

Proceedings

Direct Synthesis of MoS₂ Dendrites on SiO₂/Si Substrates by Metal Organic Chemical Vapor Deposition †

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Abstract: Controlled growth orientation of MoS₂ thin films is the key requirement to realize their vast number of applications, as material has strong anisotropic properties, in addition chemically active edge sites over inert in-plane MoS₂ flakes is more important for catalytic activities. Thermodynamically, growth of inert in-plane MoS₂ is preferred due to less number of active sites on its surface over the edge-sites MoS₂ and that making vertical growth difficult task. Here, we demonstrate for first time the chemical vapor deposition (CVD) of vertically standing molybdenum disulfide (MoS₂) dendrites, with an combination of Molybdenum hexacarbonyl (Mo(CO)₆) and Dimethyl disulfide (C₂H₆S₂) as the novel kind of Mo and S precursors, respectively. MoS₂ dendrites is a new type of MoS₂ material, SEM and TEM results demonstrated the vertically oriented growth and structure has a tree-like crystal structure with high density of edge terminated MoS₂. Moreover, leaves of those trees have sizes as small as 20 nm and consist of MoS₂ few atomics layers. On optical properties side of dendrites, structure has high absorption cover all visible range of light and strong photoluminescence with wide peak centered around green light due to quantum confinement.

Keywords: MOCVD; MoS₂ films; vertical; dendrites

1. Introduction

Among the family of transition metal dichalcogenide (TMDs), MoS₂ is one of the most extensively studied materials due to attractive properties of its thin films such as possibility to transform band structure of MoS₂ from indirect to direct bandgap with decreasing their thickness from bulk to a single layer [1], high room-temperature carrier mobility MoS₂ (was measured to be ~100 cm² v⁻¹s⁻¹) with a large switching on/off ratio exceeding 10¹⁰ [1], absorption over broad spectral range and low energy consumption [2,3]. Due to that, Molybdenum disulfide has attracted considerable interest as a promising candidate in nanoelectronics and optoelectronics for manufacturing of enhanced transistors, sensors and electronic displays. In addition, MoS₂ yielded the progressive results in the fields of solar cells, energy storages, energy conversions and catalytical applications [4]. For example, MoS₂ can perform as a highly efficient electrocatalyst for hydrogen evolution reaction [1].

Recently growth of vertically aligned MoS₂ nanosheets has been achieved and got a huge interest due to their advanced features including high aspect ratio, maximum surface area, and dense exposed edges. It has been shown that vertically aligned MoS₂ layers in comparing with horizontal sheets are much useful in diverse applications such as hydrogen evolution reaction (HER), sodium storage devices, lithium ion batteries, supercapacitors, sensors, photodetectors, and Photocatalyst, as well as for heavy metal detection. However, deposition of vertically standing MoS₂ nanosheets using

CVD is still a complicated task due to shortage of understanding growth mechanism. Vertically aligned nanosheets can be formed by powder vaporization, sputtering deposition of Mo films as an initial growth step and subsequent sulfurization and by MOCVD [8–12].

Finally, using MoS₂ in field of catalyst and sensing materials specially gas sensors is particularly interesting due to the various active sites (defects, vacancy and edge sites of MoS₂) for selective adsorption and semiconducting behaviors. Many researchers have experimentally exploited the application of MoS₂ in those fields, relied on the use of a horizontal growth of the MoS₂ nanostructure, which is relatively easy to expose and prepared by CVD synthesis and chemical exfoliation. However recently many results has been published confirm the advance of MoS₂ vertical sheets in those fields [5–7].

In this work, MoS₂ dendrites is deposited by MOCVD with tree-like structures, as Morphology confirmed by SEM and TEM. And films have strong full color photoluminescence due small sizes of structures (quantum confinement).

2. Materials and Methods

The deposition process was carried out in the hot-wall low pressure tubular CVD reactor. Mo(CO)₆ powder and C₂H₆S₂ were used for MOCVD growth of MoS₂ films (Figure 1). The Mo precursor Mo(CO)₆ was introduced into the deposition chamber by using argon as a carrier gas from the evaporator, which was maintained at temperature 30 °C, and C₂H₆S₂ were introduced in similar way under temperature 70 °C. Total pressure in the reaction chamber was fixed at 0.5 torr and deposition temperatures 350–950 °C, S/Mo ratio in reactor were 475 and Time of deposition was 30 min. The substrates (silicon wafer, silicon wafer with preliminary 100nm SiO₂ layer and fused quartz) were cleaned in acetone, alcohol and de-ionised (DI) water for 10 min each.

