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Atomic Layer Deposition of a High-*k* Dielectric on MoS_2 Using Trimethylaluminum and Ozone

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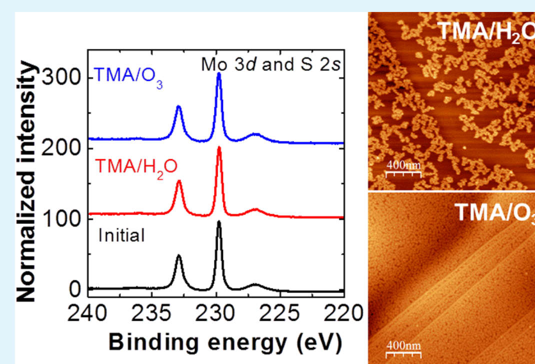
Supporting Information

ABSTRACT: We present an Al_2O_3 dielectric layer on molybdenum disulfide (MoS_2), deposited using atomic layer deposition (ALD) with ozone/trimethylaluminum (TMA) and water/TMA as precursors. The results of atomic force microscopy and low-energy ion scattering spectroscopy show that using TMA and ozone as precursors leads to the formation of uniform Al_2O_3 layers, in contrast to the incomplete coverage we observe when using TMA/H_2O as precursors. Our Raman and X-ray photoelectron spectroscopy measurements indicate minimal variations in the MoS_2 structure after ozone treatment at 200 °C, suggesting its excellent chemical resistance to ozone.



KEYWORDS: *atomic layer deposition, high-k dielectric, ozone, MoS_2*

Molybdenum disulfide (MoS_2) is a promising 2D semiconductor, with a layered structure similar to graphene and an intrinsic band gap,[1] that exhibits interesting electronic properties such as high field mobility (up to ~500 $cm^2\ V^{-1}\ s^{-1}$), low subthreshold swing (~70 mV/dec), and high current on/off ratio (~1×10^8).[2−4] To fabricate high-performance devices based on MoS_2, high-*k* dielectrics such as HfO_2[3,5] or Al_2O_3[2,4,6] with thicknesses of 10−30 nm have been used as top-gate insulators because they improve the field-effect electron mobility of the channel by reducing Coulombic scattering.[7] In these studies, the dielectric layers were deposited by atomic layer deposition (ALD) because of its unparalleled conformality and uniformity as well as its ability to control film thickness on the atomic level. However, it is difficult to deposit high-quality high-*k* dielectrics onto the surfaces of 2D semiconductors such as graphene[8] and MoS_2[9,10] because of the chemical inertness of their basal planes. Recently, Liu et al. reported that depositing uniform Al_2O_3 (~10 nm thickness) on MoS_2 could only be achieved at substrate temperatures below 200 °C via a physical adsorption mechanism.[2,9] However, physical adsorption of the precursors causes the film coverage to depend on growth parameters such as pulsing and purging times, process pressure, and cleanliness of the MoS_2 surface. For example, Yang et al.[11] could not produce uniform ALD-Al_2O_3 on MoS_2 after depositing the same number of cycles used by Liu et al. In addition, the use of low-temperature ALD raises concerns regarding high levels of impurities, such as OH and C residues,[12] in the dielectric film. To overcome these limitations and grow a uniform dielectric layer, Yang et al.[11] functionalized the MoS_2 surface with oxygen plasma prior to ALD at 250 °C. However, they observed significant interfacial oxidation, indicated by the emergence of the Mo^{6+} chemical state, and lattice disordering induced by physical plasma damage. Additionally, both Liu et al. and Yang et al. needed to deposit up to 10 nm of dielectric to produce uniform films, which is undesirable considering the constant downscaling to physical thicknesses less than 3 nm required by the microelectronics industry.

Recently, Azcatl et al.[13] reported the growth of uniform Al_2O_3 films on room temperature UV-ozone functionalized MoS_2 surface using TMA/H_2O-ALD at 200 °C due to the formation of weak S−O bonds, and suggested UV exposure is essential for this oxygen adsorption at low pressure because of the increased reactivity of radical O· generated by UV light. However, long time UV exposure could affect the optical and electrical properties of MoS_2.[14] Previous study shows that UV light exposure could induce photochemical reactivity degradation on graphene surfaces.[15] In addition, it is reported that room-temperature TMA/ozone treatment on graphene results in highly scalable high-*k* deposition with excellent conformality.[16]

In this letter, we carefully investigated how ozone-based ALD affected the MoS_2 interface. Our experimental results suggest that ozone-based ALD can be used to fabricate smooth,

