Luminescent vertically oriented nanosheets MoS$_2$ by low temperature MOCVD

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Abstract: Controlled growth orientation of MoS$_2$ 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 MoS$_2$ flakes is very important for catalytic activities. Here, we demonstrate growth dense and edge-enriched vertically oriented MoS$_2$ (V-MoS$_2$) using MOCVD technique with deposition temperature as low as 250°C. SEM results demonstrated the vertically oriented growth and high density of edge terminated MoS$_2$ sheets. While Raman and XPS confirm MoS$_2$ composition of sheets with good quality. At Room temperature, there is strong photoluminescence emission from sheets due few layer structures.

1. Introduction

Molybdenum disulfide (MoS$_2$) has been a strongly active research subject in last decade owing to their unique electronic, physical and chemical properties. MoS$_2$ consists of two-dimensional (2D) molecular layer stacked together by weak interlayer interaction. Tuning band gap and transforming MoS$_2$ from an indirect semiconductor to a direct one when decreasing its thickness from bulk to a single layer, beside high mobility and absorption over broad spectral range. making it as a promising candidate in Nano-electronics and optoelectronics for manufacturing of enhanced transistors, sensors and electronic displays because of those unique properties. In addition, MoS$_2$ famous in catalyst field and recently progressive results in the fields of energy storages, energy conversions, water disinfection with visible light and sensors applications has been reported [1,2].

The MoS$_2$ usually growth in horizontal orientation exposes the basal planes as the terminating surface, with minimal dangling bonds. This horizontal orientation growth of MoS$_2$ has been very useful for many applications, especially electronics like field effect transistor (FET), modulators and photodetectors, where high carrier mobility and fast response with in-plane transportation[1].

Recently growth of vertically aligned MoS$_2$ 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. Better performance over basal growth has been reported in many applications fields for example photodetectors with vertical orientation MoS$_2$ nanosheets show better characterization especially in PN junction structure, due to higher absorption and faster transport of photo-generated carrier due to anisotropic MoS$_2$ structure[2,3,4].
Finally, using MoS$_2$ in the field of catalyst and sensing materials, especially gas sensing, is particularly interesting due to the various active sites (defects, vacancy, and edge sites of MoS$_2$) for selective adsorption and semiconducting behaviors. Many researchers have experimentally exploited the application of MoS$_2$ in these fields, relying on the use of a horizontal growth of the MoS$_2$ nanostructure, which is relatively easy to expose and prepared by CVD synthesis and chemical exfoliation. However, recently many results have been published confirming the advance of MoS$_2$ vertical sheets in those fields [5,6,7].

2. Experiments:
The deposition process was carried out in the hot-wall low pressure tubular CVD reactor. Mo(CO)$_6$ powder and H$_2$S were used for MOCVD growth of MoS$_2$ films. 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 $30^\circ$C, and H$_2$S were used as the reacting gas. Total pressure in the reaction chamber was fixed at 2 torr and deposition temperatures 250 $^\circ$C, S/Mo ratio in reactor were 375, finally Time of deposition was 30 min. The substrates (silicon wafer, silicon wafer with preliminary 100nm SiO$_2$ layer and fused quartz) were cleaned in acetone, alcohol and de-ionised (DI) water for 10 min each and put at positions d=7 cm from entrance.

The morphology and composition of the deposited films were studied with the use of scanning electron microscopy (SEM, EDX) (Supra 55 VP), 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 1nm.

3. Results:

3.1. Composite, structure and morphology
SEM image in Figure 1, show that film composed of vertical sheets grown on Silicon substrate and similar vertical sheets grown SiO$_2$/Si and quartz substrates (not shown). It’s clear that sheets have variety in sizes from around 30 to 150 nm and random orientation of sheets. Cross section clearly show vertical growth and average length of sheets 180 nm.

XPS spectra of sheets has signal from elements Mo, S, C and O (Figure 2a). O and C signals may be due exposure to ambition atmosphere. The stoichiometry of the MoS$_2$ film has been separately confirmed with XPS and X-ray spectroscopy (EDS) (S/Mo ratio = 2.05). Mo 3d shown in figure 2b, The Mo signal mainly arises from Mo3d5/2 (228.9eV) and Mo 3d3/2 (232.1 eV) characteristic of Mo$^{4+}$ component of molybdenum disulphide (Figure 2b). The small doublets corresponding to the higher oxidation states, (Mo$^{5+}$) and molybdenum oxide (Mo$^{6+}$).
Figure 1. SEM image of vertical nanosheets, Inset: cross-section of vertically.

