Epitaxial growth of large area single-crystalline few-layer MoS$_2$ with high space charge mobility of 192 cm$^2$ V$^{-1}$ s$^{-1}$

Cite as: Appl. Phys. Lett. 105, 072105 (2014); https://doi.org/10.1063/1.4893143
Submitted: 09 May 2014 . Accepted: 02 August 2014 . Published Online: 19 August 2014

Lu Ma, Digbijoy N. Nath, Edwin W. Lee, Choong Hee Lee, Mingzhe Yu, Aaron Arehart, Siddharth Rajan, and Yiying Wu

ARTICLES YOU MAY BE INTERESTED IN

Large area single crystal (0001) oriented MoS$_2$
Applied Physics Letters 102, 252108 (2013); https://doi.org/10.1063/1.4811410

p-type doping of MoS$_2$ thin films using Nb

Chemical vapor deposition of monolayer MoS$_2$ directly on ultrathin Al$_2$O$_3$ for low-power electronics
Applied Physics Letters 110, 053101 (2017); https://doi.org/10.1063/1.4975064
Epitaxial growth of large area single-crystalline few-layer MoS$_2$ with high space charge mobility of 192 cm$^2$ V$^{-1}$ s$^{-1}$

Lu Ma,$^1$ Digbijoy N. Nath,$^2$ Edwin W. Lee II,$^2$ Choong Hee Lee,$^2$ Mingzhe Yu,$^1$ Aaron Arehart,$^2$ Siddharth Rajan,$^{2,a}$ and Yiying Wu,$^{1,a}$

$^1$Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, USA
$^2$Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio 43210, USA

(Received 9 May 2014; accepted 2 August 2014; published online 19 August 2014)

We report on the vapor-solid growth of single crystalline few-layer MoS$_2$ films on (0001)-oriented sapphire with excellent structural and electrical properties over centimeter length scale. High-resolution X-ray diffraction scans indicated that the films had good out-of-plane ordering and epitaxial registry. A carrier density of $\sim 2 \times 10^{11}$ cm$^{-2}$ and a room temperature mobility of 192 cm$^2$/V$\cdot$s were extracted from space-charge limited transport regime in the films. The electron mobility was found to exhibit in-plane anisotropy with a ratio of $\sim 1.8$. Theoretical estimates of the temperature-dependent electron mobility including optical phonon, acoustic deformation potential, and remote ionized impurity scattering were found to satisfactorily match the measured data. The synthesis approach reported here demonstrates the feasibility of device quality few-layer MoS$_2$ films with excellent uniformity and high quality.

Recently, there has been a rapidly increasing interest on investigating layered 2-dimensional (2D) materials such as MoS$_2$, WS$_2$, WSe$_2$, etc., for their promise towards a variety of next-generation electrical and optoelectronic device applications including low cost, flexible, and transparent p-FET and n-FET based on WSe$_2$,$^{11,12}$ were also reported besides demonstration of MoS$_2$-based simple integrated circuits.$^{13}$

Most of the MoS$_2$-based devices reported till date have been fabricated on flakes of MoS$_2$ mechanically exfoliated from geological samples. These exfoliated micro-flakes of MoS$_2$ have randomly distributed thickness and orientation, and are not viable for large-scale device integration. To achieve epitaxy of large-area MoS$_2$ films with uniformity and control, chemical vapor deposition (CVD) methods using various precursors such as MoO$_3$,$^{14-18}$ MoO$_2$,$^{19}$ MoCl$_5$,$^{20}$ Mo,$^{21,22}$ and (NH$_4$)$_2$MoS$_4$,$^{23,24}$ or physical vapor transport method$^{25}$ have been employed. However, these large-area films are mostly polycrystalline with small crystal grain sizes from tens of nanometers to several micrometers. In this report, we demonstrate large area vapor-solid-grown epitaxial MoS$_2$ thin films on sapphire with in-plane and out-of-plane ordering over centimeter length scales. The high quality of these films leads to record high space charge carrier mobility ($\sim 200$ cm$^2$/V$\cdot$s) for synthetic films at room temperature and current density in excess of 0.15 mA/$\mu$m. This work demonstrates the feasibility of device quality few layer MoS$_2$ layers with sufficient uniformity and quality to enable a variety of device applications based on 2D layered materials.