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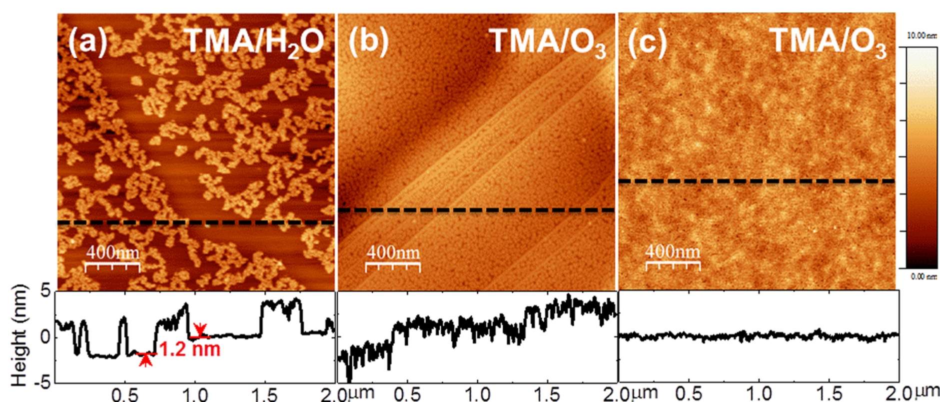

Figure 1. AFM images of the ALD-Al_2O_3 layer deposited using (a) TMA/H_2O at 200 °C (30 cycles), (b) TMA/O_3 (30 cycles) at 200 °C, and (c) TMA/O_3 (5 cycles of seeding layer at 30 °C, followed by 45 cycles of ALD at 200 °C).

uniform Al_2O_3 layers with thicknesses of 5 nm or less without noticeable oxidization of the MoS_2 interface. Ozone, compared with H_2O and oxygen plasma as oxidant precursors, has well-recognized advantages, such as higher reactivity,[17]relatively easy purging, and good compatibility with batch processes, in addition to producing lower defect-state density, lower leakage current, and fewer OH and related defect states[12,17]in the resulting ALD films. The present letter studies the reaction behavior of ozone with the MoS_2 surface and the feasibility of depositing high-*k* dielectrics using ozone-based ALD.

Figure 1a shows a representative AFM topographic image of an ALD-Al_2O_3 layer deposited on a MoS_2 flake with 30 cycles of TMA/H_2O at 200 °C. The thickness of the Al_2O_3 layer is ~3.0 nm with a vertical growth rate of ~1.0 Å/cycle, determined by the corresponding AFM line profile. In contrast to the uniform Al_2O_3 layer deposited at 200 °C by Liu et al.,[2] the Al_2O_3 layer reported in the present letter exhibits less than 40% coverage, revealed by the formation of dispersed Al_2O_3 clusters resembling the Al_2O_3-ALD film on a MoS_2 surface, as reported by Yang[11] and Azcatl[13] et al. When using TMA/H_2O, we observed more rapid Al_2O_3 growth along the step edge of the MoS_2 flake than on the terraces, indicated by the AFM line profile (~1.2 nm step height). This behavior was likely caused by the presence of dangling bonds at the edge, which commonly react more readily during initial ALD nucleation.[18] We obtained a uniform Al_2O_3 layer (RMS roughness of ~1.2 nm) by replacing water with ozone as the oxidizing agent, as shown in Figure 1b. An AFM line profile confirms the film thickness to be ~3.1 nm, grown at a rate of ~1.0 Å/cycle, which agrees well with a previously reported growth rate on highly oriented pyrolytic graphite (HOPG).[18] With the same precursor purge and pulse times as the TMA/H_2O-ALD process, using ozone enhances the Al_2O_3 film coverage and uniformity on both the MoS_2 step edges and basal planes, suggesting that the ozone facilitates initial TMA precursor nucleation on the MoS_2 by increasing the number of activation sites.[19] It is believed that the differing growth behavior at 200 °C when using TMA/O_3 is associated with the distinct interaction mechanisms of ozone with the MoS_2 surface. Different than water, ozone readily decomposes into molecular O_2 and monatomic O upon reaching the surface; the latter is considered to be the active species providing TMA nucleation sites through weak surface adsorption.[13,17,19] At higher temperatures, the complicated concomitance of O radical diffusion and desorption tends to govern the growth of the Al_2O_3 film, leading to higher surface roughness.[17,19]

In an attempt to deposit a uniform, thin Al_2O_3 layer on MoS_2, we deposited five cycles of TMA/O_3 at 30 °C as a seeding layer prior to sequential ALD at 200 °C. Figure 1c shows an AFM image of the conformal Al_2O_3 layer after 45 cycles of TMA/O_3 at 200 °C. The thickness of this oxide layer is ~5.1 nm, determined by using an ellipsometer (Sentech 800) against a reference measurement of an Al_2O_3 layer grown on H-terminated Si. In contrast to the film shown in Figure 1b, this Al_2O_3 film grown on the seeding layer has a fairly smooth surface (RMS roughness of ~0.23 nm vs RMS roughness of ~0.18 nm for clean MoS_2. Our results indicate that a thin (~5 nm or less) and uniform dielectric layer can be deposited by first depositing a thin seeding layer (~1 nm) before performing TMA/O_3-ALD at a higher temperature. Similar to ozone-based ALD on graphene,[20] it is suggested that using a seeding layer also prevents the formation of possible ozone-etch-related defects induced by high-temperature interactions between the ozone and surface.

