

Synthesis of the few layered two-dimensional molybdenum oxide atomic crystal

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Abstract. We study the effect of substrate type, source temperature, and substrate position on the morphology of Alfa molybdenum oxide (α -MoO₃) in physical vapour deposition. We found that the orientation and thickness of the MoO₃ is strongly affected by the evaporated flow and temperature. Lying down, few layered (FL) MoO₃ can be grown directly on technical substrate such as SiO₂ with typical length scale of tens of micrometres. Our studies provide a simple, catalyst-free and low cost synthesis way to prepared large size FL MoO₃ for further optical and electrical investigation such as photodetector, field effect transistors, and electrochromism.

1. Introduction

Researchers have paid much attention to two-dimensional metal oxide nanomaterials recently because of its unique optical and electric properties [1]. Among various kinds of metal oxide, molybdenum oxide (MoO₃) is a multifunctional materials that has potential application in photovoltaic devices[2], electrochromic window[3], gas sensors[4] and so on. There are three main crystalline polymorphs: orthorhombic molybdenum oxide (α -MoO₃), monoclinic molybdenum oxide (β -MoO₃), and hexagonal molybdenum oxide (h-MoO₃). α -MoO₃ is a thermodynamically stable phase with layered structures, which is made from MoO₆ octahedra (Figure 1(a)). MoO₆ octahedra forms corner-sharing chains along the [100] direction and edge-sharing chains along the [001] direction. The layers are stacked by weak van der Waals forces along the [010] direction with a layer thickness of 0.7 nm.

It's been found that the Coulomb scattering can be screened effectively due to its high dielectric constant. As a result, MoO₃ nanosheet has carrier mobility of more than 1000 cm²/Vs, which is attractive in field effect transistors[5]. The layered MoO₃ has been fabricated by a variety of synthesis methods, including thermal evaporation[6], electrodeposition[7], spray pyrolysis[8], sol-gel[9], sputtering[10], and mechanical exfoliation[11]. Recently, Di Wang prepared α -MoO₃ sheet with thickness of single-unit-cell and length scale of tens of micrometers on mica by physical vapor deposition[12]. However, direct synthesis of few layered (FL) MoO₃ on a technical substrate, for example, SiO₂ is still lacking. In this study, a simple, high-efficiency, catalyst-free synthesis technique for the preparation of FL two-dimensional MoO₃ was developed.



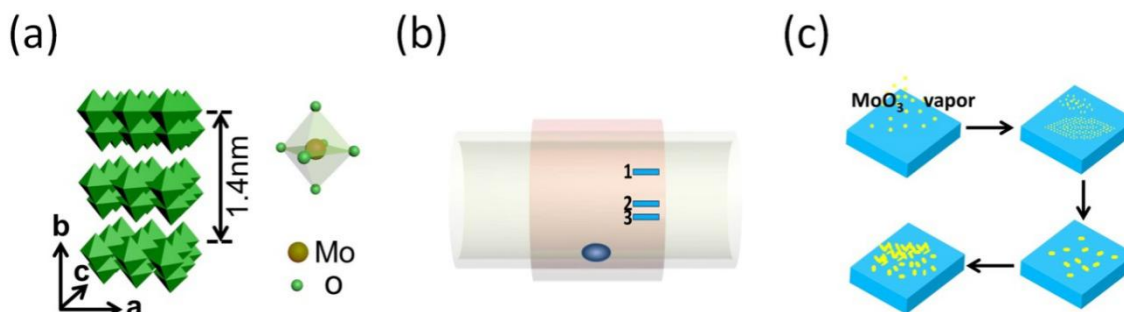


Figure 1 (a) The schematic structure of α - MoO_3 . The thickness of monolayer is 0.7 nm and a unit cell content two layers. (b) Schematic setup of tube furnace for physical vapour deposition; (c) The growth process of MoO_3 .

