

Atomic layer deposition of two dimensional MoS₂ on 150 mm substrates

Arturo Valdivia

School of EECS, Oregon State University, Corvallis, Oregon 97331

Douglas J. Tweet

Sharp Labs of America, Camas, Washington 98607

John F. Conley, Jr.^{a)}

School of EECS, Oregon State University, Corvallis, Oregon 97331

(Received 17 November 2015; accepted 21 January 2016; published 5 February 2016)

Low temperature atomic layer deposition (ALD) of monolayer to few layer MoS₂ uniformly across 150 mm diameter SiO₂/Si and quartz substrates is demonstrated. Purge separated cycles of MoCl₅ and H₂S precursors are used at reactor temperatures of up to 475 °C. Raman scattering studies show clearly the in-plane (E_{12g}) and out-of-plane (A_{1g}) modes of MoS₂. The separation of the E_{12g} and A_{1g} peaks is a function of the number of ALD cycles, shifting closer together with fewer layers. X-ray photoelectron spectroscopy indicates that stoichiometry is improved by postdeposition annealing in a sulfur ambient. High resolution transmission electron microscopy confirms the atomic spacing of monolayer MoS₂ thin films. © 2016 American Vacuum Society.

[<http://dx.doi.org/10.1116/1.4941245>]

I. INTRODUCTION

The lack of a bandgap in graphene has led to the exploration of other 2D materials, in particular, transition metal dichalcogenides (TMDs). Like graphene, TMDs exist in a bulk state consisting of stacked planes held together through weak van der Waals forces. Each plane consists of a transition metal (M) from groups 4–10 and a group 16 chalcogen (X) to form a stoichiometric ratio of MX₂. Two dimensional TMDs that exhibit properties distinct from their bulk forms have recently come under intense investigation as building blocks for van der Waals heterostructure electronics.^{1–5} One of the most promising TMDs is molybdenum disulfide (MoS₂).^{6,7} The indirect bandgap (~1.2 eV) inherent to bulk MoS₂ transitions to a direct bandgap (~1.8 eV) in its monolayer state. The sizable direct bandgap makes MoS₂ a leading candidate material for low power digital electronics,^{1,8} photonics,^{1,9} sensing,¹⁰ and catalysis applications.^{11–13}

These potential applications require the preparation of high quality monolayer MoS₂ over large areas.^{14,15} As with initial work on graphene, mechanically exfoliated MoS₂ has formed the base of much research into electronics applications.^{5,8,10} However, the lack of scalability renders mechanical exfoliation impractical for manufacturing. Chemical vapor deposition (CVD) has been shown to yield MoS₂ on various substrates,^{3,6} but exhibits drawbacks such as a lack of uniform electrical properties, poor process stability, and the high temperatures required (typically above 650 °C).^{14–17}

A natural technique for the synthesis of 2D materials is atomic layer deposition (ALD). In ALD, film growth occurs via sequential, purge separated, self-limiting reactions of the precursors on the surface of the substrate. Sequential self-limiting surface reactions allow for precise thickness control, high conformality, and scalability to large surface areas, making ALD an ideal candidate for growing few layer

TMDs.¹⁸ Recently, ALD of monolayer MoS₂ thin films was reported for the first time using molybdenum (V) chloride (MoCl₅) and hydrogen disulfide (H₂S) precursors.¹⁹ A shortcoming of this work was that single crystal ⟨0001⟩ orientation sapphire substrates (rather than Si) were required and depositions were limited to 2-in. diameter wafers. ALD of thick many layer MoS₂ films on SiO₂ and Si substrates was recently reported using molybdenum hexacarbonyl [Mo(CO)₆] and dimethyldisulfide [CH₃-S-S-CH₃] and Mo(CO)₆ and H₂S; however, monolayer growth was not achieved in either of these studies.^{20,21}

In this work, we demonstrate that low temperature ALD can be used to deposit monolayer to few layer MoS₂ uniformly across 150 mm diameter SiO₂/Si and quartz substrates. MoS₂ material quality is assessed using Raman spectroscopy, photoluminescence, x-ray photoelectron spectroscopy, and transmission electron microscopy. The impact of postdeposition sulfur anneals on MoS₂ material quality is investigated.