LEIS microscopy is an extremely surface-sensitive technique capable of detecting chemical species in the topmost layer of deposited films.[21] In Figure 2, ex situ LEIS spectra of the

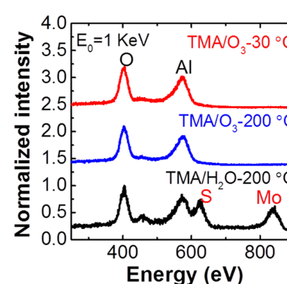

Figure 2. LEIS spectra of the topmost layers of ALD-Al_2O_3 films deposited using TMA/O_3 (30 cycles) at 30 and 200 °C as well as TMA/H_2O (50 cycles) at 200 °C.

surface elemental compositions show only O (404 eV) and Al (573 eV) peaks, originating from the Al_2O_3 layer, for the samples prepared using ALD with TMA/ozone precursors The absence of S (625 eV) and Mo (838 eV) signals, regardless of substrate temperature, from the underlying MoS_2 substrate indicates that 30 cycles of ALD produced full-coverage films. In contrast, we detected four peaks assigned to O, Al, S, and Mo on the surface after 50 cycles of TMA/H_2O-ALD, clear evidence of incomplete film coverage. Because the Mo scattering cross-section is four times larger than that of S

atoms,[21] the peak ratio of S and Mo atoms suggests that more S than Mo is present in the first layer, in agreement with the stoichiometry of MoS_2. These LEIS results, which complement our AFM images, suggest that ozone-based ALD more effectively deposits uniform dielectric layers on MoS_2.

Figure 3a, b show the ex situ Raman spectra of a monolayer-thick MoS_2 flake exposed to ozone at 30 or 200 °C for 10 s; we

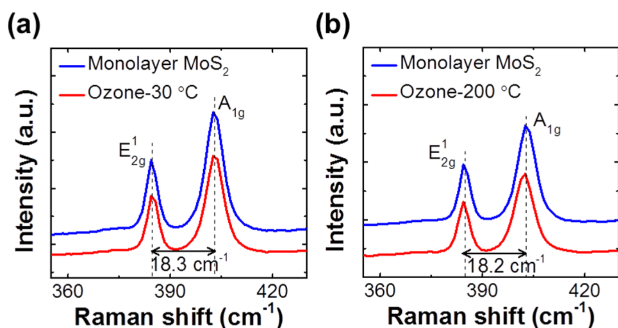

Figure 3. Raman spectra of as-exfoliated monolayer MoS_2 (top) after O_3 treatment (bottom) at (a) 30 °C for 10 s and (b) 200 °C for 10 s.

assessed the thickness of the flake by interpreting the ~18.2 cm^{-1} separation between the two peaks present. Raman spectroscopy has been widely used to study the 2D crystalline structure of MoS_2 because of its ability to detect its characteristic phonon modes.[21] The prominent peak observed at low Raman shifts of around ~384 cm^{-1} is attributed to S–Mo–S in-plane motion (E^1_{2g} mode), whereas the peak at ~402 cm^{-1} is assigned to out-of plane motion (A_{1g} mode).[22] These two Raman active modes have been reported to shift with changes in thickness,[23] strain,[24] temperature,[25] and doping;[26] therefore, they are considered a signature of the stoichiometric MoS_2 lattice structure. Figure 3a shows that exposing MoS_2 to ozone at 30 °C for 10 s (~380 g/Nm^3, P[O_3]= ~150 Torr) does not observably alter its Raman signals compared with its as-exfoliated peaks. At 200 °C for 10 s, the S–Mo–S out-of-plane A_{1g} mode at ~402 cm^{-1} shifts down by ~0.6 cm^{-1} and broadens by ~0.3 cm^{-1}. We recorded Raman spectra from up to five positions on each sample to ensure that this peak shift was not caused by measurement errors; additionally, our Renishaw Raman spectroscopy instrument can detect Raman frequency shifts as low as 0.1 cm^{-1}. This finding agrees with an in situ Raman study performed on top-gated single-layer MoS_2 transistors,[26] in which electron doping caused the A_{1g} mode to red-shift and broaden, but did not affect the E^1_{2g} peak. In the present letter, the absence of noticeable alterations to the MoS_2 Raman active modes and the lack of the MoO_3[27] Raman frequency at ~820 cm^{-1} suggests that exposing the MoS_2 to ozone did not significantly disorder its lattice. Reports have shown that MoS_2 is relatively stable in oxygen-rich environments at temperatures up to 370 °C[27] because of its high Mo–S dissociation binding energy (~368 kJ/mol).[28] Therefore, our Raman analysis of monolayer MoS_2 suggests that the improved coverage of the Al_2O_3 film when using TMA/O_3 as precursors can be traced to the relatively weak interaction between the oxygen species and MoS_2; the sulfur and oxygen interactions that do occur are not strong enough to alter the MoS_2 lattice at room temperature, but can supply additional activation sites for initial TMA nucleation. Although, in this case the formation of possible weak S–O bond could not be excluded during ozone exposure, which is beyond the detections of our ex situ Raman studies.