The vapor-solid grown MoS$_2$ films are of significantly higher crystalline quality than previous attempts.$^{21}$ This can be attributed to the control of the grain nucleation, and the high growth. We used a template (sapphire, space group: R-3c) that shares some symmetry with the MoS$_2$ (space group: P6$_3$/mmc) structure, and is thermally stable up to relatively high temperature. It has been shown previously that under similar conditions, the use of an epitaxial template led to significantly better crystal quality.$^{16,24,26-28}$ In previous reports of CVD-grown MoS$_2$, while out of plane ordering was evident from X-ray diffraction (XRD) measurements in the (0001) direction, no in-plane ordering, such as that evidenced from off-axis geometry, was apparent. We attribute this to significant twist in the mosaic caused by the large number of independent grains.

In this work, the control of grain nucleation was achieved by the supersaturation of sulfur vapor. Single-crystal (0001)-orientated sapphire substrates were solvent cleaned and 5 nm of molybdenum was deposited by sputtering using AJA Orion RF/DC Sputter Deposition Tool. 8.0 mg of MoS$_2$ powder (purchased from Sigma Aldrich) was placed in a small quartz tube which was then put inside a larger quartz tube (inner diameter: 1 cm) along with the Mo-coated sapphire wafer. The larger quartz tube was pumped down by a mechanical pump, sealed and heated to 1100°C for 4.5 h and then cooled down to room temperature at a rate of 0.5°C/min. The scheme of synthesis set-up is shown in Figure 1.

Nucleation is the first step in the crystallization process. Nuclei formed in this step can continue to grow into crystalline domains. In order to get single-crystal MoS$_2$ films with
good crystalline nature, the nuclei density should be minimized, which can be achieved by a controlled low supersaturation. In our vapor-solid synthesis, initially sulfur vapor reacts with the surface Mo metal and creates the seed crystal. Sulfur pressure needs to stay at a low value to reduce the nucleation density. It is difficult to control the amount of sulfur by using elemental sulfur itself because the super saturation is very high compared to the small amount of Mo metal on the substrate. We reduced the sulfur pressure by using MoS2 powder as a sulfur source to get a lower sulfur pressure during the synthesis. Thermogravimetric analysis (TGA) of MoS2 shows that above 950°C, sulfur can be gradually released and detected by mass spectrometer.\(^{29-32}\) The decomposition of MoS2 powder at high temperature can provide sulfur to sulfurize the Mo metal on sapphire substrate. The equilibrium between MoS2 powder and sulfur vapor inside the quartz tube would provide a sulfur vapor pressure of 0.023 Pa at 1100°C.\(^{30}\) According to the pressure-temperature phase diagram of Mo-S system,\(^{33}\) this pressure is the lowest sulfur pressure at which pure MoS2 phase can be produced. The total amount of sulfur that MoS2 can release under vacuum at ~1000°C for 4.5 h is about 0.099%,\(^{30}\) which is calculated to be the amount of sulfur that the Mo layer on substrate needed to get MoS2 phase (see calculation result in the supplementary material\(^{34}\)).

During the synthesis, the following reactions occur:

\[
\text{MoS}_2 \text{ powder} \quad \text{(surface)} \rightarrow \text{MoS}_x \quad (x < 2) \quad + \quad \frac{2-x}{2} \text{S}_2, \quad (1)
\]

\[
\text{Mo} \quad \text{(on sapphire)} \quad + \quad \text{S}_2 \rightarrow \text{MoS}_2 \quad \text{(on sapphire)}. \quad (2)
\]

The (0001)-orientated sapphire was chosen to be a good Van der Waals epitaxy substrate due to its atomically flat surface without dangling bonds on the surface. Both theoretical\(^{35,36}\) and experimental\(^{37,38}\) study show that the surface of (0001)-orientated sapphire is terminated by one Al layer because in this situation the dangling bonds on the surface are either completely filled or empty to form an auto-compensated neutral surface. Thus, the lattice matching condition has been relaxed dramatically.

