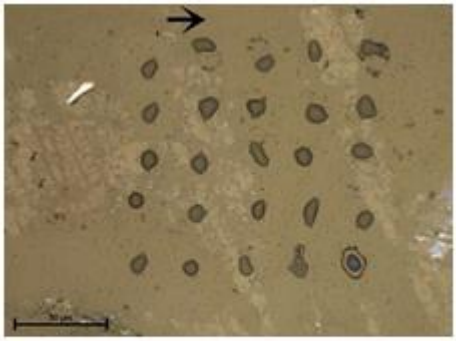


(c)

Fig. 2. (a,b) Raman spectra and optical image after transferring MoS_2 on the carbon.(c) Optical image for 5x5 matrix points that created by 0.5 M H_2SO_4.

D. Fabrication of MoS_2 transistor

Transistor fabrication has been started by cleaning substrate and material by nitrogen gas ,and then to find a suitable shadow mask wafer and place it on the substrate ,after that to start deposit 20 nm Cr and 50 nm of Au ,after patterning we removed the shadow mask from the substrate ,our device is ready to go probe station

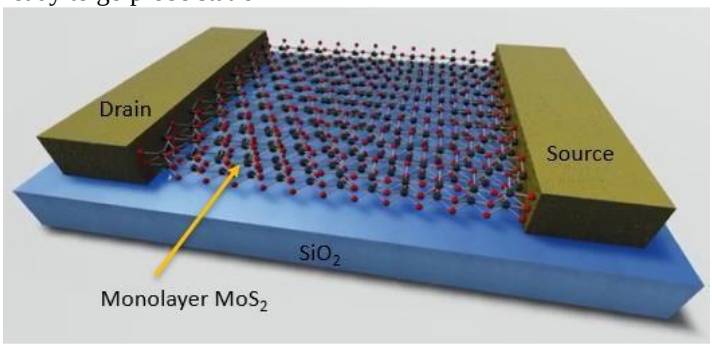


Fig 3. schematic illustration of a transistor.

IV. RESULTS AND DISCUSSION

A. Morphology of Two-Dimensional MoS_2

Optical images of 2D-MoS2 has shown in Figure 4.The size of the triangle was between 12 to 15µm. The flake size of the MoS_2 increased in the range of 35 to 45µm when the amount of the metal source was increased. And in the specific parameters

that we reported in experimental section we are able to synthesis a very large area of MoS2 as a continuous monolayer layer.

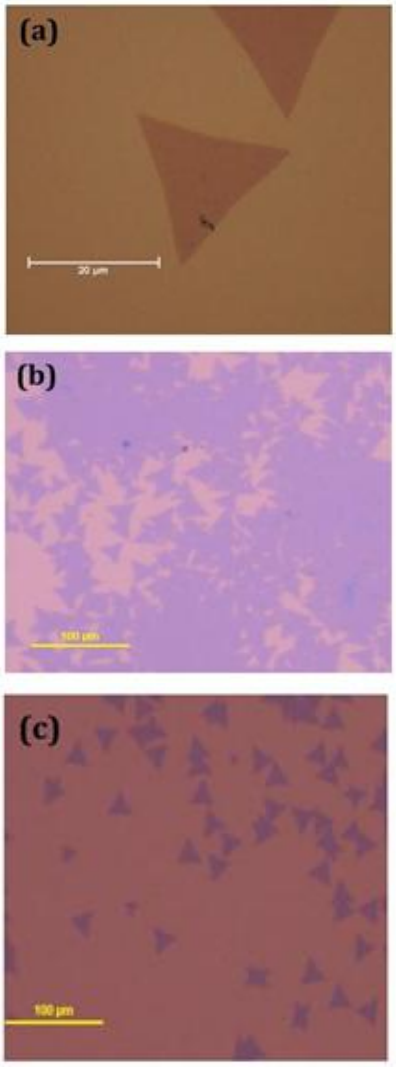


Fig 4. Optical images for MoS2 monolayer.

B. *SEM images of MoS_2*

Scanning electron microscope image of triangular MoS_2 monolayer grown on a 320 nm SiO_2/Si substrate. The figure has shown the 60° corners of a selected triangular with a clean surface. Therefore, another advantage over exfoliation techniques is that the crystal axes can be immediately detected by inspection.