2. Experimental and Results

The MoO_3 sheets were synthesized by thermal physical vapor deposition method under air condition. The substrates of SiO_2 were ultrasonic cleaned in acetone, alcohol, and distilled water successively. Each cleaning step lasted for 10 minutes. The substrates were then removed from the distilled water and were dried with nitrogen gas. 0.1 g of MoO_3 powder was placed in an Al_2O_3 crucible at the center of a quartz tube (Figure 1(b)). The substrates were placed at the low temperature region. The distance between the substrate and powder is 12-16 cm. The temperature of the source was increased to 780 °C from room temperature in 70 minutes, maintaining for 120 minutes, and then cooled down to room temperature naturally. The crystallization process of MoO_3 is realized by gas-solid mechanism. After the powder of MoO_3 is sublimated as gaseous species in the high temperature region, it will diffuse to the low temperature region, and then be recrystallized on the substrate[13].

There are different morphologies on diverse substrates, for example, silicon, silicon oxide, textured silicon (T-Si) substrate, and Mo plate at same temperature in Figure 2. The α - MoO_3 plates are densely packed on Si, SiO_2 , and T-Si. On the Si substrate in the Figure 2(a), the α - MoO_3 nanosheets are rectangular with thickness of ~200 nm, width of ~1 μm , and length of ~12 μm . Some small nanosheets were also observed; maybe due to short growth time, or the finite space for crystallization. On SiO_2 surface (Figure 2(b)), the nanosheets with thickness of ~150 nm, width of ~2 μm , and length of ~5 μm were observed. There are many nanosheets with thickness of ~500 nm, width of ~3 μm , and length of ~10 μm on the T-Si (Figure 2(c)). There are obvious differences between MoO_3 on the Mo plate (Figure 2(d)) and MoO_3 nanosheets on Si, SiO_2 , and T-Si. It grows longer with typical length of 30 μm , and thicker and smaller in width. The morphology difference may be due to the difference in surface roughness[14]. The Mo surface is rougher than the Si and SiO_2 in submicrometer scale. The deposited MoO_x species on the surface is not easy to diffuse on the Mo surface, which leads to slower growth in width and thickness, but faster growth along the length.