The surface morphology of the samples was characterized by atomic force microscope (AFM, Veeco Instruments DI 3000). Crystalline nature was examined by a Bruker D8 High-Resolution Triple Axis X-Ray Diffractometer. Raman spectra were obtained by Renishaw spectrometer with a 10 mW laser at 514 nm.

Device fabrication started with standard lithography using a i-line stepper projection aligner followed by e-beam evaporation of Ti/Au/Ni metal stack for Ohmic contact. The devices were then mesa isolated using BCl3/Ar plasma chemistry in an inductively coupled plasma/reactive ion etching (ICP-RIE) system at 30 W RIE power. An Agilent B1500 parameter analyzer was used to measure room temperature current-voltage characteristics on Transfer Length Method (TLM) pads of width 100 μm. Dielectric deposition was done at 250°C using a Picosun SUNALE R-150B Atomic Layer Deposition tool. Low temperature I-V measurements were done using a Lake Shore cryogenic setup equipped with liquid Helium closed-loop circulator.

Figure 2(a) is a digital image of the as-grown MoS2 film with mirror-like appearance due to its atomically smooth surface (The RMS roughness of the MoS2 film was ~0.53 nm in a 5 μm × 5 μm area by an AFM scan). Figure 2(c) is a SEM image of the MoS2 film, which demonstrates the uniformity and continuity of the film in a large scale. The inset of Figure 2(c) is the SEM image of the area scratched by tweezers, which shows the lateral layered structure of the MoS2 film. In fact, the surface of as-grown MoS2 sample reported here appeared to be smoother compared to that of 4–5 nm MoS2 film exfoliated from geological MoS2.\(^{39}\) The thickness of the MoS2 film from sulfurizing 5 nm Mo is approximately 7.0 nm based on AFM measurement (Figure 2(b)). The 2–θ/ω XRD scan (Figure 3(a)) only the (0001) family diffractions of MoS2 and the diffraction of sapphire (0006) peak, which a preferred growth orientation of MoS2 with the c-axis parallel to that of sapphire substrate. Thickness fringes near the MoS2 (0002) peak suggest a sharp interface (Figure 3(b)) and confirmed the thickness ~7 nm estimated from AFM scan (see the calculation of thickness from fringes thickness in the supplementary material\(^{14}\)).

The off-axis (10–13) 2–θ/ω XRD scan (Figure 3(b)) across the full range of θ = 360° six peaks at MoS2 (10–13)
the length of 7 MoS2 unit cells equals to the length of sapphire substrate. To understand the in-plane orientations of the two basal planes in Figure 4. The MoS2 film and the sapphire substrate are rotationally commensurate.

The 30° rotation between the epi-layer and the substrate reduces the in-plane lattice mismatch to 13.0% with \( \sqrt{3}a(\text{MoS}_2) = 5.47\,\text{Å} \), \( a(\text{sapphire}) = 4.758\,\text{Å} \). For the unrotated case, the lattice mismatch of MoS2 and sapphire with \( a(\text{MoS}_2) = 3.16\,\text{Å} \) and \( a(\text{sapphire}) = 4.758\,\text{Å} \) would have been 50.5%. The lattice mismatch of 13% is still relatively high, but as shown previously, Van der Waals epitaxial materials can tolerate a mismatch of 13% is still relatively high, but as shown previously, Van der Waals epitaxial materials can tolerate a mismatch of 13%.