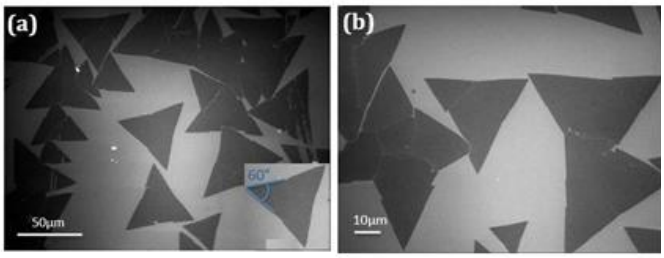
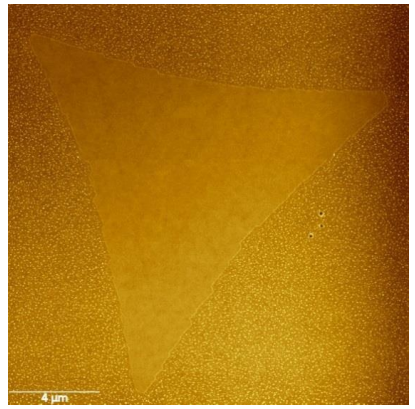
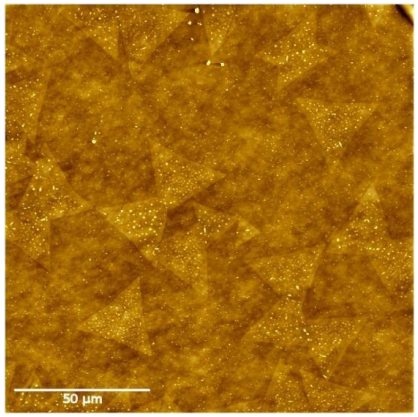


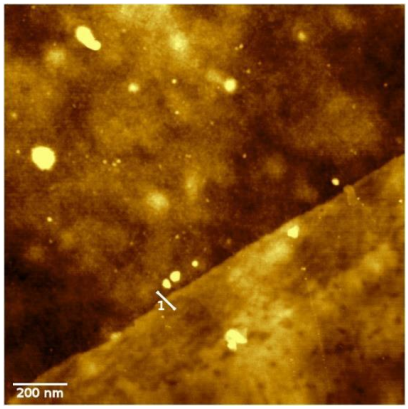
Fig. 5 :(a,b) SEM images monolayer MoS2.

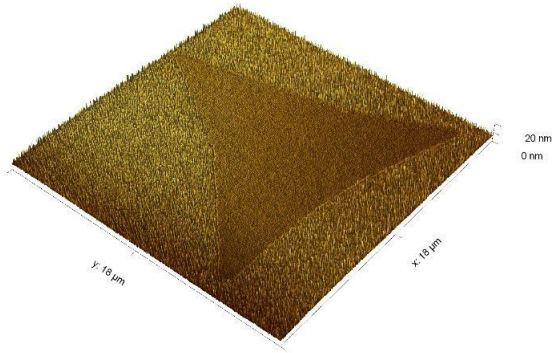
C. *Atomic force microscopy AFM of MoS_2 monolayer*

This date has been shown a strong sign that synthesized MoS2 is monolayer. The thickness that we measured by using AFM can be considered less than 0.85 nm, we will take a note that bilayer MoS2 is about 1.3 nm.









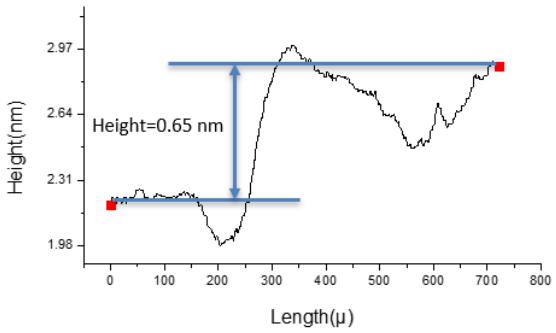
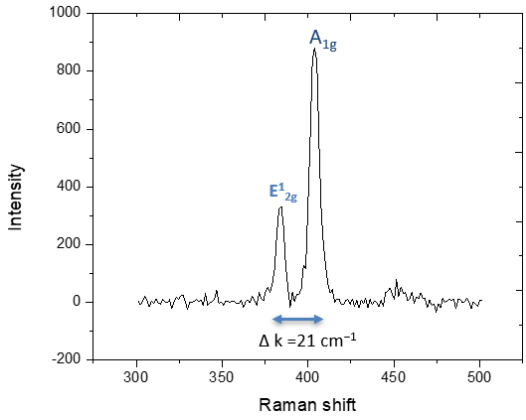


Fig. 6 :(a,b) AFM images monolayer MoS_2 and height evaluation.

