Low Temperature Plasma Enhanced Atomic Layer Deposition of Two-Dimensional Molybdenum Disulfide

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Abstract: In this report we present a plasma enhanced atomic layer deposition (PEALD) method to produce few layer molybdenum disulfide (MoS_2). The films are synthesized at low temperature (300 C°) with non-toxic elemental sulfur (S_8) and molybdenum pentachloride ($MoCl_5$). The as produced films have angstrom level surface roughness. Moreover, due to the small steric factor of $MoCl_5$ only two cycles are required to reach a flat bilayer film.

Keywords: Two Dimensional Materials, Plasma Enhanced Atomic Layer Deposition

1. Introduction

Two dimensional materials promise a new generation of applications due to some unique electronic properties. Of this class of materials, none is more studied than MoS_2. Above all, its ability to work reliably as a transistor with an atomic layer thick gate length [1] or with a one nanometer single wall carbon nanotube [2] has given the material a unique spotlight. Its non-toxic nature has allowed it to grow into biological and environmental fields [3,4] and its unique structure has given it a advantage in hydrogen evolution reactions [5], lithium ion batteries [6], dynamic memory cells[7], and multiterminal memtransistors [8]. Yet, many difficulties in the synthesis of this material remain.

Molybdenum disulfide (MoS_2) synthesis has typically required extensive annealing times, high temperatures, and toxic chemicals to produce. Predominately, the reliable synthesis of large area MoS_2 has proven to be difficult. Multiple authors have reported on chemical vapor deposition methods (CVD) by which a variety of different grain sizes, layer thicknesses, and crystal shapes have been reported with little variance in synthesis conditions [9–14]. Furthermore, for many applications, high temperature CVD synthesis is not acceptable based on maximum substrate or other material temperature constraints and the long times necessary for growth are undesirable. To combat this, low temperature methods are currently in development.

There have been many successes in low temperature synthesis of MoS_2. These largely include atomic layer deposition (ALD) [15–18] routes with some attempts at plasma synthesis[19–22] and low temperature CVD [23]. Unfortunately, the low temperature field is currently limited to the use of hydrogen disulfide (H_2S) a highly toxic compound. Furthermore, plasma enhanced chemical vapor deposition synthesis methods rely on a predeposited molybdenum film which is then taken to a reactor to be sulfurized by H_2S. In recent cases many authors have moved towards a more direct synthesis approach with plasma enhanced atomic layer deposition (PEALD) [24,25], but these still require the use of an H_2S plasma. Furthermore, due to the carbon precursors employed and their steric factors, the surfaces result in variously arranged MoS_2 flakes with surface voids that are not evenly arranged on the surface.

In this report we show that atomic layer synthesis of molybdenum disulfide is possible in a quick process with S_8 and $MoCl_5$ at low temperatures. The as synthesized films are crystalline and have angstrom level surface roughness.

2. Experimental

MoS_2 was synthesized in a tube reactor using an inductively coupled plasma. The reactor was a cylindrical quartz tube of 1 inch in diameter with an inner tube diameter for precursor injection of 3/8 inches. A function generator coupled to a power amplifier and pi matching network were used to send RF signals into the reactor to ignite an H-mode discharge at 125W.

Plasma enhanced atomic layer deposition steps proceed as follows. $MoCl_5$ was heated in a containment vessel that was attached to the reactor. The system was purged initially for one minute under 30 sccm of argon flow. Then an H-mode argon discharge was ignited to heat up a sapphire substrate that was attached to a nickel rod approximately one inch from the inlet of the precursor injection in the reactor. After one minute, $MoCl_5$ was carried into the system for 10 seconds where it reacts with surface sites on the sapphire substrate. Then the remaining gas was purged with 60 sccm of argon for 30 seconds. Then S_8 was carried into the system by 30 sccm of argon and an H-mode discharge was ignited with a total flow of 60 sccm of argon (30sccm to carry S_8 in and 30 sccm pure argon). After 60 seconds the discharge is turned off and 60 sccm of argon was carried through the system for 30 seconds. Only 2 cycles were needed to produce the films. During the process the substrate temperature reaches a maximum around 320 Celsius.

Film characterization was done using a 532 nm Witec Alpha300R Confocal Raman Microscope to take Raman