Figure (a, b)2. XPS for MoS$_2$ (a) XPS survey and (b) Mo 3d spectra.
Raman spectroscopy shown in Figure 3, two strong characteristic Raman modes $E_{12g}$ and $A_{1g}$ were observed at 382 cm$^{-1}$ and 407 cm$^{-1}$, corresponding to in-plane vibration of molybdenum and sulfur atoms, and out-of-plane vibration of sulfur atoms, respectively. (FWHM of $E_{2g}$ is 18 cm$^{-1}$ and $A_{1g}$ around 8 cm$^{-1}$). The frequency difference ($\Delta f$) between the $E_{12g}$ and $A_{1g}$ modes can be reliably used to count the number of MoS$_2$ layers. The $\Delta f$ value observed is $\sim$25 cm$^{-1}$, This indicates the presence of five or more layers of MoS$_2$ in the Nanosheets [8]. Finally, the mode of 1LA around 227 cm$^{-1}$ mode which use as indicator for distortion and defects in MoS$_2$ sheets, indicate defective structure of sheets due to low temperature growth[9].

Although Exist of Raman modes $E_{12g}$ and $A_{1g}$ is indicator of crystalline structure of MoS$_2$ at 382 cm$^{-1}$ and 407 cm$^{-1}$, Sheets did not show any XRD reflections. this can explanation by that, first, in XRD spectrometer in powder geometry reflections only from planes parallel to substrate can be observed. second, sheet has small thickness and random orientations as can be seen from SEM image.

![Raman spectrum of vertical nanosheets](image)

Figure 3. Raman spectrum of vertical nanosheets.

3.2. optical properties

Optical characterization constitutes the most direct and perhaps the simplest approach for probing structure-property relationships in solids. In this work both absorption and photoluminescence used to characterize vertical nanosheets.

The UV-visible spectra of the vertical sheets deposited on quartz substrate are shown in Figure 4a, spectrum is a plot of absorbance against incident photon wavelength at normal incidence and at room temperature. Spectrum show peaks belong to C,B and A excitons around 475, 650 and 700 respectively.

From the UV-Vis spectrum (Figure 4), it is possible to calculate the direct optical energy band gap values of materials with plotting the graph of $(\alpha h\nu)^2$ versus photon energy. according to the Tauc relation, $(\alpha h\nu)^2 = B(\nu - E_g)$. Where $\alpha$ is the absorption coefficient (calculated using relation $\alpha = (1/d) \ln(1/T)$ with $T=10^{-A}$, where A is absorbance), $h\nu$ is the photon energy in eV, $E_g$ is the band gap energy, and B is a constant. As it shown in figure 4b, The estimated value of direct band gap is 2.23 eV.
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 vertical sheets show strong photoluminescence emission. At room temperature peak around 670 nm correspond to emission from exciton A energy (1.87) eV, shoulder at longer wavelengths maybe due to bound exciton (Figure 5a). While at 77 K we see big change of spectrum where peak at 670 become more broaden with shift to longer wavelengths. And new very wide peak appear at shorter wavelength centered around 560, (Figure 5b).

Nanosizes sheets 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, while bigger has red emission as in few layer films [10]. According to that, we believe the origin of the higher value of direct bandgap and broad emission peak centered s 560 can be result of quantum confinement, as film consist of high number of small sheets in range of few tens nanometers, while emission at exciton A due to bigger sheets as confirm few layer structures of sheets.

Figure 4(a,b). absorbance and estimated direct optical bandgap (a) absorbance and (b) bandgap.
Figure 5(a,b). Photoluminescence of MoS$_2$ vertical sheets (a) 300 K and (b) 77 K.

4. Conclusions

 Attempt has been made in this study to deposit molybdenum disulphide thin films with vertical nanosheets 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 optical properties of the deposited films were also studied.

 Random and small size of sheets change of optical properties of film due to quantum confinement effects, leading to increase of optical bandgap and new emission band.
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