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**CONTINUOUS ULTRA-THIN MOS₂ FILMS GROWN BY
LOW-TEMPERATURE PHYSICAL VAPOR
DEPOSITION (POSTPRINT)**

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AFRL/RXAN**

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Interim Report**

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14. ABSTRACT Uniform growth of pristine two dimensional (2D) materials over large areas at lower temperatures without sacrifice of their unique physical properties is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into functional devices. This Letter describes a vapor phase growth technique for precisely controlled synthesis of continuous, uniform molecular layers of MoS ₂ on silicon dioxide and highly oriented pyrolytic graphite substrates of over several square centimeters at 350° C. Synthesis of few-layer MoS ₂ in this ultra-high vacuum physical vapor deposition process yields materials with key optical and electronic properties identical to exfoliated layers. The films are composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements from contacts with separation on the order of centimeters.					
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Continuous ultra-thin MoS₂ films grown by low-temperature physical vapor deposition

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Uniform growth of pristine two dimensional (2D) materials over large areas at lower temperatures without sacrifice of their unique physical properties is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into functional devices. This Letter describes a vapor phase growth technique for precisely controlled synthesis of continuous, uniform molecular layers of MoS₂ on silicon dioxide and highly oriented pyrolytic graphite substrates of over several square centimeters at 350 °C. Synthesis of few-layer MoS₂ in this ultra-high vacuum physical vapor deposition process yields materials with key optical and electronic properties identical to exfoliated layers. The films are composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements from contacts with separation on the order of centimeters. © 2014 AIP Publishing LLC.

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Molybdenum disulfide is a naturally abundant material with a layered atomic structure giving rise to remarkable mechanical (e.g., low shear strength for solid lubrication)¹ and catalytic (e.g., hydrodesulfidization)² performance. Few-layer MoS₂ and other transition metal dichalcogenides (TMDs) have recently shown exciting technological potential in nano-electronic device development such as a thickness-³ or strain-tunable⁴ direct band gap^{5,6} enhanced photoluminescence⁷ with sensitivity to ambient environments,⁸ and other properties with promise for diverse sensor^{8,9} and optoelectronic device applications.¹⁰ The thin TMD materials examined in the aforementioned studies have been synthesized primarily by chemical or mechanical exfoliation—both approaches generally lacking scalability and uniformity over appreciable areas (>10 μm). Chemical vapor deposition is emerging as a technique to produce continuous transition metal dichalcogenide films, over larger areas (>10 μm²) approaching those of exfoliated crystals;¹¹ however, the lack of pristine quality, wafer-scale synthesis of continuous two dimensional (2D) TMDs, and their heterostructures is currently a major hurdle impeding both fundamental understanding and device development progress.

Here, results from few-layer MoS₂ growth under non-equilibrium physical vapor deposition (PVD) growth of continuous MoS₂ films of 3–6 molecular layers at a growth temperature of 350 °C are shown. This is accomplished by maximizing atomic mobility during growth through the use of incident atoms with kinetic energies just below the lowest energy threshold for defect formation (i.e., vacancy creation by sputtering of S atoms), which is reported to be approximately 8 eV.¹² The materials were grown on amorphous SiO₂ and (002) oriented graphite substrates in an ultra-high vacuum environment to minimize surface and interface contamination.

Examination of the materials via transmission electron microscopy (TEM) and atomic force microscopy (AFM) revealed that they were continuous and of uniform thickness with well-aligned basal planes over 4 cm² areas. Materials grown via this PVD technique possess characteristics typical of few-layer MoS₂ films produced by exfoliation, including an equivalent dependence of Raman peak shifts on thickness⁵ and a direct band gap of approximately 1.9 eV.¹³

