Self-Limiting Layer Synthesis of Transition Metal Dichalcogenides

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This work reports the self-limiting synthesis of an atomically thin, two dimensional transition metal dichalcogenides (2D TMDCs) in the form of MoS₂. The layer controllability and large area uniformity essential for electronic and optical device applications is achieved through atomic layer deposition in what is named self-limiting layer synthesis (SLS); a process in which the number of layers is determined by temperature rather than process cycles due to the chemically inactive nature of 2D MoS₂. Through spectroscopic and microscopic investigation it is demonstrated that SLS is capable of producing MoS₂ with a wafer-scale (~10 cm) layer-number uniformity of more than 90%, which when used as the active layer in a top-gated field-effect transistor, produces an on/off ratio as high as 10⁸. This process is also shown to be applicable to WSe₂, with a PN diode fabricated from a MoS₂/WSe₂ heterostructure exhibiting gate-tunable rectifying characteristics.

Two-dimensional (2D) materials, and the heterostructures that can be created from them, have been widely studied due to their atomic-scale thickness, flexibility and unique electrical/optical properties. However, there is still a need to develop a layer-controlled synthesis method capable of producing a uniform 2D material over large areas in order to ensure the reliable operation of optoelectronic devices whose properties are dependent on the number of 2D material layers. The well-established CVD process has allowed large-area graphene sheets to be used in various practical applications, as this process is self-limited through a surface-catalyzed process based on the lower solubility of carbon in Cu than in Ni. Since it is this self-limiting behavior that makes it possible to achieve monolayer (1L) graphene over 95% of the target growth area, achieving a similar self-limiting behavior is clearly an important first step in the development of any new process for the large-area uniform growth of 2D materials.

Transition metal dichalcogenides (TMDCs) and their relevant 2D heterostructures (e.g., MoS₂/WSe₂ and MoS₂/graphene) have been the most heavily studied semiconducting 2D materials. Most recent research has been devoted to synthesizing uniform and layer-controlled TMDCs over large areas, such as chemical vapor deposition and transformation of Mo and MoOₓ thin film, but unlike graphene, the self-limiting growth of TMDCs with wafer-level layer controllability and uniformity has not yet been achieved. Atomic layer deposition (ALD) is known to be self-limiting, as the growth rate is dependent on the adsorption of precursor molecules rather than growth conditions such as exposure time, but as growth occurs through the formation of multi-layer islands it is difficult to achieve the layer controllability needed when compared to other techniques such as CVD. Maximizing the self-limiting behavior of the ALD process is therefore essential to achieving the layer controllability needed for a 2D structure, which requires not only careful optimization of the process conditions (e.g., temperature, pressure, exposure of precursor/reactant), but also the careful selection of the precursor and reactant. Moreover, since the ALD process is entirely based on surface reaction, it is important to understand the surface characteristics of the material being deposited. For example, the ALD of metal oxides or metals on graphene is made difficult by the chemically inactive nature of the graphene surface. As 2D TMDCs also have a chemically inactive surface, it is reasonable to expect they will exhibit a unique growth behavior during ALD when compared to conventional materials that are rich in dangling bonds.

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In this study, the self-limiting layer synthesis (SLS) of a 2D TMDC (MoS$_2$) is achieved through ALD by combining precursor exposure, purging, reactant exposure and a final purging into a single cycle. In this way, a point is reached at which the number of layers produced is determined purely by the growth temperature; a unique behavior that is directly attributable to the chemical inactivity of the 2D MoS$_2$ surface. The characteristics and layer uniformity achieved are subsequently assessed through spectroscopic and microscopic analysis, and the universality of the process itself is tested by applying it to the fabrication of a MoS$_2$/WSe$_2$ heterostructure for use in a diode.