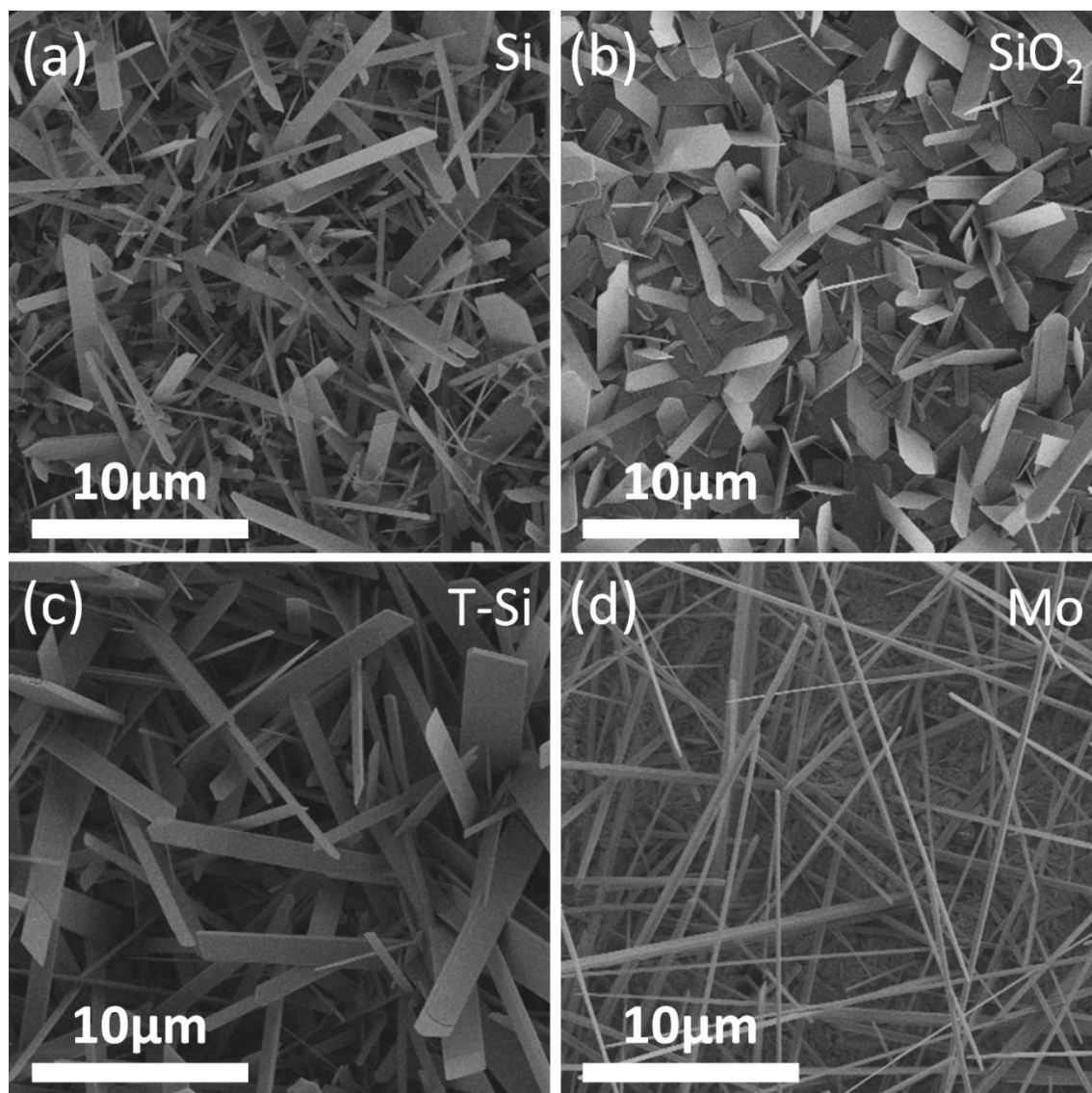


Figure 2. SEM images of MoO_3 on the different substrates at 780°C . (a) silicon wafer; (b) silicon wafer with 300 nm thick silicon oxide; (c) textured silicon wafer; (d) Mo plate.

In order to confirm the crystal structure of $\alpha\text{-MoO}_3$ nanosheets, the Raman of MoO_3 nanosheets (a confocal Raman microscope by Renishaw inVia Reflex with a 532 nm laser as excitation) was conducted, the X-ray diffraction (XRD) spectroscopy in a Rigaku-MiniFlex600 using the $\text{Cu K}\alpha$ radiation (1.546\AA), with 40 kV and current of 40 mA was carried out, and high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) experiments were conducted on JEOL 2100F operated at 200 kV (HRTEM). Figure 3(a) presents a typical Raman spectrum of MoO_3 nanosheets. The peaks at 339 and 666 cm^{-1} are corresponding to Mo-O₃ stretching mode, which is along [001]. The peak at 819 cm^{-1} is corresponding to Mo-O₂ stretching mode. The peak at 995 cm^{-1} is corresponding to Mo=O stretching mode of the terminal oxygen. The XRD pattern (Figure 3(b)) shows the strongest diffraction peaks for MoO_3 , for example, 12.5° , 25.4° , 38.7° , which correspond to (020), (040), (060) planes, respectively. In the Figure 3(c), the lattice spacing is 0.391 nm and 0.374 nm , which is in accord with the orthorhombic structure of MoO_3 phase, and with the lattice constants of $a=3.96\text{ \AA}$, $b=13.86\text{ \AA}$, $c=3.7\text{ \AA}$ (JGPDS 05-0508). The

SAED diffraction pattern indicates that the growth direction along (001) and (100) planes, which is normal to (010) plane.