The morphology and composition of the deposited films was studied with the use of scanning electron microscopy (SEM, EDX) (Supra 55 VP) and transmission electron microscope (TEM) (JOEL 2100F), RAMAN spectrum measured by spectrometer (Horiba) with reflection geometry. X-ray photoelectron spectroscopy (SPECS HAS 3500) was used for chemical analysis.

Photoluminescence (PL) measured using home-made Argon laser with standard lock-in amplifier configuration. laser Argon beam modulated by chopper and then focused on sample, PL emission collected by lens on monochromator with PMT detector, signal from chopper send to lock-in amplifier as a reference signal, used integral time 3 S and resolution 1 nm.

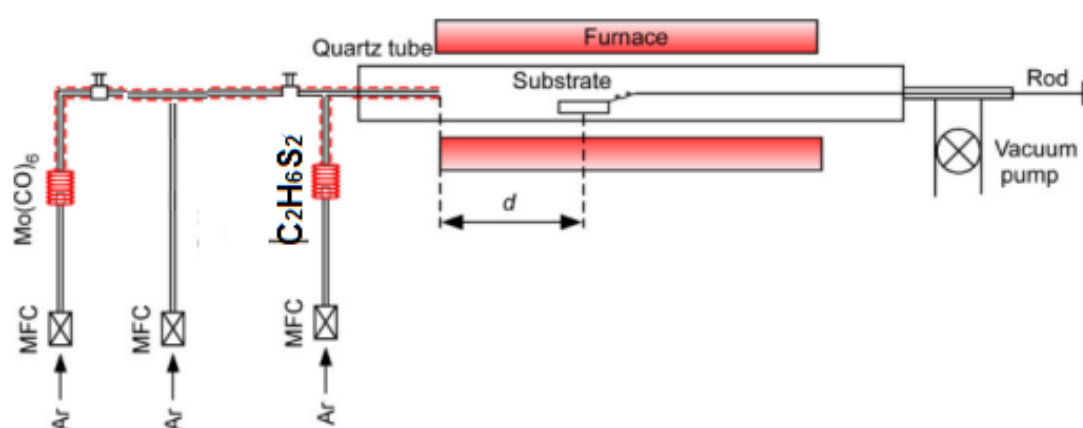


Figure 1. Schematic picture of reactor used in experiments.

3. Results

3.1. Morphology, Structure and Composition

Scanning electron microscopy (SEM) gives valuable information regarding the shape and size of microstructure, in Figure. 2, SEM images of the film deposited at SiO₂/Si substrate, film compose of dendrites with random orientation to each other. Cross section of film, clearly show vertical dendrites growth of with height around 650 nm. Films deposited on Si and quartz substrates has similar morphology without any noticeable change.