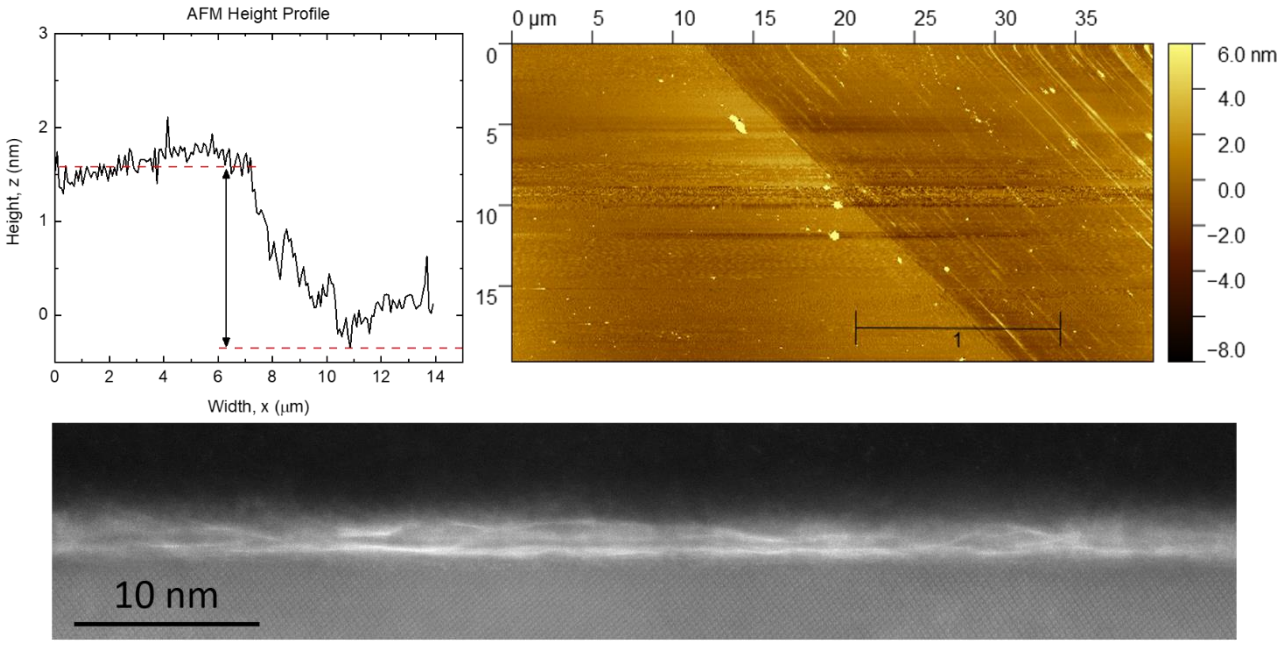

Fig. 1. AFM height images are shown which indicate that the film is 2 nm thick. TEM images further corroborate the AFM images.

images. TEM was carried out by FEI Titan G2 80-300 TEM/STEM. Atomic force microscopy was carried out in force tapping mode using a Bruker nanoscope v multimode 8 with QNM.

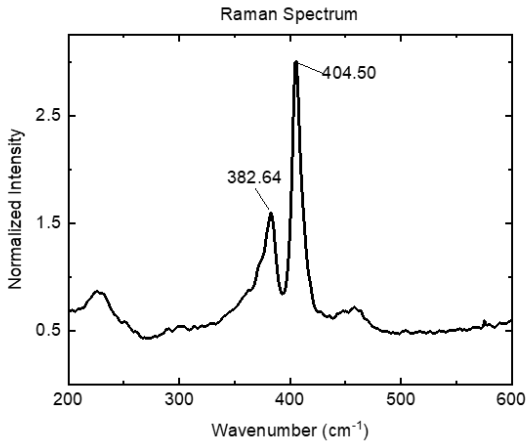

Fig. 2. Raman spectrum taking of the MoS_2 thin film. The peaks correspond to a bilayer crystalline MoS2 film [26].

3. Results and Discussion

Raman peak locations at 404.5 and 382.6 show that the film is crystalline MoS_2 and is two layers thick which can be seen in Figure 2 [26]. To verify the thickness of the material, AFM was used in force tapping mode. A stainless-steel blade was used to scratch a portion of the MoS_2 from the sapphire substrate. The sapphire has a much higher hardness than the blade used which leaves the underlying sapphire untouched during scratching. In Figure 1 the thickness of the film and the area over which the thickness was taken is shown. It is clear that the thickness of the material is on the order of 2 nm and that the roughness of the film is on the order of angstroms. In the bottom of Figure 1 are the TEM images which demonstrate the film uniformity and bilayer nature across the sapphire surface.

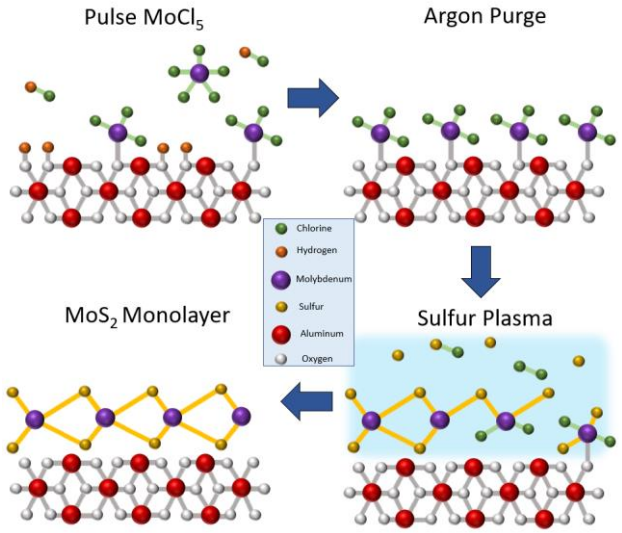

Fig. 3. Example of PEALD film growth. The small steric factor of the molybdenum precursor on the surface can contribute to a much higher density of saturated surface species

One of the reasons for the bilayer formation after only two cycles of deposition result from the steric factor of the $MoCl_5$, see Figure 3 [27]. Upon reaction with a surface oxygen site, $MoCl_5$ should reduce to form a molybdenum trichloride oxide compound which does not take up

significant space on the lattice site of the sapphire substrate. This allows for a high surface density of molybdenum precursor during the initial deposition cycle as compared to a precursor that might have significantly longer atomic chains that would prevent the adhesion of a high number of initial atoms and hence require more cycles.

4. Conclusion

In conclusion, atomically thin polycrystalline MoS_2 films were synthesized using an inductively coupled quartz tube reactor. The films were synthesized in under 10 minutes utilizing nontoxic elemental sulfur at low temperature. The reason for the low cycle number was due to the steric factor of the initiating precursor, $MoCl_5$, which allowed for a high density of surface attachment and hence few cycles to initiate full film formation.

5. References

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