Induced Synthesis of Vertically Oriented Multilayer MoS\(_2\) via CVD Method

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Abstract. Fabrication of nanostructured MoS\(_2\) for photodetector applications has become increasingly attractive due to its atomically thin profile and favorable bandgap. In this paper, vertically oriented multilayer MoS\(_2\) (V-MoS\(_2\)) are grown directly on a SiO\(_2\) substrate by chemical vapor deposition (CVD) with TiO\(_2\) being adopted as an induced precursor for the first time. The interim morphologies of the synthesized MoS\(_2\) are investigated and the growth mechanism of the MoS\(_2\) film is proposed.

1. Introduction

With the age of two-dimensionally (2D) layered materials approaching, two-dimensional transition metal sulfides (TMDs) have been considered as the promising candidates for photodetectors due to their 2D conjugated structures, large specific surface area, low electrical noise, and broad band response [1-5]. Especially, MoS\(_2\) becomes an alternative material for the photodetection chips of the next generation, on account of its atomically thin profile and favorable bandgap [6]. However, monolayer MoS\(_2\) can only absorb a small portion of incident light due to its ultrathin thickness (0.72 nm), which usually leads to the low quantum efficiency for the MoS\(_2\)-based devices [7-8]. To conquer the drawbacks of optical absorption, researchers have devoted significant efforts by preparing multilayer [9] and bulk MoS\(_2\) [10], or combining it with other semiconductor materials [11-12]. However, the relevant bandgap becomes indirect, meanwhile the carrier mobility has been greatly reduced. Even for high-quality parallel-oriented multilayer or bulk MoS\(_2\)-based heterostructure, the photoelectric response becomes undesirable, as the carrier mobility of interlayer is non-ideal. In contrast, vertically oriented multilayer MoS\(_2\), which has the advantages of both strong light absorption and quick longitudinal in-plane carrier transport, may show significant potential in optoelectronic devices.

To date, high quality MoS\(_2\) have been exploited via many different methods, including mechanical exfoliation, chemical vapor deposition (CVD) and epitaxial growth [13-15]. However, it is extremely difficult to obtain vertically oriented multilayer MoS\(_2\) (V-MoS\(_2\)) on the SiO\(_2\) substrate, because the lattice mismatch between MoS\(_2\) and SiO\(_2\) is very high. What’s more, most synthesis methods require templates, surfactants or self-assembly [16], which often need multi-step and costly operations. In this paper, a high-quality V-MoS\(_2\) were developed on the TiO\(_2\) coated SiO\(_2\) substrate, by introducing ultrathin TiO\(_2\) into the interlayer of MoS\(_2\) and SiO\(_2\) to induce the growth direction of MoS\(_2\). Spectroscopic and microscopic results reveal that the synthesized V-MoS\(_2\) are highly crystalline. The
induced epitaxial growth method herein opens a new avenue to synthetize vertically oriented materials with excellent optoelectronic performances.

2. Experimental Sections

2.1 Growth of V-MoS₂ nanosheets array
The V-MoS₂ was grown on a Si wafers substrate with a SiO₂ layer of 300 nm deposited through a chemical vapor deposition (CVD) method. The MoO₃ powder (2 g) was placed in a ceramic boat and the SiO₂/Si substrate covered with a layer of sputtered titanium dioxide layer (10-30 nm) for inducing the growth direction of MoS₂ was faced down and mounted on the top of boat. A separated ceramic boat filled with sulfur powder (20 g) was placed close to the ceramic boat filled with MoO₃ powder, as shown as in figure 1. After the reaction chamber was heated to 800 °C for 40 minutes in an argon environment, the sample was taken out until the furnace down cooled to room temperature.

2.2 Characterization
Surface morphology of the samples was examined with commercial scanning electron microscope (SEM, FEI VS600) and optical microscope (Nikon, 50I POL). Energy Dispersive Spectrometer was used to obtain the distribution of elements (EDS, FEI VS600). Raman spectra was obtained with a confocal microscope system (Bruker, Dimension Fast Scan) with a 100× objective (NA=0.9) under ambient condition. A 532 nm laser with a low laser power (50 μW) was applied to measure photoelectronic performance.