II. EXPERIMENT

ALD was conducted using a table top Arradance Gemstar ALD system that was specially modified to handle H₂S gas.²² Substrate heating was performed using a platen holder to temperatures up to 475 °C at a base pressure of 3 × 10^{−3} Torr. MoCl₅ and H₂S precursors were alternately pulsed into the chamber using 20 sccm of N₂ as a carrier gas. The solid precursor MoCl₅ was heated to a temperature of 70 °C. The ALD pulse sequence included an additional “soak” step after each precursor pulse to ensure adequate time for reaction between the reactant (MoCl₅ or H₂S) and the respective surface species.²³ In all depositions, the MoCl₅ was pulsed first. The pulsing sequence used consisted of: 500 ms pulse MoCl₅/5 s soak/10 s N₂ purge/40 ms pulse H₂S/5 s soak/10 s N₂ purge. ALD MoS₂ thin films were deposited on 150 mm diameter (1) n-type Si wafers with

^{a)}Electronic mail: jconley@eeecs.oregonstate.edu

280 nm of thermally grown SiO₂ and (2) quartz wafers. Prior to ALD, the SiO₂/Si substrates were patterned with photoresist, and the oxide was etched via reactive ion etching to a depth of 40 nm, as shown in Fig. 1. After the etch process, the photoresist was ashed and the surface of the wafers was cleaned with piranha solution (sulfuric acid and hydrogen peroxide) followed by a 20–30 s short dip in dilute hydrofluoric acid. The SiO₂ mesas were created to promote the nucleation of MoS₂.¹⁶ Following deposition, some as-deposited films were annealed in a sulfur environment by either (1) flowing 50 sccm H₂S or (2) flowing Ar carrier gas over elemental sulfur heated to roughly 120–130 °C. All anneals were performed in a tube furnace for 30 min between 600 and 900 °C.

Raman analysis and photoluminescence (PL) was conducted using a WiTec Confocal Raman Microscope Alpha300 RA system with a 532 nm excitation laser. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALAB 250. Transmission electron microscopy (TEM) was performed on a FEI TITAN 80–200 TEM/SEM with ChemiSTEM technology.

III. RESULTS AND DISCUSSION

Shown in Fig. 2 are photographs of two 150 mm quartz wafers placed on a chemwipe (a) pre- and (b) post-ALD. Following 50 ALD cycles of MoCl₅ and H₂S at 475 °C, the quartz wafer in Fig. 2(b) changes to a dark yellow (color online) shade that is visually uniform across the full wafer.

Shown in Fig. 3(a) are Raman spectra comparing the etched and unetched regions of a patterned SiO₂/Si wafer following 50 cycles of ALD at 375 °C. The characteristic in-plane (E_{2g}^1) and out-of-plane (A_{1g}) vibrational modes of MoS₂ appear in both Raman spectra near 382 and 404 cm⁻¹, respectively, indicating an ordered S-Mo-S atomic arrangement.^{24,25} The dashed lines at 383 and 408 cm⁻¹ indicate the position of these two peaks measured in a bulk MoS₂ sample. The E_{2g}^1 and A_{1g} peaks in the unetched region are more distinct and of a higher intensity compared to those observed in the etched region, indicating preferential growth of MoS₂ in the unetched region. Deposition of MoS₂ was also attempted on a blanket SiO₂/Si wafer with no patterning. Raman analysis of the blanket SiO₂/Si substrate showed the absence of both the E_{2g}^1 and A_{1g} peaks, suggesting that the enhanced growth on unetched regions of SiO₂ may be due to residual photoresist acting as additional nucleation sites.¹⁶

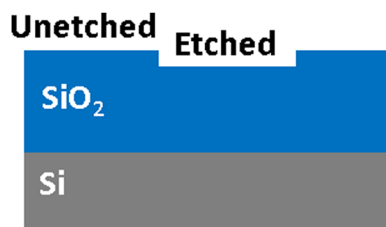


FIG. 1. (Color online) Schematic cross section of patterned SiO₂/Si substrate.