Triple-axis rocking curve scan was also measured to confirm the single crystalline nature (Figure 3(d)). A full width at half maximum (FWHM) of 15.552 arc sec at MoS2 (0002) diffraction was found to be about one-half of that of exfoliated single-crystalline MoS2.21 The narrow rocking curve FWHM suggests that the MoS2 films grown by vapor-solid method had high crystalline quality with relatively low density of defects. The two characteristic Raman peaks of MoS2 were observed with \( E_{2g} \) at 381.2 cm\(^{-1}\), and \( A_{1g} \) at 406.5 cm\(^{-1}\) with a peak separation of 25.3 cm\(^{-1}\) confirming the film had the characteristics of bulk (or several-layer) MoS2 (Figure 3(e)).

The carrier mobility, which is strongly dependent on the crystalline quality as well as on the background impurity of the 2D film, plays a critical role in transport properties and hence device performance. Theoretical calculations and experiments show that while charge impurity limited scattering in single-layer MoS2 is \( \sim 17\text{cm}^2\text{V}^{-1}\text{s}^{-1} \) without the high-\( \kappa \) dielectric screening effect, the intrinsic phonon-limited mobility of single-layer as well as multilayer MoS2 is expected to be as high as 320–410 cm\(^2\) V\(^{-1}\)s\(^{-1}\) (Refs. 45 and 46). Without the high-\( \kappa \) dielectric, few-layer MoS2 films have been shown to have mobility from 10 to 100 cm\(^2\) V\(^{-1}\)s\(^{-1}\) (Refs. 47–49), which can be enhanced to several hundred cm\(^2\) V\(^{-1}\)s\(^{-1}\) with a high-\( \kappa \) dielectric environment.47,48,50 However, the high mobility values reported were on exfoliated samples, rather than on large area synthetic MoS2. In this report, we show that high space charge mobility approaching the phonon-limited values can be achieved using the synthesis method described here.

In a log-log scale (Figure 5(a)), the current-voltage (I-V) curves exhibited two distinct slopes with a linear dependence on \( V \) at low-bias regime (0–10 V) and a quadratic dependence at higher (>20 V) bias regime. Further, for various TLM spacing (d), the current at higher bias was found to have \( V^2/d^2 \) dependence, indicating space-charge nature of the transport. The I-V curves were thus fitted with the space-charge transport equation

\[
I = \frac{Q \mu t L}{d} V + \frac{2\varepsilon_0 \mu L}{\pi d^2} V^2.
\]  

Here, \( q \) is the electron charge, \( \mu \) is the electron mobility, \( t \) is the thickness of MoS2 film (=7 nm), \( L \) is the width of TLM pads (=100 \( \mu \)m), \( d \) is the TLM pad spacing, and \( \varepsilon_0 \) is the dielectric constant of bulk MoS2 (=7.6). From the resulting fit (Figure 5(b)), an electron mobility of 120 (±20) cm\(^2\) V\(^{-1}\)s\(^{-1}\) and a carrier density of \( 2 \times 10^{14} \text{cm}^{-2} \) were extracted. Interestingly, from the I-Vs measured in a direction perpendicular (in-plane) to the direction of measurement as reported above, an electron mobility of 250 (±50) cm\(^2\) V\(^{-1}\)s\(^{-1}\). With a lattice mismatch to 13.0% and additional epitaxy, a constant of bulk MoS2 (\( C_{14} \)) with respect to sapphire: (a) top view and (b) side view.

FIG. 3. (a) 2θ/θ XRD Scan of MoS2 film on sapphire (blue index: MoS2 diffraction peaks, black index: sapphire (0006) diffraction peak); (b) XRD Scan at MoS2 (10–13) position; (c) Phi Scan at MoS2 (10–13) diffraction position and sapphire (01–12) position; (d) Triple-Axis Rocking Curve Scan at MoS2 (0002) diffraction position; and (e) Raman spectra of MoS2 film. (Cps = counts per second).