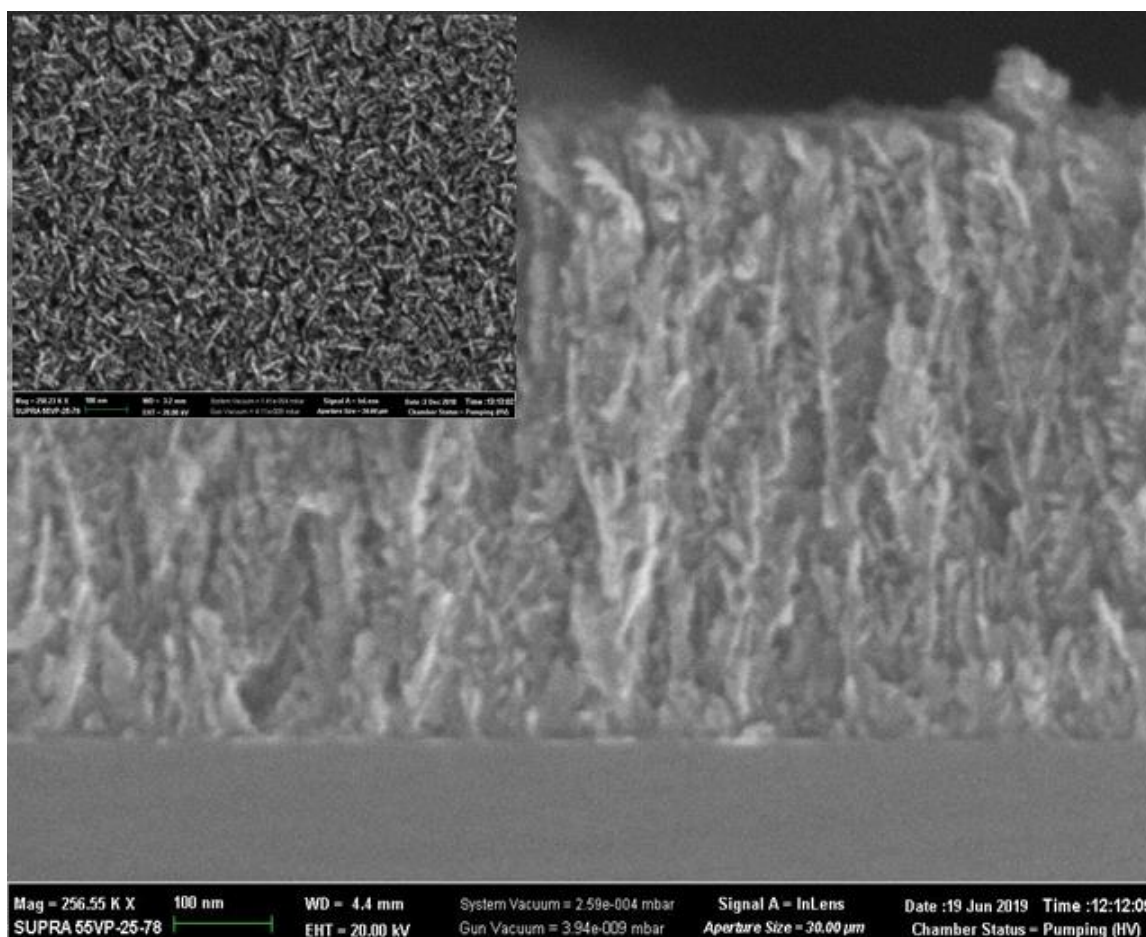


Figure 2. SEM cross section of vertically standing dendrites MoS₂. Inset: top-view of film.

Using TEM, it's possible to see higher resolution and more detailed view. For TEM view, film put on grid by scratching method. In Figure 3 nano-scale view of film, clear tree shape with nanosizes leaves. Leaves also have few nanometers of thickness, as it's transparent for electron beam. sizes can be as small as 20 nm and thickness can reach few layers, Electron beam diffraction of film consist of rings belong to planes belong to 2H MoS₂.