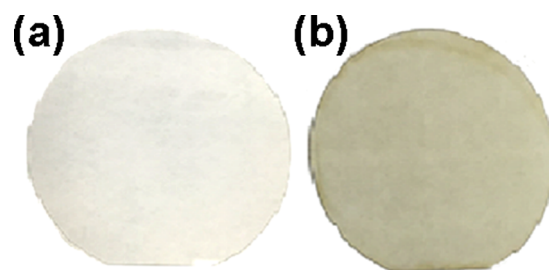


FIG. 2. (Color online) Photographs of 150 mm quartz wafers: (a) uncoated and (b) after 50 cycles of ALD MoS₂ at 475 °C.

Shown in Fig. 3(b) are plots of Raman intensity versus wave number for 50 cycle ALD MoS₂ as-deposited at either 375 or 475 °C on the unetched region of a patterned SiO₂/Si wafer. The E_{2g}^1 and A_{1g} peaks are significantly sharper and of higher intensity at the 475 °C deposition temperature, indicating higher quality growth.

The properties of the as-deposited ALD MoS₂ films are improved by annealing in a sulfur ambient. Shown in Fig. 4(a) are plots of Raman intensity versus wave number for as-deposited and sulfur annealed MoS₂ films from the unetched region of a patterned SiO₂/Si wafer. All data were normalized to the Si peak at 520 cm⁻¹ (not shown). For

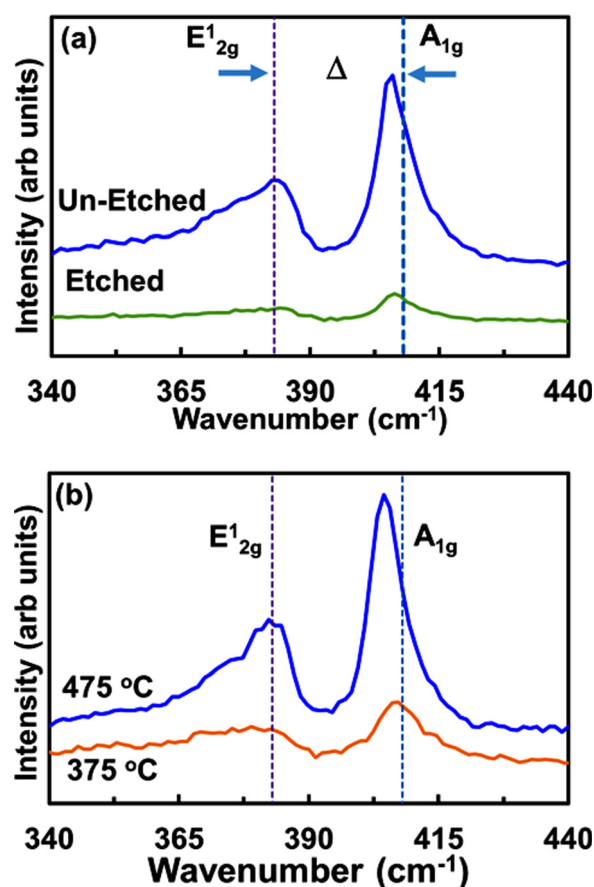


FIG. 3. (Color online) (a) Raman spectra of 375 °C as-deposited ALD MoS₂ films on etched and unetched regions of a patterned SiO₂/Si wafer. (b) Raman spectra comparing ALD MoS₂ as-deposited at either 375 or 475 °C on the unetched region of a patterned SiO₂/Si wafer. The vertical dashed lines indicate the position of the E_{2g}^1 and A_{1g} peaks for bulk MoS₂.

