Chemical Vapor Deposition Growth of Crystalline Monolayer MoSe2

Xingli Wang,†,§,†) Yongji Gong, §,†) Gang Shi,† Wai Leong Chow,† Kunttal Keyshar,† Gonglan Ye,† Robert Vajtai,† Jun Lou,† Zheng Liu,†,# Emilie Ringe,†,§,* Beng Kang Tay,§,#,* and Pulickel M. Ajayan†,§,*

†Department of Materials Science & NanoEngineering, Rice University, Houston, Texas 77005, United States, §NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798 Singapore, ▲Department of Chemistry, Rice University, Houston, Texas 77005, United States, ‡School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore, and *CNRS-International-NTU-Thales Research Alliance (CINTRA), Nanyang Technological University, 639798 Singapore. †X.W. and Y.G. contributed equally to this work.

ABSTRACT

Recently, two-dimensional layers of transition metal dichalcogenides, such as MoS2, WS2, MoSe2, and WSe2, have attracted much attention for their potential applications in electronic and optoelectronic devices. The selenide analogues of MoS2 and WS2 have smaller band gaps and higher electron mobilities, making them more appropriate for practical devices. However, reports on scalable growth of high quality transition metal diselenide layers and studies of their properties have been limited. Here, we demonstrate the chemical vapor deposition (CVD) growth of uniform MoSe2 monolayers under ambient pressure, resulting in large single crystalline islands. The photoluminescence intensity and peak position indicates a direct band gap of 1.5 eV for the MoSe2 monolayers. A back-gated field-effect transistor based on MoSe2 monolayer shows n-type channel behavior with average mobility of 50 cm2 V-1 s-1, a value much higher than the 4–20 cm2 V-1 s-1 reported for vapor phase grown MoS2.

KEYWORDS: transition metal dichalcogenides · molybdenum diselenide · transistors · two-dimensional materials · chemical vapor deposition · monolayer

Monolayer transition metal dichalcogenides (TMDs) such as MoS2 have recently attracted tremendous interest due to their narrow band gap (ranging from 1.1 for MoTe2 to 2.0 eV for WS2),1–3 indirect to direct band gap transition, efficient hydrogen evolution when used as catalysts,1–6 etc., enabling a wide range of applications from electronics and optoelectronics to energy conversion.7–13 Among the more than 40 types of compounds in the TMD family, MoS2 is arguably the most extensively studied due to its promising semiconducting properties. Studies indicate that the less well-studied selenides may however be superior to sulfides in many aspects owing to a narrower band gap (1.5 eV in MoSe2 vs 1.9 eV in MoS2), a 10-fold narrower line width, and tunable excitonic charging effects.14,15 While progress in synthetic methodologies allows for monolayer and single-crystal growth of MoS2 with lateral dimensions reaching hundreds of micrometers,16,17 there remain significant challenges related to controlled, reproducible, and large area growth of the selenides.

Monolayer molybdenum diselenide (MoSe2) is in fact a “three-layer” structure consisting of top and bottom Se layers sandwiching Mo layers.2 In multilayer arrangements, layers are stacked together with weak van der Waals

* Address correspondence to emilie.ringe@rice.edu, ebktay@ntu.edu.sg, ajayan@rice.edu.

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interactions between Se atoms; in this “bulk” form, MoSe2 has been used as a host for intercalation,19 lubricants,20 and catalysts.21 Akin to MoS2 and WSe2,1,5,22 the band structure of MoSe2 varies with the number of layers. Decreasing thickness changes the band structure of MoSe2 from indirect (as in a bulk crystal) to direct (as in a monolayer); meanwhile, the band gap increases from 1.1 to 1.5 eV.15 Such tunable properties of MoSe2 render it an ideal material for various electrical and optical applications. Recently, back-gated field effect transistors were fabricated on ultrathin MoSe2 films,23 achieving an on/off ratio as high as 10^6 and an intrinsic mobility up to ~50 cm^2 V^−1 s^−1 at room temperature, which was shown to increase nearly 4-fold at 78 K. Given such properties, monolayer to few-layers MoSe2 appears to be a tremendous candidate for applications in electrical and optical devices.

However, synthesis of good quality, large-scale MoSe2 remains a challenge, with very few methods reported.25–29 Several chemical approaches produce MoSe2 nanocrystals, such as the sonochemical reaction between Mo(CO)6 and Se at 0 °C,24 the solvothermal conversion of MoO3 to MoSe2,25 and the reduction in the WSe2 system.37 Growth at 750 °C for 20 min yielded a high coverage of triangular domains, as shown in Figure 1a. Similar to CVD grown MoS2,38 MoSe2; they appear in optical images as darker areas. Their occurrence may indicate the presence of defects in the first layer, which act as nucleation sites for the second layer growth. Similar to CVD grown MoS2, MoSe2 islands can merge together, forming a continuous film as shown in Figure 1d. The thickness of a grown triangle, 0.8 nm as measured by atomic force microscopy (AFM, Figure 1e), confirms that the sample is a monolayer; the domain-to-domain and film thickness homogeneity are

