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Controllable growth and characterizations of hybrid spiral-like atomically thin molybdenum disulfide

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ABSTRACT

Monolayer MoS_2 is an emerging two-dimensional semiconductor with wide-ranging potential applications in novel electronic and optoelectronic devices. Here, we reported controlled vapor phase growth of hybrid spiral-like MoS_2 crystals investigated by multiple means of X-Ray photoemission spectroscopy, scanning electron microscopy, atomic force microscopy, kelvin probe force microscopy, Raman and Photoluminescence techniques. Morphological characterizations reveal an intriguing hybrid spiral-like MoS_2 feature whose lower planes are AB Bernal stacking and upper structure is spiral. We ascribe the hybrid spiral-like structure to a screw dislocation drive growth mechanism owing to lower supersaturation and layer-by-layer growth mode. In addition, the electrostatic properties of MoS_2 microflakes with hybrid spiral structures are obvious inhomogeneous and dependent on morphology manifested by kelvin probe force microscopy. Our work deepens the understanding of growth mechanisms of CVD-grown MoS_2, which is also adoptable to other TMDC materials.

1. Introduction

Following the boom of graphene, two-dimensional (2D) transition metal dichalcogenides materials (TMDCs) have emerged as an important layered crystals, exhibiting intrinsic semiconducting, metallic and even superconducting behaviors [1–3]. Generally, TMDCs have the formula MX_2, where M represents a transition metal from groups IV-VI (e.g. Mo, W, Ti, or Nb), while X is a chalcogen atom (S, Se, or Te). More than 40 types of TMDCs can occur depending on the combination of chalcogen and metal atoms [4–6]. Among the variety of TMDCs being investigated, MoS_2 is a representative one with good chemical stability, excellent optical and electronic properties. Monolayer MoS_2 has been fabricated to many prototype devices with advanced functionalities, such as field-effect transistors (FETs) and photo detectors [7,8]. Photoelectric devices fabricated from monolayer MoS_2 have recently been shown to have excellent photoresponsivity up to 880 A/W at a wavelength of 561 nm, which are superior to graphene-based devices with a similar geometry [8,9].

For realizing the high-performance of MoS_2-based devices, exploring an approach to high-crystalline MoS_2 with atomically flat surface and interfaces is necessary. The chemical vapor deposition (CVD) method, a powerful way to large-scale graphene, allows the growth of single-crystalline MoS_2 microflakes directly on arbitary substrates [10–13]. Although CVD growth of MoS_2 has been well developed, controlled synthesis of MoS_2 with different morphologies and stacking styles is still not achieved and the mechanism is not clear absolutely. For example, Y. J. Cao et al. reported that the dendritic triangle shape MoS_2 microflakes can be synthesized by controlling the carrier gas flow rate [14]. Recently, spiral-like WSe_2 was synthesized by L. Chen et al. and the transistors based on it show the room-temperature hole mobility over 44 $cm^2\ v^{-1}\ s^{-1}$ and a large current on/off ratio of 1×10^6 [15]. The controlled growth and characterizations of spiral-like MoS_2 structures are essential to realize the applications in electronic and optoelectronic devices.

In this contribution, we controlled synthesized novel hybrid spiral-like MoS_2 crystals through increasing the growth temperature to 1000 °C. The combined atomic force microscopy and scanning electron microscopy were used to investigate the hybrid spiral structure with clear steps and helical fringes. The underlying growth mechanism is proposed to be combined layer-by-layer growth and screw dislocation drive mode. Moreover, electrostatic properties of MoS_2 with hybrid spiral structures have been shown to exhibit distinctive surface potential and charge distributions,

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which may have important implications on the applications of MoS_2-based devices.

2. Materials and methods

The experiments were carried out in a commercial CVD furnace (KJMTI Corporation, OTF-1200) with a 3 in.-diameter quartz tube and double heating zones in the length of 20 cm separated at border to border distance of 5 cm. The growth temperature and carrier gas flow rate were controlled with a proportion integration differentiation (PID) temperature controller and a mass flow controller, respectively. A quartz boat loaded MoO_3 powders (4N purity, Aladdin) was placed at the 2nd heating zone while another loaded sulfur powders (5N purity, Aladdin) was placed at the center of the 1st heating zone of the furnace and at ~15 cm away at the upstream side. A third quartz boat with clean SiO_2 (300 nm thick)/Si substrates in 1× cm^2 size was placed in the 2nd heating zone at the downstream side. The SiO_2/Si substrates were initially cleaned in DI water, acetone and isopropanol, following 3 h bath in H_2SO_4/H_2O_2 (volume ratio: 3:1) and then 5 min air plasma spurting to remove the possible organic contaminations. Upon roughly pumping, nitrogen (N_2, 5N purity) gas flow was introduced to purge the quartz tube at 150 sccm (standard cubic centimeters per minute) for 20 min. Then, the 2nd heating zone was rapidly heated up to 800 or 1000 °C and maintained for 15 min with a decreased N_2 gas flow of 100 sccm. Sulfur powders were maintained at the temperature being melting point of ~120 °C during the reaction process, so that sulfur vapor could be slowly carried by N_2 gas flow to the reaction zone. The system was maintained at pressure of 1 kPa during the entire growth run. Subsequently, the furnace was switched off following the growth process for cooling down to room temperature undisturbedly with N_2 gas flow.