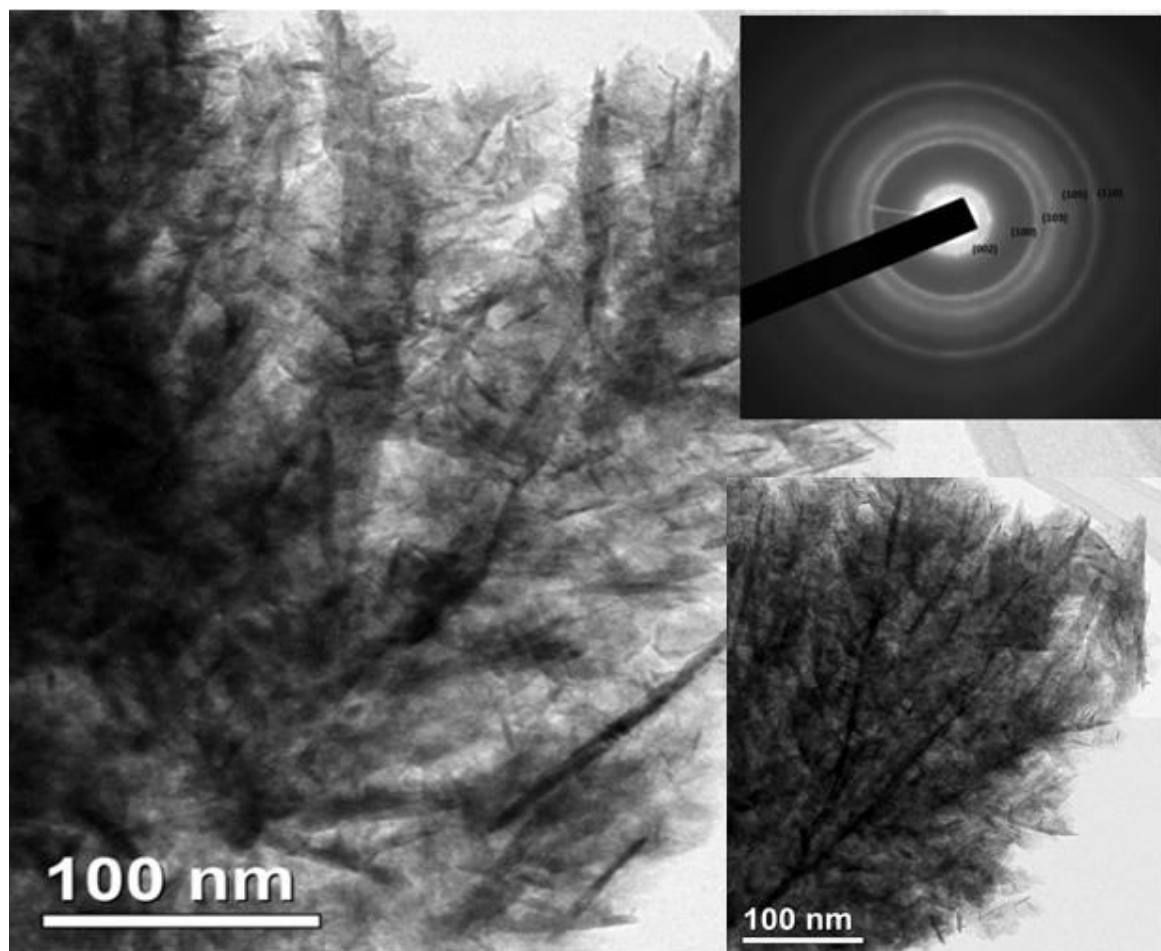


Figure 3. TEM view of tree shape nanostructures with electron diffraction of it.

Crystallinity of film studied by XRD and RAMAN spectroscopy. as shown in Figure 4b, All reflections can be indexed as the pure hexagonal MoS₂ phase with lattice constants of $a = 3.161 \text{ \AA}$ and $c = 12.299 \text{ \AA}$ and in agreement with standard file JCPDS No. 37-1492. However, Due to fact, XRD spectrometer in powder geometry reflections only from planes parallel to substrate can be observed. it's clear that strong Reflection (002) originate from horizontal layer, while reflections (100) and (101) maybe refer to vertical structures.

Further information on Crystallinity has been got by Raman spectroscopy, where number of layer and texture of film can be obtained. Figure 4a show RAMAN spectrum of film, two strong characteristic Raman modes E₁2g and A₁g were observed at 381.2 cm^{-1} and 405.5 cm^{-1} , corresponding to in-plane vibration of molybdenum and sulfur atoms, and out-of-plane vibration of sulfur atoms, respectively. The frequency difference between the E₁2g and A₁g Raman modes is $\sim 24 \text{ cm}^{-1}$, which indicates the presence of around four or more layers of the MoS₂ in nano-structures, confirming TEM results.

Finally, Composition and stoichiometry measured by EDX and XPS. Spectra of film has signal only from elements Mo, S, C and O. Oxygen and Carbon signals maybe due exposure to ambient atmosphere. The stoichiometry of the MoS₂ film has been separately confirmed with XPS and X-ray spectroscopy (EDS) (S/Mo ratio ~ 2.1), Figure 5. However, Films deposited in temperature less than 350 has stoichiometry much less than 2 due to catalyst mechanism of reaction between precursors.