The PVD synthesis process is based on magnetron sputtering, and is, therefore, easily scalable to allow growth of very thin TMD films over very large areas (>1 m²) on diverse substrate materials due to the low processing temperatures. PVD possesses additional advantages in the cleanliness of the interfaces processed in the ultra-high vacuum environment (base pressure was <5 × 10⁻⁹ Torr for all growth experiments) and the precise atomic scale thickness control for well-defined interfaces. This work is an extension of the authors' prior efforts examining PVD process parameters and growth orientation control of nano-crystalline MoS₂ films,^{14,15} but with emphasis on low temperature growth and large-scale synthesis of few-layer MoS₂. All films were grown via magnetron sputtering using a solid 3.3 cm diameter MoS₂ target of 99.95% purity. The SiO₂ and highly oriented pyrolytic graphite (HOPG) substrates were introduced via a vacuum load-lock and mounted on an electrically grounded, heatable, and rotatable fixture. Square Si substrates with a 1000 nm thermally grown SiO₂ with dimensions of 2 cm × 2 cm were ultrasonically cleaned in a series of solvents and rinsed with deionized water. HOPG samples 1 cm × 1 cm (SPI, Grade 1) were mechanically cleaved immediately prior insertion into a sample vacuum load-lock. In this work, the samples were heated to 350 °C and allowed to rotate at approximately 100 rotations per minute while

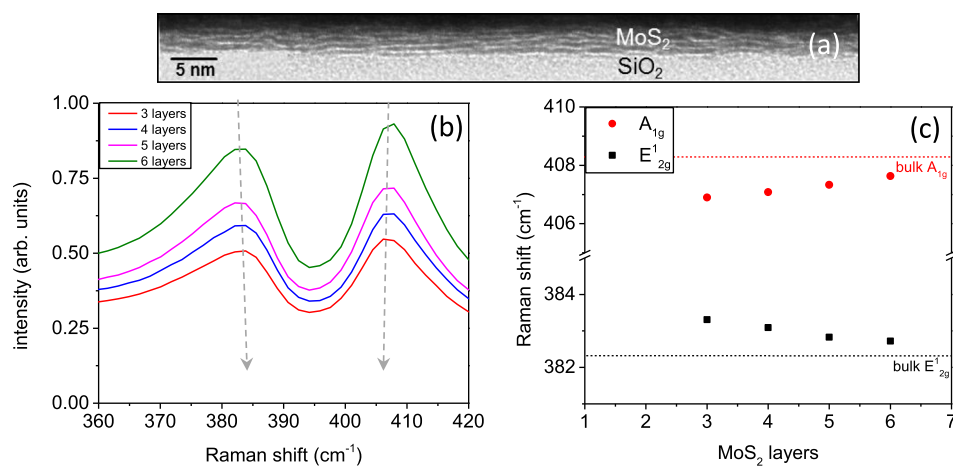


FIG. 1. Typical cross-sectional microstructure of MoS₂ films synthesized at 350 °C is shown for a five layer sample on SiO₂ in (a). The Raman spectra of films for a range of thicknesses are shown in (b). The frequency shift between in-plane and out-of-plane Raman peaks is correlated to the number of layers (c) by measurement of film thickness in the TEM.