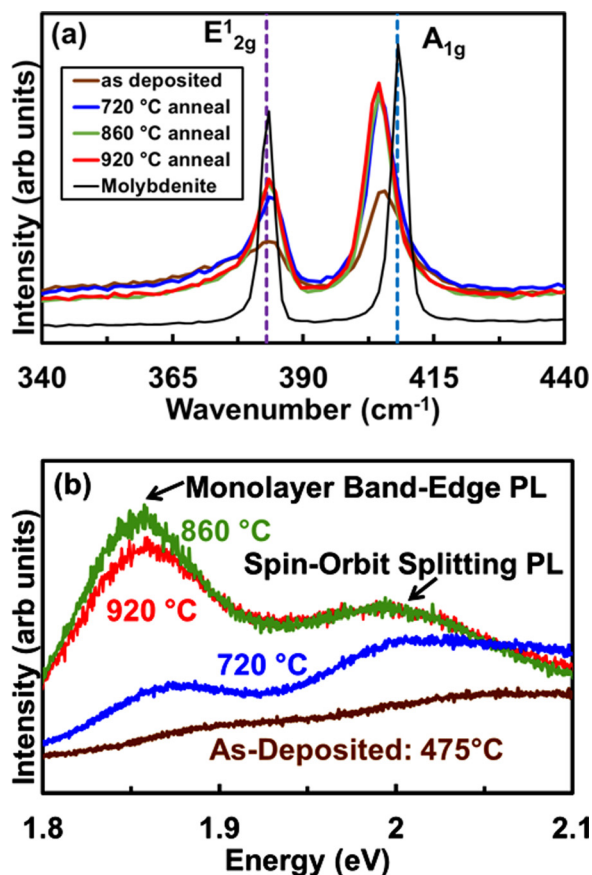


FIG. 4. (Color online) Raman spectra of 475 °C as-deposited and sulfur annealed ALD MoS₂ films showing (a) the region of the E_{12g} and A_{1g} peaks (a molybdenite spectrum is shown for reference) and (b) the region of the band-edge monolayer photoluminescence and spin-orbit splitting peaks.

reference, a Raman spectrum of bulk molybdenite is also shown. The full width half max (FWHM) of the E_{12g} and A_{1g} peaks are an indication of crystalline quality. After the sulfur anneal, the two characteristic MoS₂ peaks become narrower, stronger, and more symmetric. The FWHM of the E_{12g} peak for the as-deposited ALD films is 18.3 cm⁻¹. The FWHM is reduced to 11.8 cm⁻¹ after annealing in sulfur ambient at 720 °C and further reduced to 4.2 cm⁻¹, comparable to CVD MoS₂,¹⁵ after annealing at 920 °C. This suggests improved crystallinity with high temperature sulfur anneals. Even after the sulfur anneals, the FWHM of the E_{12g} peak is still broader than 3.7 cm⁻¹, the FWHM of MoS₂ monolayers mechanically exfoliated from bulk MoS₂.¹⁵

Plots of PL versus energy in Fig. 4(b) show that in addition to the sharpening of the E_{12g} and A_{1g} peaks, the sulfur anneals result in the appearance of a strong PL peak at 1.86 eV, consistent with band edge emission from the direct bandgap of monolayer MoS₂.^{11,26} The broad peak near 2.0 eV has been attributed to spin-orbit splitting from the band edge and is also associated with monolayer semiconducting MoS₂.^{27,28} The PL peak is below the detection limit in the as-deposited films, begins to appear at 720 °C, strengthens at 860 °C, and decreases somewhat at 920 °C. Similar results are seen for H₂S anneals.

XPS spectra for as-deposited 475 °C ALD MoS₂ films, along with films annealed in H₂S at 600, 860, and 900 °C are

shown in Fig. 5. The Mo3d_{5/2} peaks and the S2p_{3/2} peaks are resolved in Figs. 5(a) and 5(b), respectively, and correlate well to what has been previously reported in literature for MoS₂.⁶ The ratio of the S2p_{3/2} and Mo3d_{5/2} peaks may be used to determine the stoichiometric ratio of the as-deposited and annealed films. The as-deposited films showed a S/Mo ratio of 1.4, indicating sulfur deficiency. This is consistent with the presence of the 236 eV peak in these films, which has been attributed to the Mo⁶⁺ state.²⁸ After H₂S annealing at 600 °C and above, the S/Mo ratio increased to the desired value of 2.0 and the 236 eV peak almost completely disappears, indicating that the H₂S anneal is effective in improving stoichiometry as well as reducing defects.