**Self-limiting layer synthesis of MoS$_2$**

Figure 1(a–c) contains AFM images and height profiles of tri-, bi- and mono-layers of MoS$_2$ transferred onto a SiO$_2$ substrate (scale bar = 0.5 μm). (d) Raman spectra and (e) PL spectra of tri-, bi- and mono-layer MoS$_2$ on SiO$_2$. (f) Raman peak distances for MoS$_2$ with various SLS cycles and growth temperatures.
E\(^{1\_2g}\) and A\(_{1g}\) is often used to determine the number of MoS\(_2\) layers, as an increase in layers is accompanied by a softening of the E\(^{1\_2g}\) mode frequency and a stiffening of the A\(_{1g}\) mode frequency\(^{29,31}\). In this case, the calculated peak distances of 20.2 cm\(^{-1}\) for 1L, 21.1 cm\(^{-1}\) for 2L, and 23.3 cm\(^{-1}\) for 3L all agree well with previously reported values for MoS\(_2\)\(^{29,32,33}\). Thus, both the AFM and Raman results show that it is the growth temperature that determines the number of MoS\(_2\) layers by SLS.

The PL spectra of the synthesized MoS\(_2\) are shown in Fig. 1(e) as a function of the number of layers obtained. Note that the 1L MoS\(_2\) spectrum exhibits a strong PL signal at 1.89 eV and a weak, wide PL signal at 2.05 eV, which correspond to the A\(_3\) and B\(_3\) direct excitonic transitions of MoS\(_2\)\(^{4,34}\). These signals weaken in the case of 2L MoS\(_2\) and become negligible with 3L MoS\(_2\), as the increasing number of layers induces a transition from a direct to an indirect band gap. This is concordant with previous results regarding the dependence of the PL signal on the number of layers\(^{4,34,35}\) and further confirms the growth temperature dependent nature of the SLS of MoS\(_2\).

Given the good temperature performance of this FET at 10 K, a top-gated FET with Au(10 nm)/Ti(50 nm) electrodes and an ALD Al\(_2\)O\(_3\) (40 nm) gate insulator. The room temperature requirements make proper selection of the precursor essential, with MoCl\(_5\) being used in this study due to its higher thermal stability relative to other metal organic precursors.

The uniformity of the MoS\(_2\) obtained through SLS was evaluated at different scales through Raman mapping of the peak distances between the A\(_{1g}\) and E\(^{1\_2g}\) modes. The Raman map of the 1L SLS MoS\(_2\) in Fig. 2(a) shows a perfectly uniform distribution at a micrometer scale (20 \(\mu\)m × 20 \(\mu\)m), with statistical analysis (see Supplementary Fig. S6) revealing the average peak distance and standard deviation to be 20.3 and 0.6, respectively. Uniformity at a wafer-level scale was measured by synthesizing 1L, 2L and 3L MoS\(_2\) onto 1.5 \(\times\) 9 cm\(^2\) SiO\(_2\) substrates; the substrate size being limited by the diameter (~3 cm) and length (15 cm hot zone) of the tube furnace used. It is clear from Fig. 2(b) that the color of the SLS MoS\(_2\) is certainly dependent on the number of layers, but to assess the cm-scale uniformity, Raman spectra were measured at nine different positions along the length of the SLS MoS\(_2\). The peak distances and full-width at half-maximum (FWHM) of the E\(^{1\_2g}\) and A\(_{1g}\) modes are plotted in Fig. 2(c) for each position, from which we see that with all samples the variation in peak distance and FWHM of the E\(^{1\_2g}\) and A\(_{1g}\) modes with position is quite small (~2% for peak distance, ~5 and ~4% for the FWHM of E\(^{1\_2g}\) and A\(_{1g}\) respectively). In addition, the Raman peak distance varies from 20.2 to 23.4 cm\(^{-1}\) as the number of layers is increased, confirming that good uniformity and layer control is achieved at the wafer level through the SLS of MoS\(_2\).

The crystallinity and electrical performance of the 1L SLS MoS\(_2\) was evaluated through high-resolution TEM (HRTEM) analysis and by using its in a top-gated field-effect transistor (FET). The low-magnification TEM image in high magnification TEM image of 1L SLS MoS\(_2\) in Fig. 2(d) reveals triangular, dark-contrast regions of 2L MoS\(_2\), but as these represent only about 4% of the total area, the 1L SLS MoS\(_2\) can be considered to have near-perfect (\(>95\%\)) micrometer-scale layer uniformity. This growth of 2L MoS\(_2\) on 1L MoS\(_2\) could be due to the energetically favorable adsorption of MoCl\(_5\) on defect sites such as sulfur vacancies or grain boundaries, as such adsorption of molecules is seen with graphene\(^{26,27}\).