positioned 7 cm from the MoS₂ target. Throughout the process, the temperature was measured with an IR pyrometer calibrated with a thermocouple for each substrate material. The chamber was then filled with ultra-high purity argon gas at a constant flow rate of 25 sccm to a pressure of 15 mTorr (2 Pa). Conditions for controlling the orientation of MoS₂ films in similar vapor phase growth processes were outlined by the authors in prior works,^{14,16} but employing additional control over the desorption and diffusion kinetics of MoS₂ by modulating the power to the sputter source and also by controlling the magnetic and electrostatic fields adjacent to the substrate were necessary in the present work. Films were grown layer by layer over incrementally longer time intervals at a constant rate of approximately 0.15 nm per second in order to precisely build their thickness to the desired number of layers. Raman spectroscopy was then employed to characterize E_{2g}¹ (in-plane vibrations) and A_{1g} (out-of-plane vibrations) peaks indicating atomic ordering into crystalline hexagonal MoS₂. The growth time on SiO₂ was correlated to the resulting thickness by examining cross sections of several samples grown for different durations in the TEM to precisely identify the number of molecular layers. Samples were prepared for study in the TEM by evaporating a layer of gold onto the surface to protect the MoS₂ layers from damage during focused ion beam processing. A typical film cross-section on a thermally grown silicon oxide wafer ($R_a = 5$ nm) is shown in Fig. 1(a) for a five layer thick sample. The atomic layers are parallel with spacings measured to be 0.63–0.68 nm (close to accepted spacing for bulk crystal of 0.66 nm); however, atomic scale boundaries isolate individual crystalline domains with characteristic lengths on the order of 5–10 nm. Despite the nanoscale size of the domains, the materials are apparently bonded through the domain boundaries because large areas (>mm²) of intact films can be lifted off the substrates via solution-based techniques. Additionally, four indium contacts were placed at the corners of an approximately 1 × 1 cm² in a van der Pauw geometry on films 3–6 layers thick to measure room-temperature resistance values of 1–5 × 10⁻⁴ Ω-m.

Examples of Raman spectra (514 nm excitation wavelength) for samples grown at different times are shown in Fig. 1(b). The difference between the E_{2g}¹ and A_{1g} peak shifts (measured by fitting of a Gaussian function to each Raman peak) are plotted against film thickness, as shown in

Figure 1(c). Raman spectroscopy has been used to generate topographical surface maps allowing characterization of the number of MoS₂ layers and thickness uniformity.^{17,18} In these works, the contrast in such maps spatially resolves the frequency difference between A_{1g} and E_{2g}¹ peaks in the Raman spectra, revealing the number of layers at a particular region of a sample. This mapping technique is effective, but not practical over the cm² length scale of interest in this work; therefore, a modified Raman technique was developed to evaluate uniformity over large areas. The Raman peak separations for samples of the thickness measured by observation in the TEM were plotted to make a calibration curve relating A_{1g} and E_{2g}¹ peak separations to the number of layers as shown in Fig. 1(c). The peak separations were consistent with those reported in the literature for exfoliated films of the same thickness.¹⁷ Physical vapor deposition (Fig. 2(a)) was used to grow a four-layer MoS₂ sample on an oxidized silicon wafer with an area of 4 cm² (Figure 2(b)) under identical processing conditions as those used to generate the calibration curve (Fig. 2(c)). Raman spectra were collected over the sample area in 500 μm intervals along the sample length and width. The frequency difference between the E_{2g}¹ and A_{1g} peaks was measured at the approximate positions identified on the sample as shown in Fig. 2(b). The minimum (24.1 cm⁻¹) and maximum (24.3 cm⁻¹) frequency values were obtained over the 4 cm² area shown in Fig. 2(b), indicating the minimum and maximum thicknesses, respectively, on the sample surface. These values are plotted on the MoS₂ thickness calibration curve in Figure 2(c). The maximum observed frequency difference between the peaks indicates a maximum possible thickness difference of less than 0.5 molecular layers, or about 3 Å. In conjunction with TEM results, it appears that the films are uniform to within one atomic diameter over the entire 4 cm² area. The relationship between processing conditions and this exceptional thickness uniformity is discussed in more detail later in this work.

Another hallmark of monolayer thin MoS₂ is photoluminescence (PL) due to the presence of a direct band gap at approximately 1.9 eV. Figure 3 shows the Raman shift as well as the PL from 3 and 5 layer MoS₂ samples grown on SiO₂. The PL spectra are relatively broad as they were taken at room temperature, but are similar to spectra reported by other authors.⁷ This photoluminescence was observed for sputtered films with thicknesses up to 6 molecular layers.