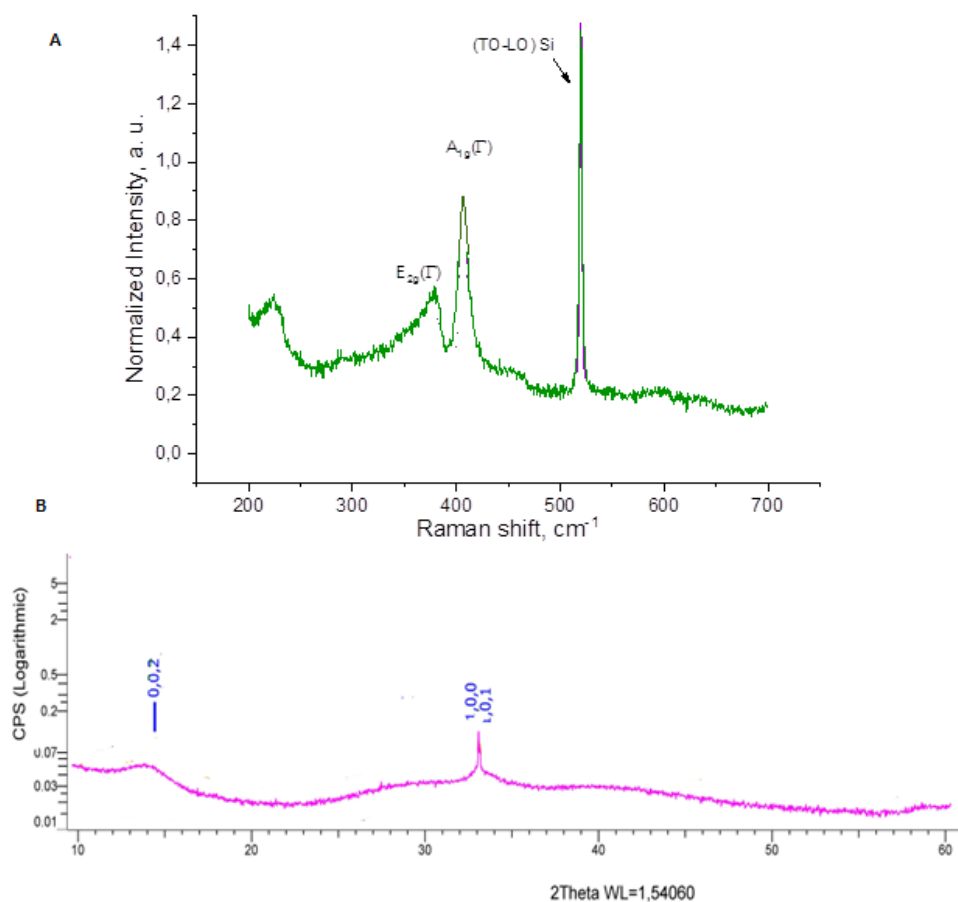


Figure 4. (a), Raman spectrum. (b), XRD for film on silicon substrate.