Assessing the thickness of a 2D film is challenging. It has been shown that the number of MoS₂ layers present in a thin film may be determined by the frequency and separation (Δ) between the E_{12g} and A_{1g} peaks.^{24,25} It was reported that Δ increases with the number of S-Mo-S layers, with a monolayer having $\Delta \sim 19$ cm⁻¹ and bulk like (>5 layers) MoS₂ having $\Delta \sim 25$ cm⁻¹.^{24,25} Shown in Fig. 6 is a plot of average Δ versus the number of ALD cycles for as-deposited 375 °C films. Qualitatively, Δ increases with the number of ALD cycles. Also shown are 50 cycle 475 °C films both as-deposited and annealed at 920 °C. The Δ 's for the 25 and 50 cycle 375 °C as well as for the 50 cycle 475 °C as-deposited films are in the range of 22–23 cm⁻¹, correlating roughly to bilayer growth in the previous reports.^{24,25} It should be noted

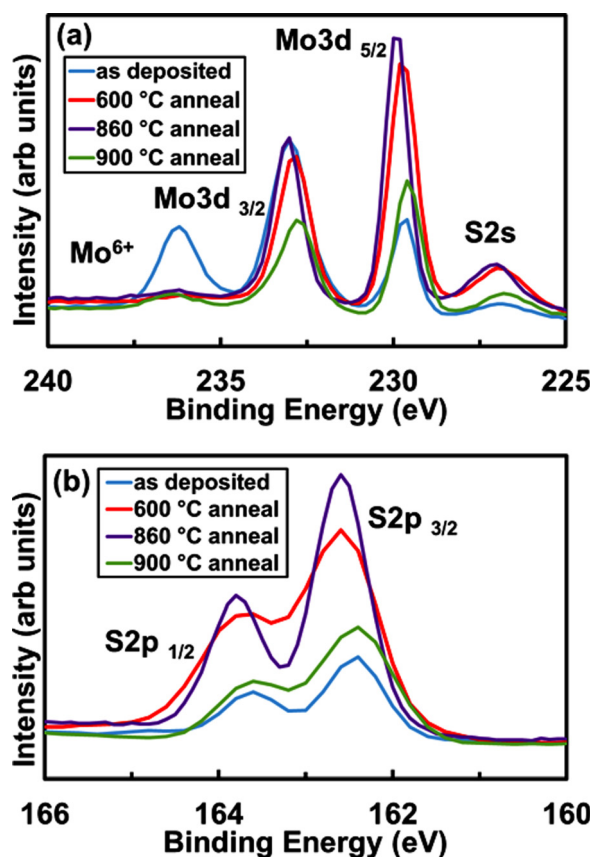


FIG. 5. (Color online) XPS spectra of (a) Mo3d_{3/2} and (b) S2p_{1/2} peaks for ALD MoS₂ films as-deposited at 475 °C and H₂S annealed at either 600, 860, or 900 °C.

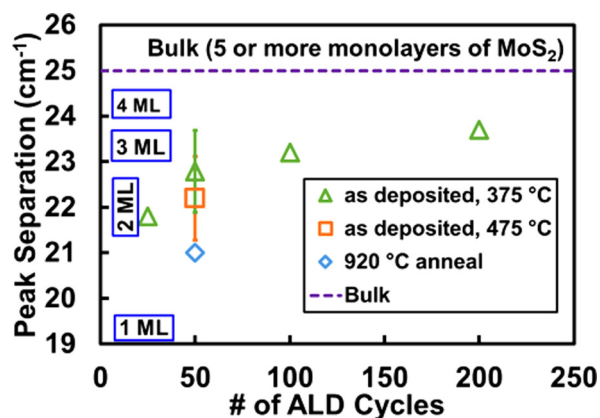


FIG. 6. (Color online) E_{2g}^1 - A_{1g} average peak separation (Δ) versus number of ALD cycles for 375 °C ALD MoS₂ films as-deposited on the unetched regions. Also shown are 475 °C films, as-deposited and annealed in sulfur at 920 °C.

however, that the position of the A_{1g} peak may be sensitive to defects and substoichiometry. As indicated by the XPS results in Fig. 5, the as-deposited films are substoichiometric. Thus, the correlation here between Δ and the number of monolayers for the as-deposited films should be considered tentative. The Δ after annealing at 920 °C in sulfur decreases to about 21 cm⁻¹, suggestive of a mix of 1 and 2 monolayers.^{24,25} This reduced Δ could be due either to an actual reduction of film thickness or improvement of stoichiometry (XPS results in Fig. 5 indicate that stoichiometry is improved by annealing). In either case, the accompanying appearance of clearly visible PL and spin orbit splitting peaks in Fig. 4(b) strongly suggests a mix of 1 and 2 monolayer regions.