The as-synthesized sample was systematically characterized by Scanning Electron Microscopy (SEM, FEI Helios 600i), X-Ray Photoemission Spectroscopy (XPS, thermo fisher ESCALAB 250xi), Atomic Force Microscopy and Kelvin Probe Force Microscopy (AFM/KPFM, Agilent 5500) and confocal Raman and photoluminescence techniques (Raman/PL, WITec alpha 300R). The XPS investigations were performed using monochromatic Aluminium K_α X-Ray with light spot size of approximately 1 mm^2. The binding energy was calibrated by assigning the corresponding C 1s peak at 284.5 eV. The topography and corresponding height profile of sample were characterized using AFM in tapping mode. In our experiment, we used a platinum-iridium (Pt/Ir)-coated silicon cantilever (SCM-PIT from Bruker, USA) in tapping mode to perform KPFM measurements. The topography and surface potential signals of sample were simultaneously measured with a mechanical drive frequency of ~75 KHz and an Ac modulation of 0.2–0.3 V at ~10 KHz. Raman and PL spectra/mapping, were carried out under a 532.0 nm laser light and Si-based CCD detector at ambient conditions. The laser power was maintained below 1 mW to avoid local heating and oxidation to obtain a satisfactory signal-to-noise ratio while maintaining acceptable data acquisition duration and avoiding drift. The 520.0 cm^{-1} phonon mode from the silicon substrate was used for calibration of the Raman shift. The emitted signal was collected by a Zeiss 100× objective (N.A=0.9) and dispersed by a 1800 lines/mm grating for Raman measurements and a 600 lines/mm grating for PL measurements.

3. Results and Discussion

The SEM image of sample 1 (Fig. 1a) shows many equilateral and merged triangle shaped crystals in lateral size of ~30 μm which are assigned to single-crystalline MoS_2 microflakes. The inserted plot of temperature *vs* time in Fig. 1a reveals that the first sample is synthesized at accustomed growth temperature of 800 °C and no additional layer is observed, in consistent with

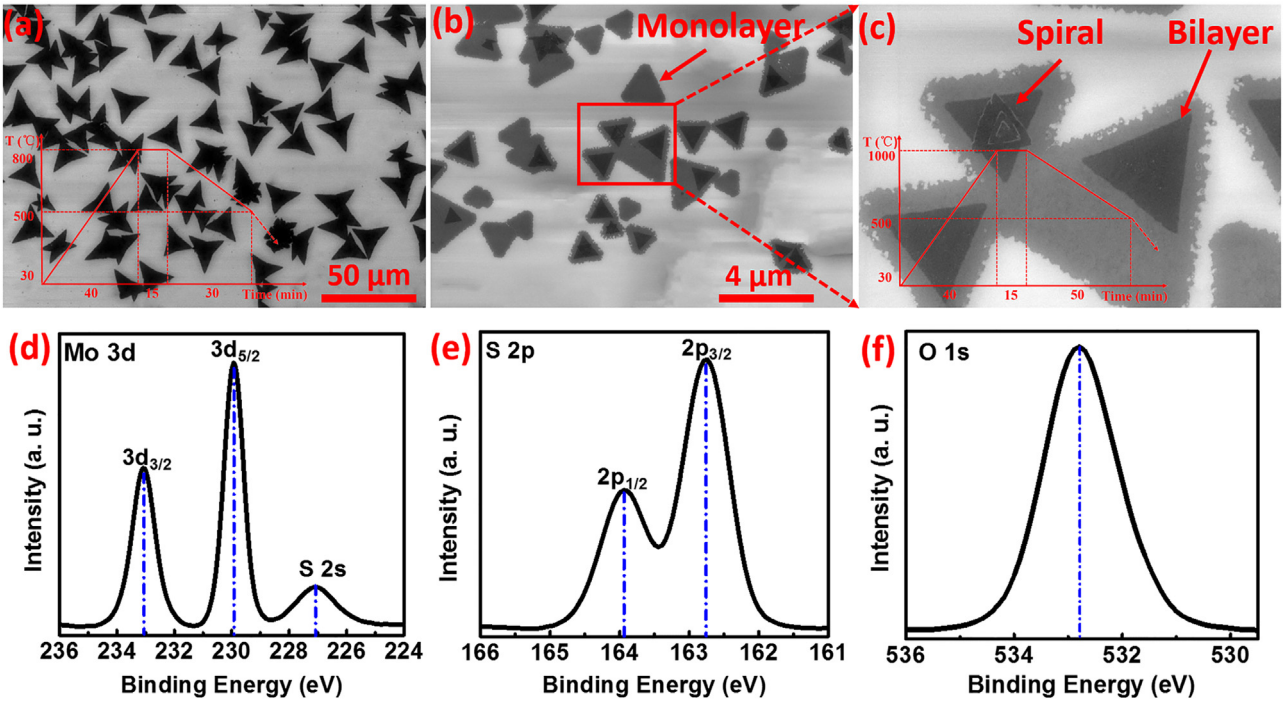

Fig. 1. (a) The SEM image of monolayer MoS_2 crystals and the corresponding plot of temperature *vs* time for sample growth (Inset). (b) The representative SEM image exhibiting monolayer and stacked few-layer MoS_2 microflakes. (c) The zoomed-in high magnification SEM image showing hybrid spiral-like and stacking bilayer MoS_2 crystals. The corresponding plot of temperature *vs* time for sample growth is inserted. (D-f) The corresponding XPS narrow scans of Mo 3d, S 2p and O 1s core level spectra for hybrid spiral-like sample.