In the HRTEM image of the 1L SLS MoS\(_2\) in Fig. 2(e), selected regions exhibit a honeycomb-like with a lattice spacing of 0.27 or 0.16 nm depending on whether it involves (100) or (110) planes. A six-fold coordination symmetry is also clearly evident in the fast Fourier transform (FFT) image in the inset of Fig. 2(e). The approximate grain size is 80–100 nm, though this could potentially be improved through further optimization of the process and substrate conditions. The electrical performance of the 1L SLS MoS\(_2\) was evaluated by using it in the fabrication of a top-gated FET with Au(10 nm)/Ti(50 nm) electrodes and an ALD Al\(_2\)O\(_3\) (40 nm) gate insulator. The room temperature performance of this FET at 10\(^{-5}\) mTorr is shown in Fig. 2(f), which reveals an n-type behavior; the
0.2 cm²/V·s field effect electron mobility in the linear regime of the transfer curve agreeing with a previous report of a MoS₂ FET. Interestingly, this 1L SLS MoS₂ FET also has a low subthreshold swing value of ~0.36 V/dec and an excellent on/off current ratio of ~10⁸ that is higher than anything previously achieved with 1L MoS₂ and is in fact comparable with a single crystal.

Vertically stacked heterostructure. If the proposed self-limiting growth mechanism of SLS is valid, then it would be expected to apply to other 2D materials. This was therefore tested using mechanically exfoliated WSe₂ flakes on a SiO₂(300 nm)/Si substrate, as demonstrated by the microscopy (OM) images in Fig. 3(a). This WSe₂ flake was confirmed through AFM and Raman analysis (See Supplementary Fig. S8(a–c)) to contain regions of both 2L WSe₂ (#2) and 12L WSe₂ (#3). The AFM image of the SLS MoS₂ produced on this WSe₂ flake at 800 °C (Fig. 3(b)) shows that a thickness of 1.3 nm (or 2L WSe₂) was obtained, indicating that 1L MoS₂ is deposited on both 2L WSe₂ and the SiO₂ substrate under these conditions. Figure 3(c) shows the Raman spectra obtained at 3 different points of the SLS MoS₂ on WSe₂/SiO₂. In the SiO₂ region (#1), E₁²g and A₁g Raman peaks for MoS₂ are observed at 385.2 and 405 cm⁻¹, respectively, with the peak distance of 20.2 indicating that 1L MoS₂ was obtained as expected. Raman peaks of WSe₂ (i.e., the sum of the E₁²g and A₁g peaks at 249.8 cm⁻¹) are observed in the 2L WSe₂ region (#2) along with peaks for MoS₂ (E₁²g at 378.4 cm⁻¹ and A₁g at 404.8 cm⁻¹), indicating that MoS₂ was also synthesized on the WSe₂ flake. Furthermore, the absence of any Raman peaks related to MoSe₂ (E₁²g at 286 cm⁻¹ and A₁g at 244 cm⁻¹) or WS₂ (E₁²g at 356 cm⁻¹ and A₁g at 420 cm⁻¹) indicates that there is no significant mixing or alloying between the two 2D materials. There is, however, a notable 7 cm⁻¹ downshift in the E₁²g peak of MoS₂ in the 1L MoS₂/WSe₂ region relative to the MoS₂/SiO₂ region. A similar downshift has been reported in the case of an interlayer-coupled 1L MoS₂/1L WSe₂ heterostructure fabricated by transferring individual MoS₂ and WSe₂ flakes, with this being attributed to interaction between MoS₂ and WSe₂. Meanwhile, the absence of any MoS₂ Raman peaks in the 12L WSe₂ (#3) region indicates that there is effectively no growth of MoS₂ on 12L WSe₂, further supporting the idea that the self-limiting nature of the SLS process is layer dependent.