Cross-sectional TEM images are shown in Fig. 7 for 50 cycle 375 °C ALD MoS₂ on the unetched region of the patterned SiO₂/Si substrate. The high resolution TEM in Fig. 7(b) verifies the existence of 1–2 monolayers of MoS₂. The intensity profile in Fig. 7(c) indicates the atomic lattice spacing to be approximately 0.29 nm for the (100) planes, consistent with the 0.31 nm atomic spacing of exfoliated hexagonal MoS₂.²⁹

Finally, to confirm that the MoS₂ crystals are lying flat with their basal planes parallel to the substrate surface, rather than at a random or some other orientation, a polarization test was performed with the Raman instrument. The E_{2g}^1 peak is due to vibrational modes in the basal plane, while A_{1g} peak is due to perpendicular modes.²⁴ By polarizing the incident laser beam and rotating the analyzer polarization, the A_{1g} peak should be eliminated if the MoS₂ crystals are indeed lying flat on the substrate. Figure 8 shows Raman measurements taken with the analyzer in two positions 90° apart on a 50 ALD cycle sample deposited at 475 °C and annealed at 860 °C in sulfur. The A_{1g} peak is almost entirely suppressed while the E_{2g}^1 peak is unaffected, confirming that the MoS₂ crystals have the desired orientation parallel to the surface.

IV. SUMMARY AND CONCLUSIONS

In summary, ALD of monolayer to a few layered MoS₂ thin films was achieved uniformly across 150 mm quartz and patterned SiO₂/Si wafers using alternating pulses of MoCl₅

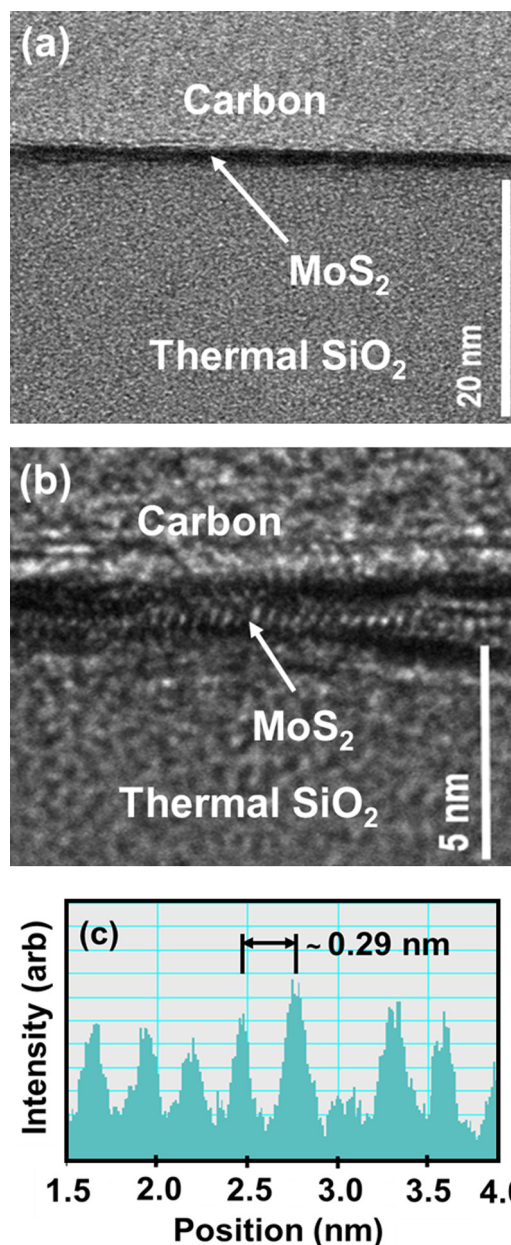


FIG. 7. (Color online) (a) TEM cross section of 50 cycle 375 °C ALD MoS₂ film as-deposited on unetched SiO₂/Si, (b) high resolution TEM image, and (c) intensity profile showing the atomic spacing.