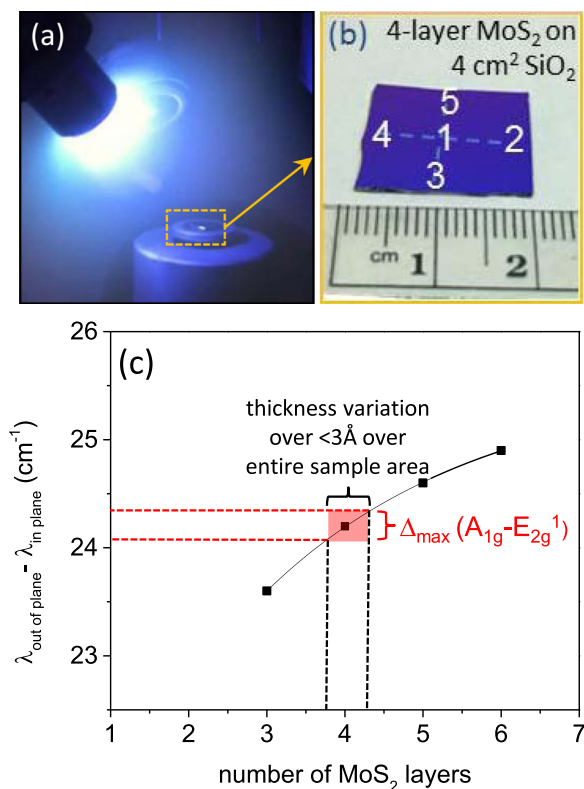


FIG. 2. (a) Photograph of 4 layer MoS_2 film growth process on a $2\text{ cm} \times 2\text{ cm}$ wafer (b). The uniformity of the film was characterized with Raman spectroscopy at different locations on the sample surface as indicated in (b). Data from the numbered locations allowed calculation of a thickness difference of approximately 3 \AA (c).

Very little to no PL intensity was observed for thicker films or bulk MoS_2 due to the decrease in the intraband relaxation rate from the excitonic states with decreasing film thickness, which thereby enhanced photoluminescence.¹³ It was also verified that the measured PL intensity did not originate from the thermally oxidized (SiO_2/Si) substrate itself.

The MoS_2 films on SiO_2 show layer by layer growth without island formation in atomic force microscopy (Fig. 4(a)). Imaging of film surfaces was performed in peak-force quantitative nano-mechanical mapping mode. The high-resolution

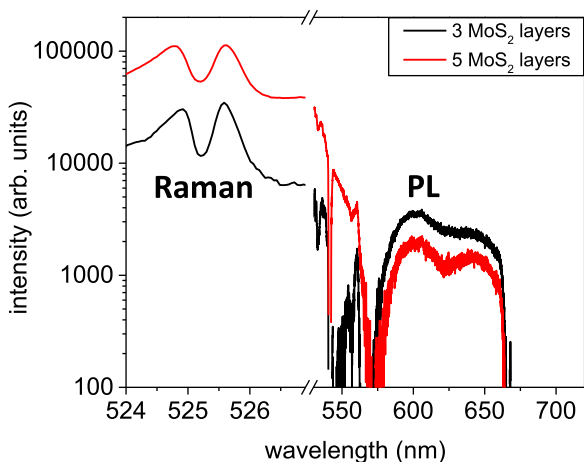


FIG. 3. Semi-log plot of Raman and PL for samples of 3 and 5 layer samples show how Raman intensity increases with the total MoS_2 volume sampled and PL quantum efficiency increases as material thickness is reduced.