D. Raman spectrum of a synthesized MoS_2

To be assured that the domains imaged by SEM in Figure 5 were indeed monolayer MoS2, we characterized them by applying Raman spectroscopy (Figure 7). Two characteristic Raman vibration modes can be seen in the spectra in Figure 7a, the E1 2g mode representing the in-plane vibration of molybdenum and sulfur atoms and the A1g mode related to the out-of-plane vibration of sulfur atoms. The frequency difference between these two modes depends on the number of layers of MoS_2. Here, the fitting results show that these two modes are located at E12g 387 cm−1 and A1g 408 cm−1, respectively, giving a frequency difference Δk of 21 cm−1. It is indicating that MoS_2 is monolayer, I will take a note that Δk for 2 layers, 3 layer sand 4 layers are 22.6, 23.6 and 24.6 cm−1.[16].



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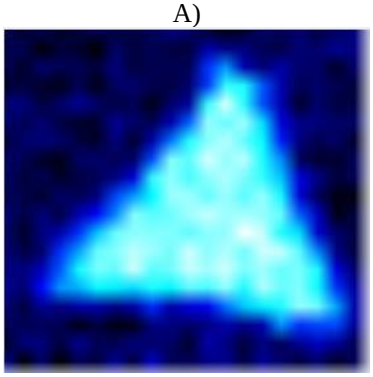


B)

Fig. 7. (a) Raman spectrum and (b) Raman map of the MoS2 domain, plotting the spatial variation of the magnitude of the frequency difference between A1g and E2g. Laser excitation of 532 nm was used.

E. Photoluminescence (PL) spectrum of a 2D-MoS2 atomic layers

Figure 8 shows the typical PL spectra from a synthesized MoS2 domain. A strong PL signal is located at 1.8 eV, which can be associated to the A1 excitation of MoS2. 2D images of the PL intensity of different domain shapes have also been measured by stepping a focused excitation laser (532 nm) across the sample and integrating the PL signal from each point.

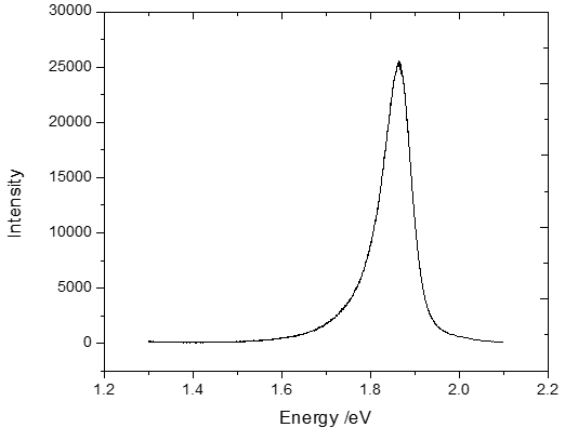


Fig 8. Photoluminescence (PL) spectrum of a synthesized MoS2 domains.

F. Electrochemical HER test for continuous MoS2 monolayer on Carbon

Recent focus on electrochemically produced clean renewable energy demands urge for the findings of efficient catalysts. The consumption of hydrogen gas is virtually harmless. On the other hand, it's a traditional production of natural gas reforming is extremely toxic and energy consumable. Luckily, electrochemistry can potentially provide a low cost, clean and renewable strategy by the electrolysis of water. Renown catalysts for this reaction are the platinum group metals. But their high cost and poor natural occurrence make it impossible for widespread applications. Since the last decade, transition metal dichalcogenides have demonstrated catalytic ability in this domain. The results below confirm previous studies on MoS2's capability to facilitate the evolution of hydrogen electrochemically. In principle, glassy carbon electrode is reputed for being a poor hydrogen evolution catalyst. However, when a monolayer of MoS2 is deposited onto the electrode, the over potential is found to be reduced. This confirms the results from previous findings [16].