and H₂S. MoS₂ deposition was favored in unetched SiO₂ regions of patterned SiO₂/Si wafers. The as-deposited films show the characteristic Raman modes (E_{2g}^1 and A_{1g}) and E_{2g}^1 - A_{1g} separation associated with monolayer to few layer MoS₂. Raman polarization tests confirm the MoS₂ crystals have the desired orientation parallel to the surface. High temperature H₂S and sulfur annealed films produce a sharpening of the E_{2g}^1 and A_{1g} peaks as well as the appearance of the band edge PL and spin orbit splitting peaks, further indication of the presence of monolayer MoS₂. Hi-resolution TEM images confirm the presence of monolayer to bilayer MoS₂ films. XPS measurements indicate that a substoichiometric sulfur ratio in the as-deposited films is increased to the stoichiometric S/Mo ratio after annealing in H₂S at

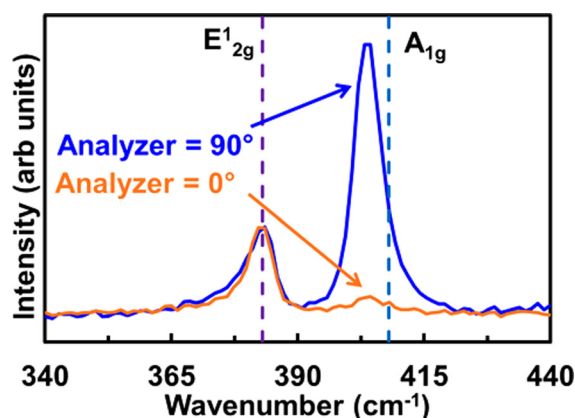


FIG. 8. (Color online) Raman spectra taken with the analyzer polarizer rotated at 90° and at 0°. Both in-surface (E_{2g}¹) and normal-to-surface (A_{1g}) oscillations come through at 90° but at 0° the Raman light scattered from modes normal-to-surface (A_{1g}) are blocked, suggesting the MoS₂ crystals have their c-axis normal to surface.

600 °C and above. Overall ALD is shown to be a promising method for uniform deposition of monolayer MoS₂ over large surface areas. The small crystallite sizes obtained may be suitable for application to hydrogen evolution catalysis.⁴

ACKNOWLEDGMENTS

This work was supported by Sharp Labs of America (SLA) with matching funds from the Oregon Nanoscience and Microtechnologies Institute (ONAMI) and Oregon BEST. XPS was conducted by Fallon Fumasi at the Center for Advanced Materials Characterization in Oregon (CAMCOR) at the University of Oregon. TEM was conducted with the assistance of Pete Eschbach at the OSU Electron Microscopy Facility which is supported by the National Science Foundation via the Major Research Instrumentation (MRI) Program under Grant No. 1040588.

¹Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* **7**, 699 (2012).

²A. K. Geim and I. V. Grigorieva, *Nature* **499**, 419 (2013).