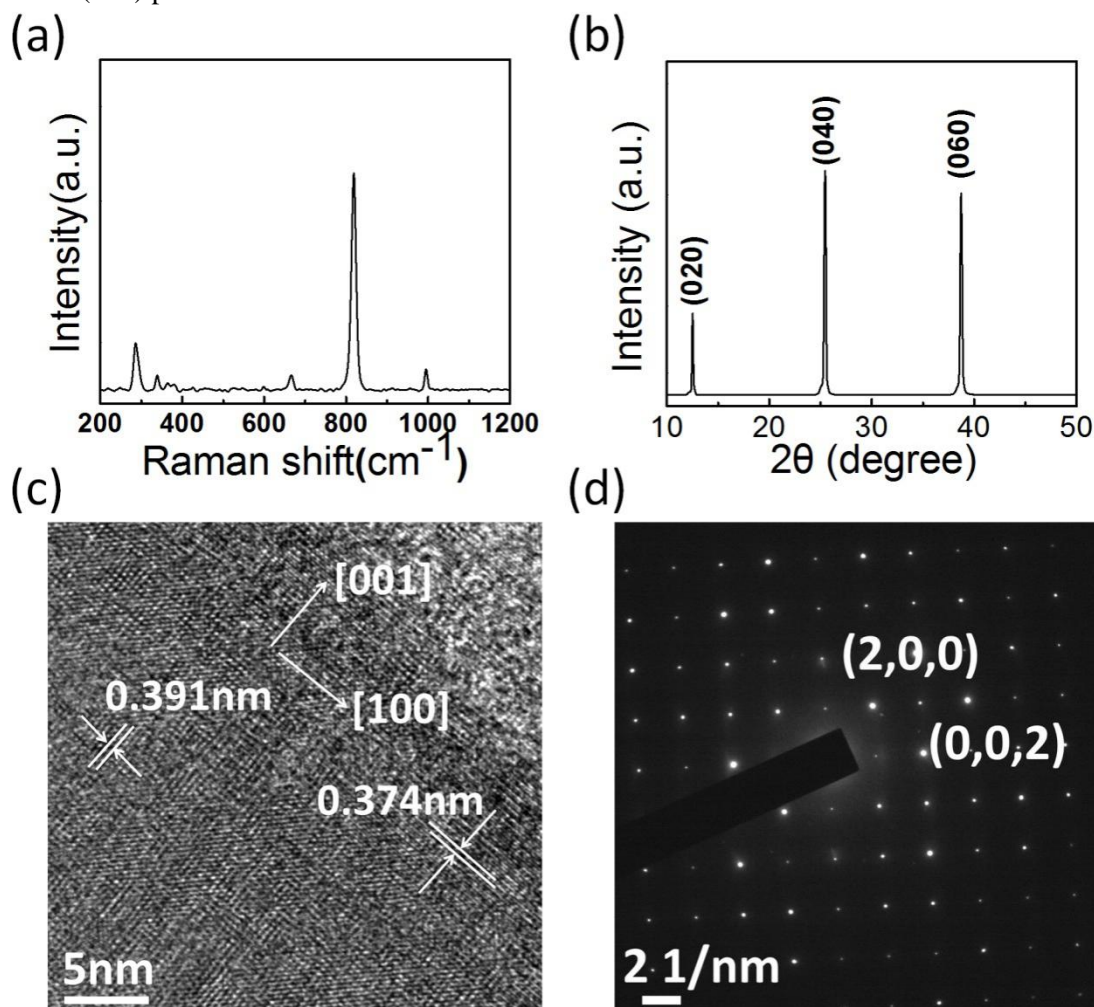


Figure 3. (a) Raman spectrum of α - MoO_3 . (b) XRD pattern of the α - MoO_3 . (c) HRTEM image of a single nanosheet. (d) The corresponding SAED pattern.