imaging was accomplished through use of a low setpoint ($<20\text{ mV}$) during sample engagement and throughout imaging, thereby preserving the tip shape. The RMS roughness of the film was approximately 0.58 nm compared to 0.26 of the substrate. This ultra-thin TMD film morphology can be attributed to the non-equilibrium sputtering process, where the incident atoms traverse sufficient distances upon arrival at the growing film surface to allow adsorption at high energy sites such as an atomic vacancy or step edge. The typical kinetic energies of incident atoms are on the order of $1\text{--}10\text{ eV}$ even after multiple scattering events within the background gas. This results in orders of magnitude greater energy input to the growing film surface as compared to the typical thermal energy associated with CVD growth, allowing increased surface mobility of incident atoms at relatively low substrate temperatures, such as the $350\text{ }^\circ\text{C}$ employed here. For a growth process with high atomic surface mobility, it is generally recognized that layer by layer, or 2D growth occurs when $\gamma_f + \gamma_I < \gamma_s$, as the surface energy of the substrate (γ_s) will be reduced by coverage with the growing film, making such growth an energetically favorable process. For MoS_2 (with a surface energy of 260 erg cm^{-2})¹⁹ grown on low surface energy substrates such as SiO_2 (259 erg cm^{-2}),²⁰ the γ_f and γ_s values are approximately equivalent; therefore, the energy associated with creating the interface would act as a barrier for 2D growth. However, layer by layer growth still occurs as shown by the AFM and TEM results presented here. A monolayer of molybdenum may be the first layer grown on the surface, according to reports of the early studies of growth of van der Waals (vdW) materials via vapor phase growth.²¹ This molybdenum layer would strongly bind to the oxide surface, as Mo has a large thermodynamic driving force to form an interfacial oxide *in situ* on an oxidized substrate.²² It is hypothesized, that after the growth of the molybdenum monolayer, subsequent adsorption of incident sulfur and molybdenum atoms would result in edges with much higher surface energies ($25\,000\text{ erg/cm}^{-2}$)²³ than the planar film surfaces parallel to the substrate surface. The high surface energy of anisotropic MoS_2 edges acting as 2D nuclei forming on this initial molybdenum base layer promotes 2D nucleation and growth, as incident atoms preferentially assemble at the reactive MoS_2 domain edges.

Further support for hypothesized growth mechanisms is indicated by the morphology and composition of the MoS_2 films grown on HOPG substrates (Fig. 4(b)). While the lower surface energy of the HOPG ($\sim 80\text{ erg cm}^{-2}$) should result in growth of isolated islands, a continuous network of granular topographic features was observed in the AFM in Figure 4(b) for the $\sim 1.5\text{ nm}$ thick film. Coverage of the HOPG surface with a transition metal layer may temper the effects of the significantly lower substrate surface energy, resulting in a similar film morphology. An example of tri-layer MoS_2 grown on a HOPG surface is shown in Figure 4(c). HOPG and hexagonal MoS_2 have in-plane lattice mismatch of approximately 30%. Despite this extreme mismatch, the capability of growing well-oriented MoS_2 with the basal planes parallel to that of the HOPG was demonstrated. This result suggests that it is possible to grow van der Waals heterostructures²⁴ by PVD techniques, allowing selection of materials based on functionality with no regard for lattice matching.