**RESULTS AND DISCUSSION**

MoSe2, an interesting 2D optoelectronic material owing to its small, direct optical bandgap, was synthesized via CVD, characterized with photoluminescence spectroscopy and electron microscopy, and implemented in a field effect transistor (FET). MoSe2 was grown from MoO3 and selenium on a clean Si wafer with a 275 nm SiO2 top layer as shown in Figure 1a. A mixture of argon and hydrogen (15% hydrogen) was used as the carrier gas and reducing atmosphere during the deposition process. Hydrogen is essential for the growth of MoSe2; without it deposition does not occur, as reported in the WSe2 system.37 Growth at 750 °C for 20 min yielded a high coverage of triangular domains, as shown in Figure 1b,c. The size of the triangles ranges from several tens to more than a 100 μm. Some triangles also exhibit small domains of double layer MoSe2; they appear in optical images as darker areas. Their occurrence may indicate the presence of defects in the first layer, which act as nucleation sites for the second layer growth. Similar to CVD grown MoS2, MoSe2 islands can merge together, forming a continuous film as shown in Figure 1d. The thickness of a grown triangle, 0.8 nm as measured by atomic force microscopy (AFM, Figure 1e), confirms that the sample is a monolayer; the domain-to-domain and film thickness homogeneity are
evidenced by the homogeneity in color present in the optical micrographs shown in Figure 1.

Raman and PL are effective methods for the characterization of crystal quality and band gap in 2D materials. A triangle with an edge of about 40 μm (Figure 2a) was characterized with Raman and PL with a laser wavelength of 514.5 nm. Spectra were collected at the edge and center of the triangular domain, as shown in Figure 2. Two main peaks appear in the Raman spectra: a sharp one at low wavenumber (239 cm⁻¹) characteristic of the A₁g mode of MoSe₂ (out of plane vibration) and a broad one at higher wavenumber (301 cm⁻¹) characteristic of the E₂g mode (in-plane vibration). The nearly identical peak position and relative intensity in the edge and center spectra suggest a high homogeneity of the grown MoSe₂. The uniformity of the Raman intensity map of the 239 cm⁻¹ peak (A₁g mode, Figure 2d) further confirms this observation. However, both PL spectra (Figure 2c) and PL peak intensity map (Figure 2e) show a stronger signal in the center of the triangle, with a decreased intensity at the edges. Only one high intensity peak at around 840 nm is present in both spectra, corresponding to a band gap of 1.48 eV, in excellent agreement with the reported 1.5 eV for monolayer MoSe₂. The crystal quality of the CVD grown MoSe₂ was characterized at the atomic level using transmission electron microscopy (TEM) and aberration-corrected scanning TEM (STEM). A MoSe₂ sample with tens of micrometers domain size was transferred to a TEM grid following a poly(methyl methacrylate) (PMMA) assisted method. The continuity of the transferred film (Figure 3a) indicated the high quality of the grown sample; folds and small particles observed on the TEM specimen were caused by the transfer process. The large domains, of the order of tens of micrometers, observed in TEM confirm the high quality produced by CVD growth. The expected hexagonal packing of single layer MoSe₂ is clearly observed in the atomic resolution high-angle annular dark field (HAADF) STEM images in Figure 3. In HAADF-STEM, the image intensity is directly related to atomic number, and the expected alternating brighter (2 Se) and darker (Mo) sites are clearly observed in the images and intensity profile presented in Figure 3. MoSe₂ sample with bilayer domains were
also characterized by STEM, as shown in Figure 3d, where the bottom part is monolayer MoSe$_2$ with a perfect crystal lattice, and the brighter top part is a bilayer stacking. Additional images showing the MoSe$_2$ lattice as well as bi- and trilayer stacking can be found in the Supporting Information.

Elemental composition and bonding in the CVD grown film was examined with X-ray photoelectron spectroscopy (XPS). Four elements are present in the spectra acquired (an example is reported in Figure 4): Mo and Se from the monolayer MoSe$_2$, as well as Si and O from the SiO$_2$ substrate. The 3d spectra of Mo and Se in the MoSe$_2$ sample (Figure 4) provide information not only about stoichiometry but also about bonding. Mo 3d$_{3/2}$ and 3d$_{5/2}$ core levels peaks are located at $\sim$231.5 and 228.3 eV, respectively, while the peak of Se 3d is located around 54.0 eV, in agreement with the values obtained in other MoSe$_2$ systems.\textsuperscript{28,42} The former positions indicate the reduction of Mo from Mo$^{6+}$ to Mo$^{4+}$; peaks are significantly shifted from their hexavalent position of $\sim$235.90 and 232.50 eV (Mo 3d$_{3/2}$ and 3d$_{5/2}$ core levels of MoO$_3$).\textsuperscript{28} The peak of Se around 54.0 eV can be divided into Se 3d$_{3/2}$ and Se 3d$_{5/2}$ with peak positions at 53.9 and 54.7 eV, respectively.\textsuperscript{37} Also, the 1:1.97 Mo/Se ratio obtained from high-resolution XPS suggests that the CVD grown MoSe$_2$ is reasonably stoichiometric. XPS indicates that there is some selenium deficiency in our MoSe$_2$ samples; such deficiencies are associated with defects and are believed to cause the PL shift and intensity decrease observed (Figure 2). The XPS elemental analysis was confirmed by electron-energy...
loss spectroscopy (EELS), in which both the Se and Mo edges were found (Supporting Information Figure S2).