FIG. 4. Relative in-plane orientation of MoS2 to sapphire substrate with MoS2 axis 30° with respect to sapphire: (a) top view and (b) side view. (Black-aluminum atom, blue-oxygen atom, purple-molybdenum atom, yellow-sulfur atom; purple dashed line-unit cell of MoS2, black dashed line-unit cell of sapphire).
mobility of 65 cm²/Vs and a carrier density of 2 × 10¹¹ cm⁻² were extracted by fitting I-Vs to Eq. (3).

This observation of anisotropic electron mobility (with a mobility-ratio of ~1.8) in few-layer MoS₂ in the two mutually perpendicular directions is in agreement with prior theoretical predictions of anisotropic electron effective mass (0.53m₀ vs 0.73 m₀) for transport in (Aₘᵦᵣₜ) and in (₁��) directions of the crystal.

To reduce the effect of surface-related defects and impurities on the mobility, the films were covered with 20 nm of Al₂O₃ by atomic layer deposition (ALD). The ALD Al₂O₃ can passivate some of the interface charge leading to less remote impurity scattering. The I-Vs measured at various temperatures between two device pads separated by 3.5 µm are shown in Figure 5(c), and displayed typical characteristics of space-charge transport. The extracted electron mobility showed weak temperature dependence while the carrier density was found to increase slightly from 1.3 × 10¹¹ cm⁻² at 10 K to 1.7 × 10¹¹ cm⁻² at 290 K. The room temperature electron mobility was found to be ~192 cm²/Vs with ALD Al₂O₃ on MoS₂, an improvement from 120 cm²/Vs which was extracted without dielectric on MoS₂.

A simple estimation of the electron mobility in few-layer MoS₂ was made based on polar optical phonon (POP) scattering, acoustic deformation potential (ADP) scattering, and remote ionized impurity scattering in 2-dimensional electron gas, assuming an electron effective mass of 0.53m₀. For remote impurity scattering, we assumed that the remote interface charge density (nᵣ) is located at the ALD/MoS₂ interface, and that the 2D carriers are in the middle of the few-layer film. Since the 2D sheet carrier in our MoS₂ film is non-degenerate (2 × 10¹¹ cm⁻²), the carrier conduction does not take place predominantly at the Fermi. The scattering time was therefore estimated at any energy “E” and weighed with density of states and Fermi-Dirac distribution over the entire energy range (see mobility calculation in the supplementary material).

Figure 5(d) shows the temperature dependent electron mobility calculated using POP, ADP, and remote impurity scattering compared with experimentally extracted mobility from our MoS₂ films. For a fixed remote impurity (nᵣ) of 1 × 10¹¹ cm⁻², the theoretically estimated mobility seems to have a close fit to those measured data points, validating our scattering time estimates. The nᵣ = 1 × 10¹¹ cm⁻² which gives a good fit between theory and experiment is also close to the actual carrier density (1.3 × 10¹¹–1.7 × 10¹¹ cm⁻²) extracted after ALD layer on MoS₂.

In conclusion, we reported the vapor-solid growth of high-quality few-layer MoS₂ films at 1100°C using sulfur vapor obtained by decomposing MoS₂ powder. The as-grown surface was found to be atomically smooth and high resolution XRD scans and Raman spectroscopy indicated excellent out-of-plane ordering and epitaxial registry of the films over centimeter length scales. The film was found to exhibit space-charge transport and an electron mobility of 192 cm²/Vs was extracted at room temperature. We also demonstrated anisotropic electron mobility (with a mobility ratio of ~1.8) in measurement directions mutually perpendicular to each other. ALD Al₂O₃ on MoS₂ was found to enhance the electron mobility which showed very weak temperature dependence from 10 to 290 K. A simple scattering model based on optical phonon, acoustic phonon and remote impurity scattering was found to exhibit a good match with the experimentally extracted mobility. This demonstration of record high electron mobility for synthetic large area few-layer MoS₂ films is highly promising for enabling a wide variety of large-scale electronic device fabrication based on layered 2D materials.