3. Results and Discussion
The V-MoS₂ was successfully grown on a TiO₂ coated SiO₂ substrate by appropriately controlling the preparation parameters. The schematic illustration of the experimental set-up is shown in Figure 1. Moderate-doped N-type Si wafer (resistivity of 0.2~0.4 Ω cm, thickness of 600 μm) with a SiO₂ layer of 300 nm was used as the substrate. The wafer was sputtered with TiO₂ film (30 nm) on the surface. The MoO₃ powder (2 g) was placed in a ceramic boat and the SiO₂/Si substrate covered with a layer of titanium dioxide layer was faced downward and mounted on the top of boat. A separate ceramic boat with sulfur powder (20 g) was placed next to the MoO₃ powder. The inert gas flowed from sulphur source to molybdenum source. At the beginning of the growth process, with the chamber temperature rising to 800 °C in an argon environment, MoO₃ powder started to transform into volatile suboxide MoOₓ under the reduction function of sulfur vapor [17]. The suboxide compounds diffused to the substrate, and further reacted with sulfur vapor, leading to the formation of V-MoS₂.

Figure 1. Schematic illustration of the experimental set-up.
An ultra-low magnification scanning electron microscopy (SEM) image of V-MoS₂ is shown in Figure 2a, which clearly exhibits a lot of microspheres. These microspheres were verified to be of V-MoS₂. Figure 2b shows the enlarged SEM image of one microsphere, which clearly demonstrates that the MoS₂ layer is uniformly standing on the TiO₂ film and interconnect with each other. A high magnification image shows the V-MoS₂ structures are composed of layered nanosheets, as shown in
Figure 2c. The MoS$_2$ nanosheets vertically extend in a random distribution with thickness of several hundred nanometers from the cross-section SEM image of V-MoS$_2$ in Figure 2d.

Figure 2. (a) An ultra-low magnification scanning electron microscopy (SEM) image of V-MoS$_2$; (b) Low-magnification and (c) high-magnification SEM images of V-MoS$_2$ obtained by CVD method; (d) Side view image of V-MoS$_2$.

The Raman spectroscopy in Figure 3a clearly shows that the vertically grown MoS$_2$ sheets in the van der Waals layers have an edge-terminated spectral feature, because the out-of-plane M-X vibration mode ($A_{1g}$) is over the in-plane M-X vibration mode ($E_{2g}$). From the Raman spectrum, the V-MoS$_2$ exhibits two Raman characteristic peaks at 407.30 cm$^{-1}$ and 381.56 cm$^{-1}$, corresponding to the $A_{1g}$ and $E_{2g}$ modes respectively. The value of $\Delta$ (25.34 cm$^{-1}$) in Fig.3a evidences the existence of MoS$_2$ [18-20]. The V-MoS$_2$ was further confirmed by Energy Dispersive Spectrometer (EDS) in Figure 3 (b, c and d). In Figure 3 (b, c and d), distributions of Mo, S and Ti elements are represented respectively, which further proved the existence of MoS$_2$.

Figure 3. (a)The Raman spectra of the V-MoS$_2$; The EDS spectra of V-MoS$_2$: (b) Mo; (c) S; (d) Ti.
In order to obtain further evidences about the interaction between TiO$_2$ and MoS$_2$, we sputtered half of a piece of the substrate with titanium dioxide, and the other without sputtered titanium dioxide. The experimental result is shown in Figure 4a. As shown in the red line marked in Figure 4a, on the part without sputtering TiO$_2$ film, MoS$_2$ of single crystal with horizontal structure was obtained. The green line marked the black rounded area consist of V-MoS$_2$. It can be seen that the formation of V-MoS$_2$ is mainly due to the presence of TiO$_2$ layer. Based on the observation, we could illustrate the formation mechanism of the V-MoS$_2$. At first, molybdenum source was rapidly sulfurized into granular MoS$_2$. Meanwhile, TiO$_2$ layer under high temperature annealed, which made the TiO$_2$ morphology change and the surface of the substrate becomes rough in Figure 4b, and then MoS$_2$ nanoparticles were orientated grown with two-dimensional direction on the TiO$_2$ surface.

Figure 4. (a) The optical micrograph of the single crystal MoS$_2$ with horizontal structure and V-MoS$_2$ on the same substrate; (b) SEM images of annealed TiO$_2$

4. Conclusion

In summary, highly dispersive V-MoS$_2$ with height of about 2 μm was synthesized via a simple CVD approach under TiO$_2$ induce. The experimental results suggest that the layer of TiO$_2$ plays an important role in controlling the structures growth direction. Moreover, a possible growth mechanism was proposed to explain the formation of the V-MoS$_2$. Considering the simple synthetic process, it is believed that these vertically oriented nanostructures can be directly used for the making of nanodevices.

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