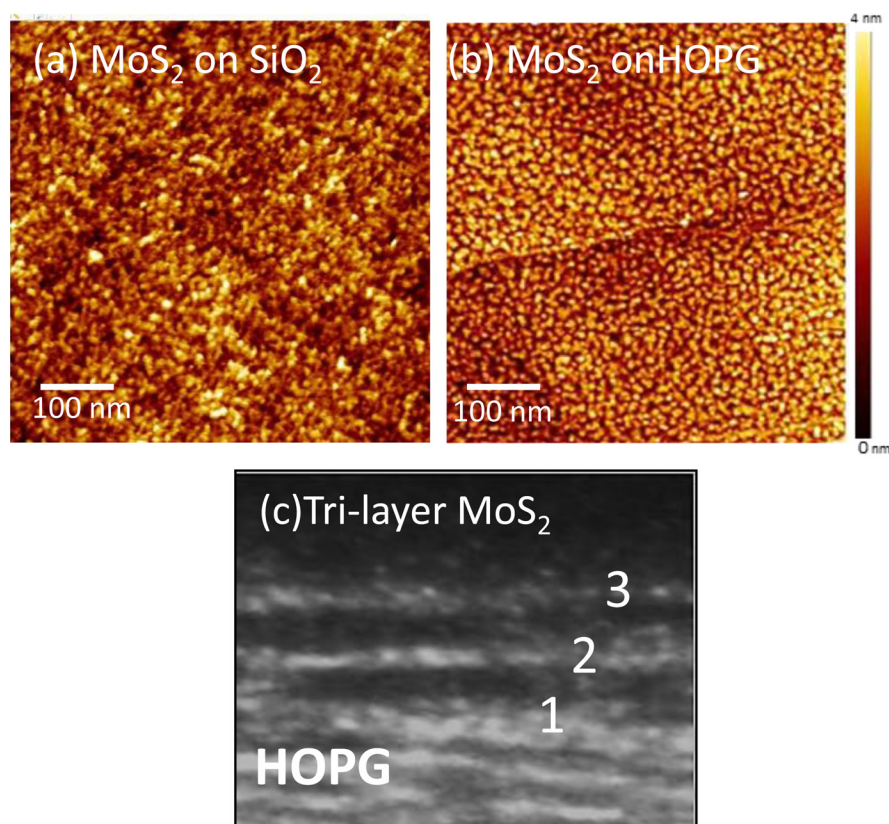


FIG. 4. AFM scans of 3 layer MoS₂ on (a) SiO₂ substrate and (b) HOPG substrate. A TEM cross-section of tri-layer MoS₂ on HOPG is shown in (c).

Film-substrate interface chemistry was examined with X-ray photoelectron spectroscopy (XPS) on these ultra-thin films, and the results support the proposed growth mechanisms for both substrates. It is presumed that Mo atoms, rather than sulfur comprise the first interfacial atomic layer, and hence, the evidence of this Mo-O interaction on the SiO₂ surface can be expected in the XPS analysis, since the MoS₂ overlayer is thin enough to allow escape of photoelectrons originating from the buried interfacial layer. Figure 5(a) shows that the total oxygen signal decreases with the increasing of MoS₂ thickness from 3 to 6 molecular layers. This is expected, as the probability of electrons escaping from the SiO₂ substrate decreases exponentially with increasing MoS₂ thickness. Evidence of the formation of Mo-O bonding at the SiO₂-MoS₂ interface comes from the examination of the high resolution scans of Mo 3d peaks from the three- and six-layer films (Fig. 5(b)). Curve fitting of the high-resolution XPS data reveals that the Mo 3d_{3/2} peak from MoO₃ (235.7 eV) decreases in intensity relative to the Mo 3d_{5/2} peak from MoS₂ (229.0 eV) as the overlayer thickness increases from three to six layers. This peak at 235.7 eV is indicative of MoO₃ formation rather than substitutional oxygen incorporated into the film during synthesis.²⁵ This suggests that the Mo-O bonds originate from the interface region (rather than from within MoS₂), indicating that the initial adlayer consists of Mo atoms bound to the O atoms of the substrate, while further deposition results in a MoS₂ film with a lower oxygen content. Moreover, the S 2s peak (226.4 eV) increases in intensity relative to the Mo 3d_{3/2} peak from MoO₃ as the film thickness increases, further supporting the model of a Mo-O interfacial layer buried by an MoS₂ overlayer.