- ³M. Chhowalla, H. S. Shin, G. Eda, L. Li, K. P. Loh, and H. Zhang, *Nat. Chem.* **5**, 263 (2013).
- ⁴A. Y. S. Eng, A. Ambrosi, Z. Sofer, P. Simek, and M. Pumera, *ACS Nano* **8**, 12185 (2014).
- ⁵Y. Lin *et al.*, *ACS Nano* **8**, 3715 (2014).
- ⁶X. Huang, Z. Zeng, and H. Zhang, *Chem. Soc. Rev.* **42**, 1934 (2013).
- ⁷W. Zhu, T. Low, Y. Lee, H. Wang, D. B. Farmer, J. Kong, F. Xia, and P. Avouris, *Nat. Commun.* **5**, 3087 (2014).
- ⁸B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nat. Nanotechnol.* **6**, 147 (2011).
- ⁹M. Tsai, S. Su, J. Chang, D. Tsai, C. Chen, C. Wu, L. Li, L. Chen, and J. He, *ACS Nano* **8**, 8317 (2014).
- ¹⁰H. Li *et al.*, *Small* **8**, 63 (2012).
- ¹¹G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, *Nano Lett.* **11**, 5111 (2011).
- ¹²Y. Li, H. Wang, W. L. Xie, Y. Liang, G. Hong, and H. Dai, *J. Am. Chem. Soc.* **133**, 7296 (2011).
- ¹³S. Shin, Z. Jin, D. H. Kwon, R. Bose, and Y. Min, *Langmuir* **31**, 1196 (2015).
- ¹⁴K. Kang, S. Xie, L. Huang, Y. Han, P. Y. Huang, K. F. Mak, C. Kim, D. Muller, and J. Park, *Nature* **520**, 656 (2015).
- ¹⁵Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, and L. Cao, *Sci. Rep.* **3**, 1866 (2013).
- ¹⁶S. Najmaei *et al.*, *Nat. Mater.* **12**, 754 (2013).
- ¹⁷X. Ling, Y. Lee, Y. Lin, W. Fang, L. Yu, M. S. Dresselhaus, and J. Kong, *Nano Lett.* **14**, 464 (2014).
- ¹⁸V. Miikkulainen, M. Leskela, M. Ritala, and R. L. Puurunen, *J. Appl. Phys.* **113**, 021301 (2013).
- ¹⁹L. K. Tan, B. Liu, J. H. Teng, S. Guo, H. Y. Low, and K. P. Loh, *Nanoscale* **6**, 10584 (2014).
- ²⁰Z. Jin, S. Shin, D. H. Kwon, S. Han, and Y. Min, *Nanoscale* **6**, 14453 (2014).
- ²¹D. K. Nandi, U. K. Sen, D. Choudhury, S. Mitra, and S. K. Sarkar, *Electrochim. Acta* **146**, 706 (2014).
- ²²N. P. Dasgupta, J. F. Mack, M. C. Langston, A. Boussetta, and F. B. Prinz, *Rev. Sci. Instrum.* **81**, 044102 (2010).
- ²³S. W. Smith, C. Beusch, D. J. Matthews, J. Simonsen, and J. F. Conley, Jr., *J. Vac. Sci. Technol., A* **32**, 041508 (2014).
- ²⁴C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, *ACS Nano* **4**, 2695 (2010).
- ²⁵H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, *Adv. Funct. Mater.* **22**, 1385 (2012).
- ²⁶K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).
- ²⁷A. Splendiani, L. Sun, Y. B. Zhang, T. S. Li, J. Kim, C. Y. Chim, G. Galli, and F. Wang, *Nano Lett.* **10**, 1271 (2010).
- ²⁸N. Kang, H. P. Paudel, M. N. Leuenberger, L. Tetard, and S. I. Khondaker, *J. Phys. Chem. C* **118**(36), 21258 (2014).
- ²⁹H. E. Swanson, N. T. Gilfrich, and G. M. Ugrinic, "Standard x-ray diffraction powder patterns," in NBS Circular No. 539 (1955), Vol. 5, available at <http://babel.hathitrust.org/cgi/pt?id=mdp.39015011413997;view=1up;seq=51>.

Atomic layer deposition of two dimensional MoS₂ on 150 mm substrates

Arturo Valdivia, Douglas J. Tweet, and John F. Conley Jr.

Citation: *Journal of Vacuum Science & Technology A* **34**, 021515 (2016); doi: 10.1116/1.4941245

View online: <http://dx.doi.org/10.1116/1.4941245>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/34/2?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

Excitation intensity dependent photoluminescence of annealed two-dimensional MoS₂ grown by chemical vapor deposition

J. Appl. Phys. **119**, 214301 (2016); 10.1063/1.4948662

Photoreflectance study of the near-band-edge transitions of chemical vapor deposition-grown mono- and few-layer MoS₂ films

J. Appl. Phys. **119**, 115703 (2016); 10.1063/1.4944437

Facile synthesis of MoS₂ and Mo_xW_{1-x}S₂ triangular monolayers

APL Mater. **2**, 092514 (2014); 10.1063/1.4895469

Scalable synthesis of layer-controlled WS₂ and MoS₂ sheets by sulfurization of thin metal films

Appl. Phys. Lett. **105**, 083112 (2014); 10.1063/1.4893978

Electrical performance of monolayer MoS₂ field-effect transistors prepared by chemical vapor deposition

Appl. Phys. Lett. **102**, 193107 (2013); 10.1063/1.4804546