For further examination of SLS MoS₂ on WSe₂, Raman mapping of the MoS₂ E₁²g peak intensity and position was compared against OM images of 1L SLS MoS₂ grown on WSe₂ flakes on a SiO₂ substrate. In Fig. 3(d), regions confirmed by Raman analysis and AFM (See Supplementary Fig. S8(d)) to be 2L WSe₂ are indicated by white arrows, with the rest being bulk WSe₂. The Raman map of MoS₂ E₁²g intensity in Fig. 3(e) shows that a strong MoS₂ E₁²g signal is observed only at 2L WSe₂ regions, indicating that MoS₂ was not synthesized on bulk WSe₂. The Raman map of MoS₂ E₁²g position (Fig. 3(f)) further supports the notion that MoS₂ grows only on 2L WSe₂, which is accompanied by a downshift relative to the MoS₂ E₁²g position on SiO₂. This confirms the validity of using SLS to produce MoS₂ on other chemically inert surfaces such as WSe₂, and indicates that the process has the potential for widespread application.
As the SLS process clearly allows for much greater layer control than previously reported methods, it represents a promising option for fabricating atomically thin functional devices such as PN diodes, light emitting diodes and inverters. To test this, a PN diode was fabricated using a 1L SLS MoS2/2L WSe2 heterostructure, with Fig. 4(a,b) showing the device structure and an OM image of the fabricated PN diode. Operation of this device is dependent on the back gate voltage, which as shown in Fig. 4(c), can be adjusted by varying the carrier concentration through electrical doping. In other words, the PN diode exhibits a gate-tunable characteristic, with an increase in gate voltage from -60 to 20 V changing the p-n rectifying configuration to n-n junction behavior. The calculated forward/reverse current ratio at $V_{ds} = 5$ V clearly shows this gate-tunable PN diode characteristic (inset of Fig. 4(c)). The forward/reverse current ratio of ~80 at $V_g = -60$ V, is higher than previously reported for a PN diode based on 1L MoS2/1L WSe2 (~50 at $V_{ds} = 8$ V)\(^4\), but drops to 1.4 at $V_g = 20$ V. This gate-tunable characteristic could be explained by a variation in carrier density with electrical doping, as consistent with a previous report\(^4\) (also explain in Supplementary Fig. S10). Also of note is the fact that this PN diode exhibits a strong PL quenching property and photovoltaic effect, indicating a rapid carrier separation at the MoS2/WSe2 junction. Figure 4(d) shows the PL spectra for 1L MoS2, 2L WSe2 and the heterostructure created from them. It is evident from this that the strong PL peak for the direct gap transition of 1L MoS2 is greatly suppressed by the WSe2 junction, which is attributed to the rapid separation of charge carriers\(^45\). Figure 4(e) shows the I-V characteristics of a MoS2/WSe2 PN diode at $V_g = -50$ V with and without illumination by an incident optical power density of 14 W/m². We see from this that the current increases with illumination due to the generation of optically excited carriers. The open circuit voltage of 0.2 V indicates a photovoltaic effect, with a calculated photoresponsivity of 33 mA/W at $V_{ds} = 1$ V. As a result, we show the potential of SLS MoS2/WSe2 structure in photovoltaic device as well as PN diode.

**Conclusion**

In summary, the synthesis of MoS2 on a SiO2 substrate has been successfully achieved through a new self-limiting process that allows the number of layers formed to be controlled by varying the growth temperature. Though the precise mechanism requires further study, this behavior is believed to be caused by the lack of dangling bonds on the surface of MoS2, and the screening effect that MoS2 layers have on the substrate's electric field. More importantly, this process can achieve excellent layer uniformity (up to 95%) over large areas at wafer-level scale. The resulting 2D MoS2 can produce n-type behavior and a high on/off ratio when used in a top-gated FET, and can be grown on other chemically inert 2D materials such as WSe2. Indeed, a PN diode based on a MoS2/WSe2 heterostructure is capable of a high forward/reverse current ratio, and exhibits a gate-tunable rectifying property attributable to