The morphology of MoO_3 depends on the source temperature. The nanosheets are sparsely dispersed on the SiO_2 (Figure 4(a)) at the source temperature of 580 °C. This may be due to the very low evaporated flow of MoO_3 . As the source temperature is raised to 680 °C, the nanosheets are more densely packed (Figure 4(b)). Typical length of the nanosheet increases from $\sim 1 \mu\text{m}$ to $2 \mu\text{m}$, and the width and the thickness increase at the same time. When the source temperature is 780 °C, a dense thick film composed of long MoO_3 nanoplates formed.

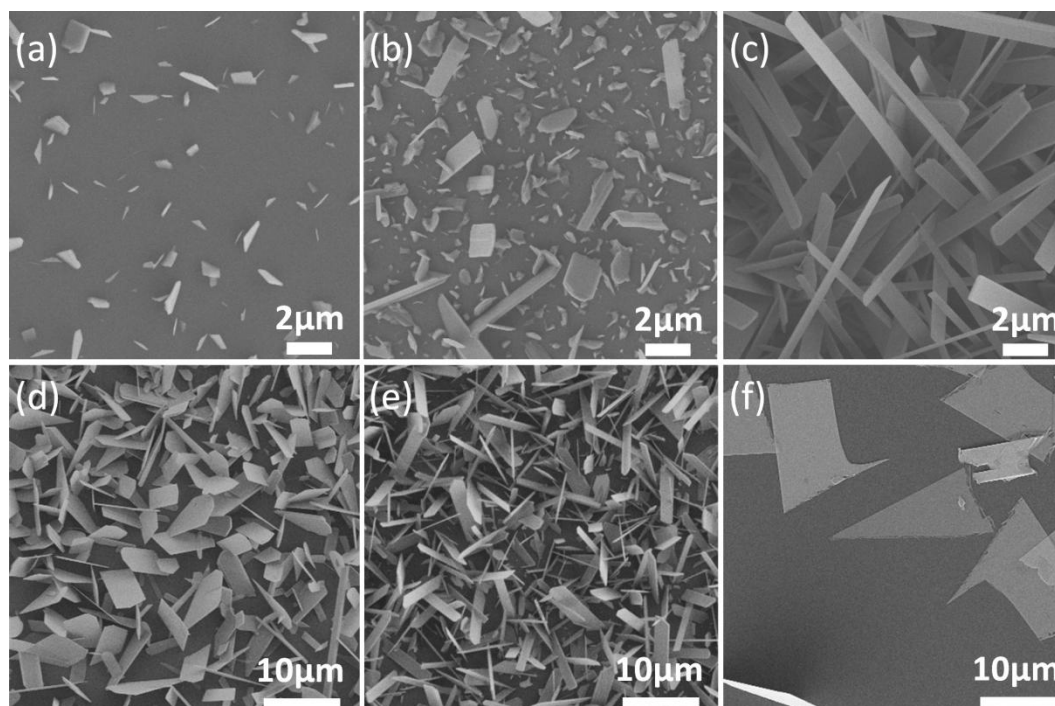


Figure 4 Effects of the source temperature and the substrate position on the morphology of the MoO_3 nanosheets. SEM images of the MoO_3 nanosheets at different source temperature of (a) 580°C , (b) 680°C , and (c) 780°C . (d), (e) and (f) are all 12.5 cm away from the source, but 0.8 cm, 2.5 cm, and 3.0 cm away from the top of the tube wall, the positions of the three substrates correspond to the positions 1, 2, and 3 in the Figure 1(c).