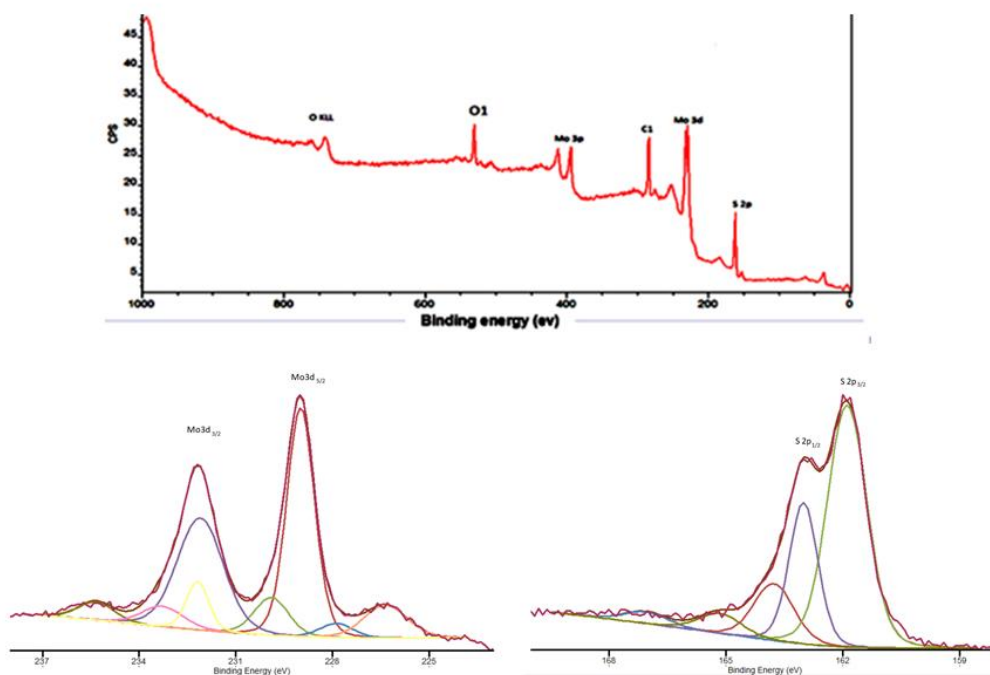


Figure 5. XPS survey of film and Mo 3d and S 2p spectra.

Generally, the dendrite structure can be formed in a non-equilibrium state during the crystal growth process. To date, a variety of materials such as metal, alloy and metal oxide have been demonstrated to form the dendrite structures [14–17]. To study mechanism growth of dendrites films deposited at different higher temperatures, as it is shown in Figure 6, dendritation reduce with increasing of deposition temperature and at high temperature film morphology become vertical sheets with small branches on their surfaces and at very high temperature growth mode is vertical walls without any dendrite structure, suggest that mechanism is limited diffusion aggregation (LDA).

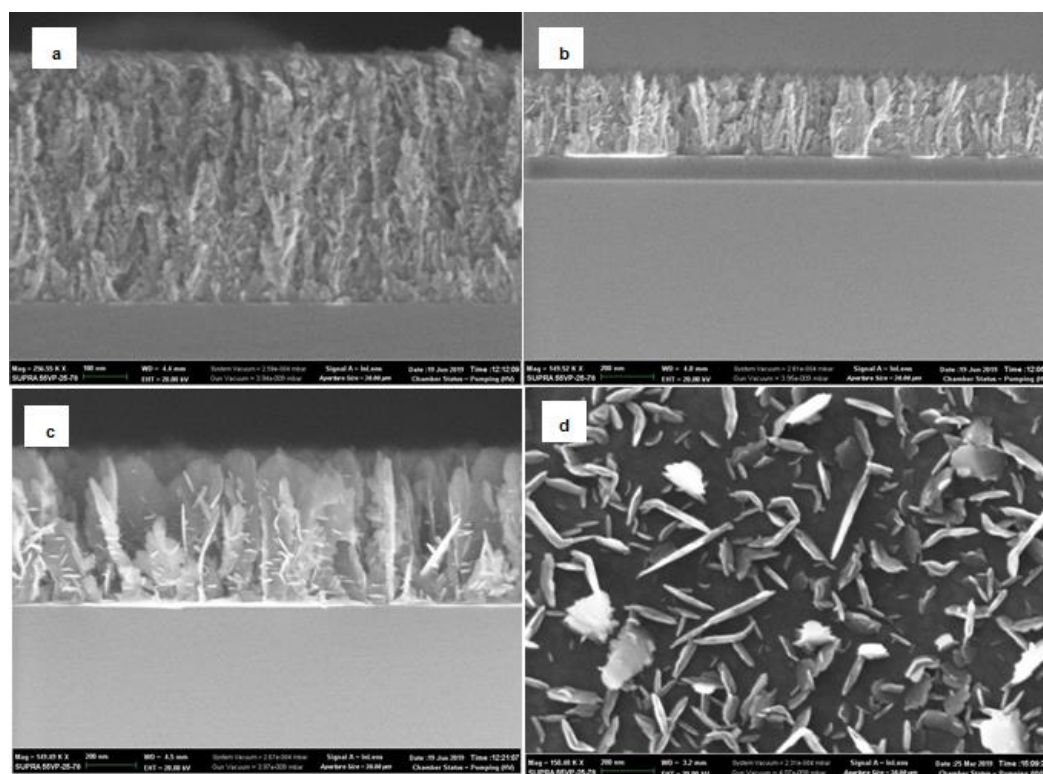


Figure 6. Effect deposition temperature on morphology of films: (a) 350, (b) 550, (c) 750, (d) 950.