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**Figure 3.** (a) OM image of an exfoliated WSe2 flake on SiO2 (scale bar = 10 μm). (b) AFM image and height profile of SLS MoS2 on 2L WSe2 region (scale bar = 0.5 μm). (c) Raman spectra for the numbered regions in Figure 3(a): #1: MoS2 on SiO2, #2: MoS2 on 2L WSe2 and #3: SLS MoS2 on 12L WSe2. (d) OM image of SLS MoS2 on exfoliated WSe2 flakes (scale bar = 10 μm) and corresponding Raman mapping results for (e) MoS2 $E_{12g}^1$ intensity and (f) MoS2 $E_{12g}^2$ position.
electrical doping by gate voltage. We therefore believe that this new method could be extended to the development of other 2D TMDCs materials and 2D heterostructures.

**Methods**

**SLS MoS\(_2\) Growth.** A tube furnace reactor was used to synthesize MoS\(_2\) directly onto SiO\(_2\) (285 nm)/Si substrates using MoCl\(_5\) and H\(_2\)S as the precursor and reactant, respectively. A bubbler containing the precursor was heated to 90 °C to ensure an adequate vapor pressure for the precursor molecules to be carried into the tube by pure argon (99.999%) carrier gas. The SLS cycle consisted of four steps, each with the same ALD procedure of: precursor exposure for 4 s, a 5 s Ar purge, 3 s H\(_2\)S reactant exposure, and a final 5 s Ar purge.

**Transfer of MoS\(_2\).** The as-synthesized MoS\(_2\) on the SiO\(_2\) substrate was spin coated with polymethyl methacrylate (PMMA) at 4000 rpm for 60 s. After curing the PMMA at 100 °C for 15 min, the sample was immersed in a 10% HF solution to etch away the SiO\(_2\) layer. The sample was then washed with DI water and transferred to a new SiO\(_2\)/Si substrate. Finally, the PMMA was removed using acetone and the sample washed with isopropyl alcohol.

**Fabrication of Top-Gated Field-Effect Transistor.** The MoS\(_2\)-based FET was fabricated from as-synthesized 1L MoS\(_2\) on a SiO\(_2\) (300 nm)/Si substrate by evaporating Au(10 nm)/Ti(50 nm) electrodes and an ALD Al\(_2\)O\(_3\) (40nm) gate insulator through conventional photolithography and reactive ion (O\(_2\) plasma) etching.

**Fabrication of PN diode.** The 1L SLS MoS\(_2\) was synthesized on WSe\(_2\) flakes at 800 °C. Then, PN diode was fabricated from an SLS MoS\(_2\)/WSe\(_2\) heterostructure on a SiO\(_2\) (300 nm)/Si substrate by evaporating Au(10 nm)/Ti(50 nm) electrodes. After etching, electrical contacts were formed between the drain electrode and 12L WSe\(_2\), and between the MoS\(_2\) and source electrode.

**Characterization of MoS\(_2\).** OM (Nikon ECLIPSE LV100ND), SEM (JEOL-6701F), Raman spectroscopy (HORIBA, Lab Ram ARAMIS; 532 nm laser excitation wavelength), AFM (VEECO, Multimode), PL (SPEX1403, SPEX; 532 nm laser excitation wavelength), XPS (Thermo U.K., K-alpha radiation), TEM (FEI Titan G2 Cube
60–300, accelerating voltage = 80 kV) and a voltage/current meter (Keithley 4200, Keithley Instruments) were all used in characterizing the SLS MoS₂ nanosheets.

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Y.K. and J.-G.S. contributed equally to this work. Y.K. and J.-G.S. carried out most experiments and analyzed the data. Y.J.P, W.J.W. and J.-H.A. made the FET devices and carried out the electrical measurement. G.H.R. and Z.L. contributed to TEM measurement. S.J.L and J.-M.M. performed PL characterization. J.S.K., P.J.J., W.J.W. and S.I. contributed to fabrication of PN diode. T.C. and H.J. contributed to AFM and SEM measurement. C.W.L. and J.P. contributed to XPS measurement and analysis data. Y.K., J.-G.S., H.L., J.P. and H.K. designed the experiment and co-wrote the paper. All of the authors discussed the results and commented on the paper.

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