To evaluate the electrical performance of the material, FETs were fabricated by electron-beam lithography. Figure 5a shows a typical optical micrograph of the fabricated device with a channel length and width of 10 and 2 μm, respectively. It has been discussed by a few authors that defects in TMDs can impact their electronic transport properties, specifically grain boundaries which have been demonstrated to undermine the performance of TMD transistors. Experimentally, we are conscious of this phenomenon and have avoided the second layer when making FET devices for consistency (for example, the optical image of our FET device in Figure 5a). The typical electrical performance data of MoSe₂ FETs is presented in Figure 5b; all the fabricated devices displayed n-type behavior, consistent with results from mechanically exfoliated samples. Field effect electron mobilities can be estimated using the equation $\mu = \frac{\Delta I_d/\Delta V_{bg}}{L/W (C_gV_g)}$, where $L$, $W$, and $C_g$ are the channel length, width, and the gate capacitance per unit area, respectively. Here, 0.5 V was used for the $V_g$. The $I$–$V$ curves (inset in Figure 5b) confirm the Ohmic contact between the tested materials and the electrodes. From the data acquired for the MoSe₂ FET shown in Figure 5b, the on/off current ratio was found to exceed $10^6$, while the electron mobilities are within $20–80$ cm² V⁻¹ s⁻¹, with an average mobility of $50$ cm² V⁻¹ s⁻¹. The similarity of this result to that for exfoliated MoSe₂ monolayer is a strong evidence of the high quality of the CVD grown sample. It is worth emphasizing that the electron mobility of the resulting MoSe₂ is much higher than that of CVD MoS₂ when measured by the same back-gated configuration ($3–20$ cm² V⁻¹ s⁻¹). In conclusion, we have demonstrated the CVD growth of monolayer MoSe₂ single crystalline islands and films. The resulting MoSe₂ is large in area, uniform, highly crystalline and has a stoichiometry very near 1:2. The direct band gap of 1.48 eV indicated by PL indicates its possible application as a semiconductor; its back-gated FET performance shows MoSe₂ as a candidate for 2D semiconductor device application with an average mobility of $50$ cm² V⁻¹ s⁻¹ and on/off ratio of $10^6$.

**CONCLUSION**

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**METHODS**

**Growth of MoSe₂**. To synthesize monolayer MoSe₂, CVD method has been developed. Selenium pellets (99.9%, Sigma Aldrich) and molybdenum oxide (MoO₃) (99%, Sigma Aldrich) powder, as Se and Mo precursor, respectively, were placed into the same alumina boat. A clean Si wafer with a 275 nm SiO₂ top layer was placed face down in the boat. The boat with precursor and substrate was placed in a fused quartz tube and located at the center of the reactor, i.e., the hot zone. The furnace temperature was raised up to 750 ºC with a heating ramp of 50 ºC/min and, after that, was held at 750 ºC for 20 min, yielding MoSe₂ triangle domains or films. After growth, the furnace was left to cool unassisted. During all the process, 50 sccm mixture of argon and hydrogen (15% hydrogen) was used as the carrier gas and reducing atmosphere during the deposition process. The growth was carried on under atmospheric pressure.

**TEM Sample Preparation and Characterization**. The TEM sample is prepared by a PMMA assisted method. First, a PMMA thin film was spin-coated on the top of the MoSe₂/SiO₂/Si substrate. After that, the SiO₂ layer was etched by 2 M KOH solution and the PMMA/MoSe₂ layer would lift off. The PMMA/MoSe₂ was then transferred onto the TEM grid (perforated carbon film with an orthogonal array of 1.2 μm diameter holes and 1.3 μm separation, mounted on a 200 mesh Au grid, Ted Pella) and air-dried; PMMA was subsequently washed off with acetone and 2-propanol.

The TEM images in Figure 3a,b were recorded at 200 kV on a JEOL 2100F. The HAADF-STEM images in Figure 3c,d were recorded on an aberration-corrected JEOL ARM CFEG operated at 80 kV.

**FET Device Fabrication**. Contacts consisting of 3 nm titanium and 35 nm gold were fabricated by e-beam evaporation. The rate of deposition of titanium was maintained at 0.01 nm/s. After the deposition, the devices were baked for 2 h at 120 ºC under vacuum.

**Conflict of Interest**: The authors declare no competing financial interest.
REFERENCES AND NOTES