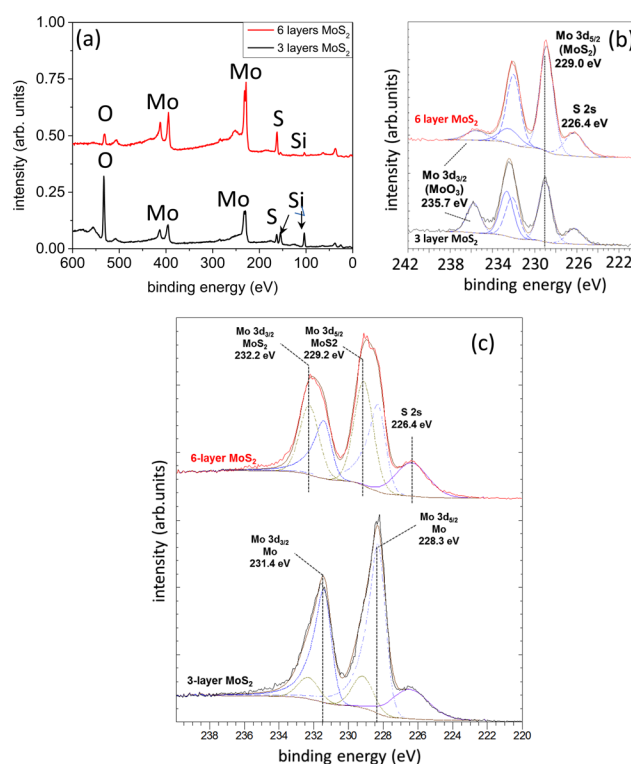


FIG. 5. X-ray photoelectron spectroscopy data for MoS₂ samples on SiO₂. The survey scans for 3 and 6 layer thick MoS₂ films (a) reveal higher silicon and oxygen peaks from the substrate due to the increased electron transparency of the thinner sample. A high resolution scan of the Mo (3d) peaks (b) reveal a diminished MoO₃ signal as the interface is buried deeper under the film and the electron transparency is reduced. For MoS₂ films grown on HOPG (c), the MoO₃ peak is absent and the Mo 3d_{5/2} peaks show strong metallic character for 3 layer films, with a much stronger Mo-S contribution for thicker films.

For film thicknesses beyond the interfacial Mo layer, XPS data provide critical validation of MoS₂ compound formation in Fig. 5(b). Here, X-ray photoelectron spectroscopy shows a single Mo 3d_{5/2} peak at to 229.0 eV (Mo IV), which is a clear indicator of covalent Mo-S bonding comprising the metal dichalcogenide, as a mixture with metallic Mo would give rise to two distinct peaks.²⁶ While analysis shows compound formation, the precise composition of the films was not directly quantified with XPS due to challenges associated with ambient contamination on molecularly thin films. It is anticipated that they may be slightly sulfur deficient, as most sputtered MoS₂ films are due to interactions with incident hydrogen or oxygen ions or atoms from ambient water that is present even within the vacuum environment employed in the current work.

Three and six layer MoS₂ films grown on HOPG were also examined with XPS (Fig. 5(c)), to demonstrate that there is no MoO₃ formation (at the interface or elsewhere) and that the nature of the Mo bonds changes from metallic Mo-Mo (distinctly characterized by an asymmetric peak at 228 eV) to Mo-S as film thickness increases. The existence of the 1T MoS₂ phase rather than the 2H phase could also give rise to this peak at 228 eV; however, annealing of the samples to 200 °C did not remove this component. High resolution sulfur peaks were also analyzed, and did not show the 1T characteristics.³ As for the MoS₂ films grown on SiO₂, the presence of metallic Mo decreased with increasing thickness, suggesting the presence of an interfacial Mo layer at the HOPG/MoS₂ film interface.

In summary, a scalable approach for uniform growth of continuous 2D TMD films on substrates >4 cm² was demonstrated. The PVD process allows a growth of MoS₂ at lower temperatures (350 °C in this work) directly on thermally grown silicon oxide and (002) graphite. The growth process is based on sputtering and is easily applicable to other transition metal dichalcogenides. The materials demonstrate the properties of exfoliated materials. Experiments with the PVD growth on diverse substrates including sapphire, borosilicate glass, and polycrystalline metals are ongoing with similar results, which will be discussed in future work. Low temperature PVD synthesis of 2D TMD materials provides a desirable combination of uniformity and scalability.

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