There are different morphologies at the different deposition position at same source temperature (Figure 4(d), (e), and (f)). Near the top of the tube wall, the nanosheets are randomly orientated, with width of $\sim 3\ \mu\text{m}$. The width gets smaller as the position gets away from the top. But at 3.0 cm away from the top, we found that most of nanosheets get parallel to the substrate. Nanosheets are sparsely distributed. The length and width are normally bigger than $10\ \mu\text{m}$. This may offer opportunity to make device easily. By observing the morphology along the tube axis, we found that the lying down MoO_3 nanosheets have grown at the position close to the source (Figure 5(a)). Normally, the evaporated MoO_3 gas will accumulate at the top of the wall and then diffuse from the center to both sides. The MoO_3 nanosheets are denser near the top of the wall, and decrease as the position gets lower. On the other hand, when the position gets near the source, the temperature gets higher. Therefore, the morphology of the as-grown MoO_3 is controlled by gas flow and the temperature.

To determine the thickness of the nanosheet, atomic force microscope was carried out. The thickness of the lying down nanosheets is ranging from several unit cells to $\sim 100\ \text{nm}$. Figure 5(b) shows that the thickness of nanosheet is $5.42\ \text{nm}$. A layer thickness is $0.7\ \text{nm}$, so it is about 8 layers. We also found that the FL MoO_3 can also be grown on Si as well. Our results show that FL MoO_3 nanosheet with tens of micrometres in length can be prepared by physical vapour deposition on technical substrate.

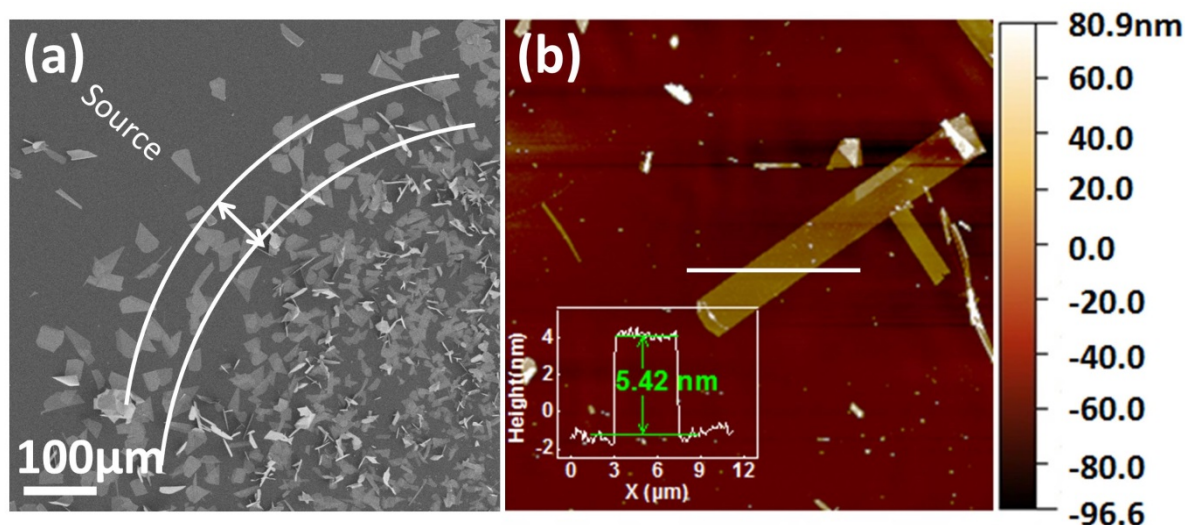


Figure 5. (a) SEM image of MoO₃ nanosheets distribution. (b) AFM image of a FL MoO₃ nanosheet, the thickness is 5.42 nm.

3. Conclusion

In conclusion, we have grown MoO₃ nanosheets on different substrate by physical vapor deposition. The morphology of MoO₃ nanoplates is controlled by the substrate type, source temperature, and substrate position. When the temperature of the source is 780 °C, FL MoO₃ atomic crystal can be fabricated on SiO₂ and Si substrate at about 12.5 cm from the source and 3 cm away from the top wall of the tube. Our findings provide a low cost and feasible way to fabricate FL MoO₃ on technical substrate, and offer the possibility to investigate the photoelectric properties of two dimensional MoO₃.

Acknowledgements

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