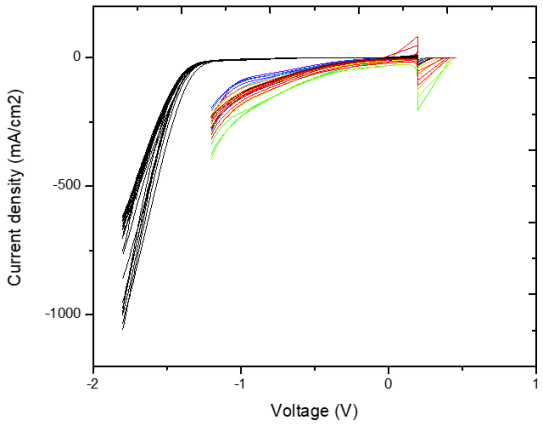
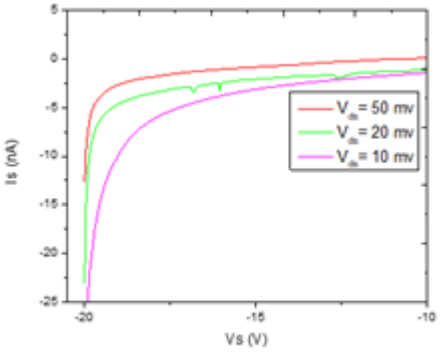


Fig 9: Electrochemical HER test for MoS_2 monolayer

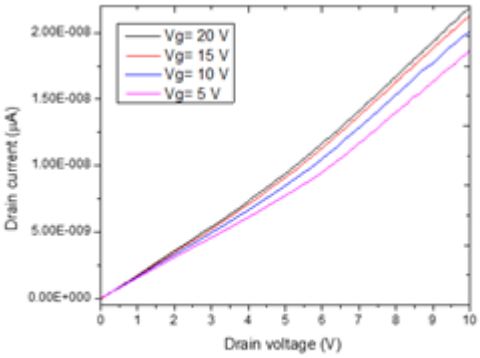
G. FET devices was measured using by using probe station.

Figure 10(b) shows IDS–VDS output characteristics of MoS2 transistor displaying tremendously high mobility, saturation current density and trans conductance for different gate overdrive voltages ranging from 5 V to 20 V with a 5 V step are applied. Our device has shown an n-type semiconductor as when we apply more voltage drain current has increased. SiO2 substrate of the device was grounded during all measurements, reducing the possible capacitive coupling between top- and backside dielectrics. Figure 10(a) shows Integration route yields have a good contact as we can see Linear behavior is observed at each Is-Vs, Is–VS curve recorded for a bias voltage ranging from 10 mV to 50 mV. Measurements are performed at room temperature, as we can see the cure has become linear and constant when Vds has increased. Fig. 10(c) shows the typical IDS–VGS transfer characteristics of device for the FET with 10 mV applied voltage. Vds Inset: Ids–Vds curve acquired for Vbg values of 0, 0.2 and 1 V.

The field-effect mobility (μFE) is calculated by the transfer characteristic using the following equation: μFE =[dIds/dVbg] × [L/(WCi Vds)].



a)



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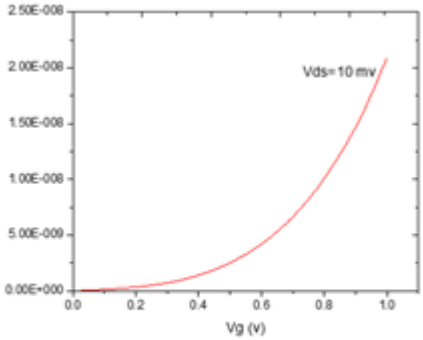

c)

Fig. 10: a) it has shown Is-vs in the voltage ranging 10 mv to 50 mv. b)I d-vd current density and transconductance for different gate overdrive voltages ranging from 5 V to 20 V with a 5 V step are concerned.c) Backgate voltage Vbg is applied to the substrate and the top gate is disconnected. Inset: I ds–Vds curve acquired for Vbg values of 0, 1 and 5V

V. Conclusion

At the end of this research report, we can conclude the following:

- Our work provides an effective method for understanding and synthesizing of monolayer MoS2 in large-sized as a continuous MoS2.
- Successful fabrication and characterization of MoS2 domains.
- Synthesized a highly crystalline and large-area MoS2 monolayer 45μm.
- Our work provides experimental method for transferring Monolayer MoS2.
- Our work provides details about experimental method for scanning electrochemical cell microscope
- Electrochemical HER test for continuous MoS2 monolayer on carbon

VI. Future Work

1. MoS2 as a sensor for contaminant materials like Pb and Cu.
2. Electrolytic phototransistor based on graphene-MoS2 Van der Waals p-n heterojunction with tunable photo response.
3. Combination of MoS2 and h-BN in order to make a capacitor.
4. Develop Transistors: syntheses a new Hetro-structures by using MoS2, h-BN, and WSe.

5. Environmental Applications of 2D Molybdenum Disulfide (MoS2)

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