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 (E1g) and out-of-plane (A1g) modes of MoS2. The separation of the E1g and A1g 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]
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 (E12g) and out-of-plane (A1g) 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 E12g and A1g 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 E12g and A1g 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.](image1)

![Fig. 2. (Color online) Photographs of 150 mm quartz wafers: (a) uncoated and (b) after 50 cycles of ALD MoS2 at 475 °C.](image2)

![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.](image3)
reference, a Raman spectrum of bulk molybdenite is also shown. The full width half max (FWHM) of the E1$_{2g}$ and A$_{1g}$ peaks are an indication of crystalline quality. After the sulfur anneal, the two characteristic MoS$_2$ 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 MoS$_2$, 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 MoS$_2$ monolayers mechanically exfoliated from bulk MoS$_2$. 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 MoS$_2$. 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 MoS$_2$. 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 H$_2$S anneals.

XPS spectra for as-deposited 475°C ALD MoS$_2$ films, along with films annealed in H$_2$S 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 MoS$_2$. 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 Mo$^{6+}$ state. After H$_2$S 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 H$_2$S 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 MoS$_2$ layers present in a thin film may be determined by the frequency and separation ($\Delta$) between the E$_{12g}$ and A$_{1g}$ peaks. It was reported that $\Delta$ increases with the number of S-Mo-S layers, with a monolayer having $\Delta \sim 19$ cm$^{-1}$ and bulk like (>5 layers) MoS$_2$ having $\Delta \sim 25$ cm$^{-1}$. Shown in Fig. 6 is a plot of average $\Delta$ versus the number of ALD cycles for as-deposited 375°C films. Qualitatively, $\Delta$ increases with the number of ALD cycles. Also shown are 50 cycle 475°C films both as-deposited and annealed at 920°C. The $\Delta$’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. It should be noted...
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 $\Delta$ and the number of monolayers for the as-deposited films should be considered tentative. The $\Delta$ 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 $\Delta$ 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 MoS$_2$ on the unetched region of the patterned SiO$_2$/Si substrate. The high resolution TEM in Fig. 7(b) verifies the existence of 1–2 monolayers of MoS$_2$. 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 MoS$_2$.29

Finally, to confirm that the MoS$_2$ crystals are lying flat with their basal planes parallel to the substrate surface, rather than at random or some other orientation, a polarization test was performed with the Raman instrument. The $E_{1g}$ 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 MoS$_2$ 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 $E_{1g}$ peak is unaffected, confirming that the MoS$_2$ crystals have the desired orientation parallel to the surface.

**IV. SUMMARY AND CONCLUSIONS**

In summary, ALD of monolayer to a few layered MoS$_2$ thin films was achieved uniformly across 150 mm quartz and patterned SiO$_2$/Si wafers using alternating pulses of MoCl$_5$ and H$_2$S. MoS$_2$ deposition was favored in unetched SiO$_2$ regions of patterned SiO$_2$/Si wafers. The as-deposited films show the characteristic Raman modes ($E_{1g}$ and $A_{1g}$) and $E_{1g}$-$A_{1g}$ separation associated with monolayer to few layer MoS$_2$. Raman polarization tests confirm the MoS$_2$ crystals have the desired orientation parallel to the surface. High temperature H$_2$S and sulfur annealed films produce a sharpening of the $E_{1g}$ 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 MoS$_2$. Hi-resolution TEM images confirm the presence of monolayer to bilayer MoS$_2$ 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 H$_2$S at
Overall ALD is shown to be a promising method for uniform deposition of monolayer MoS$_2$ 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.

7H. Li et al., Small 8, 63 (2012).