3.2. Optical Properties

Optical characterization constitutes the most direct and perhaps the simplest approach for probing structure-property relationships in solids. The spectrum of absorbance for film deposited on quartz substrate is shown in Figure. 7a, (spectrum measured at normal incidence and at room temperature), and the estimated value of direct band gap 2.2 eV and it's bigger than monolayer bandgap, Figure 7b.

Moreover, PL of MoS₂ has Two active optical transitions denoted as mode A and mode B appearing at 1.85 and 1.95 eV (in the visible region). Our film show strong photoluminescence emission. At room temperature peak around 580 nm, and this peak wide to cover all visible range of light, Figure 7c.

nanosizes sheets Previously reported as useful way to tune emission of MoS₂ depending on size of sheets peak emission blue shifted to green light for few tens nanometers size sheets while smaller sheets has emission in blue or ultra violet range of light, and bigger has red emission as in few layer films [13]. According to that, We believe The Origin of The higher value of direct bandgap and broad emission peak centered around 580 is a result of quantum confinement due to few tens nanosizes structures.

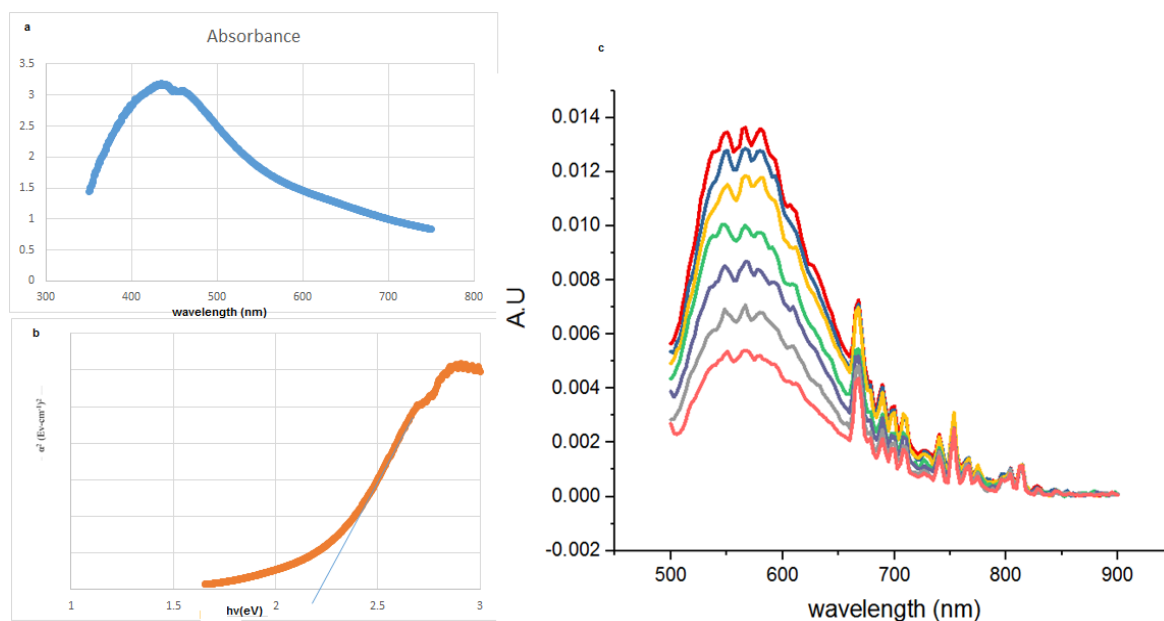


Figure 7. (a) absorbance (b) estimated direct optical bandgap, (c) low temperature PL from 300 to 10 K.

4. Conclusions

Attempt has been made in this study to deposit molybdenum disulphide Dendrites by MOCVD in a single growth step, without any pre-deposition of Mo films by other growth techniques or the use of any complex series of steps at the pre- and post-deposition steps and in a single furnace zone. Stoichiometry, thickness, morphology, as well as the optical properties of the deposited films were also study.

EDX and XPS confirmed the expected elements in film and stoichiometry is 2.1 S. while study by XRD, TEM and Raman spectroscopy confirm crystallinity of film. On optical properties side, film show full color photoluminescence and higher value of bandgap 2.2 eV due to quantum confinement.

We believe those structures can have strong potential in many applications specially in catalysts, optoelectronics and illuminant materials, due to their special features like high surface area and high density of edge states, strong absorption and emission in all visible range of light.

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