To consolidate the evidence of the chemical stability of MoS_2 against ozone etching, which can degrade device characteristics,[20] we used ex situ XPS to examine the binding energies of Mo 3d, S 2s, and S 2p core states for MoS_2 after 30 ALD cycles at 200 °C using TMA/O_3 or TMA/H_2O, and compared them with those of an as-exfoliated MoS_2 crystal. Shown in Figure 4a,

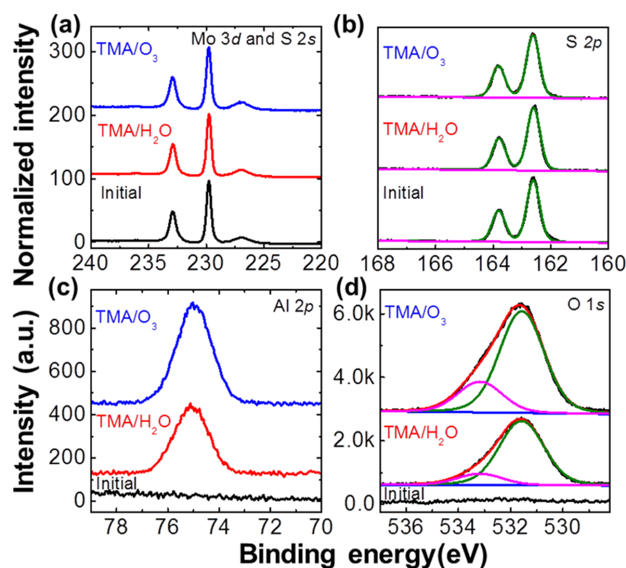

Figure 4. XPS spectra of MoS_2 samples after ALD at 200 °C with TMA/O_3 or TMA/H_2O precursors, deposited with reference to an initial MoS_2 crystal. (a) Mo 3d and S 2s, (b) S 2p, (c) Al 2p, and (d) O 1s core levels.

b, we assign the binding energies at ~232.96 and ~229.83 eV to the Mo $3d_{3/2}$ and Mo $2d_{5/2}$ chemical states, whereas we assign the peaks at ~227.05 and ~162.7 eV to the S 2s and S 2p core levels, which originate from the corresponding Mo(IV) and S(II) chemical states in the MoS_2 crystal.[11] For both samples, depositing Al_2O_3 on MoS_2 significantly decreases the intensities of the Mo and S peaks because of XPS signal attenuation; we also observed similar peak-intensity attenuation in the S 2p region at ~162.7 eV. The good overlap of the Mo 3d and S 2p peaks over those of as-exfoliated MoS_2 suggest no detectable Mo oxidation or S substitution with O in the S–Mo–S lattice; the detection limit of XPS system used in this work is about 1%; these XPS results support the fact that MoS_2 demonstrates better chemical stability against ozone treatment compared with that of graphene, in which ozone exposure at 200 °C leads to graphene surface damage arising from ozone etches,[19,20] but no apparent evidence of MoS_2 interface structure changes is seen in our Raman and XPS investigations. Compared to pretreating MoS_2 with oxygen plasma,[11] using ozone could be a less damaging way of depositing dielectric films.

Figure 4c, d shows the XPS binding energies of Al 2p and O 1s in the Al_2O_3 layers deposited by ALD at 200 °C with TMA/O_3 and TMA/H_2O precursors, respectively. For both samples, the Al 2p peaks are composed of a predominant chemical state centered at ~74.9 eV; we measured the binding energy difference between Al–O to be ~456.6 eV, which agrees well with the previously reported binding energies of Al 2p for O–Al–O in fully oxidized Al_2O_3 films.[29] The peak intensity of the

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Al 2p state in the TMA/O_3 film is ~50% greater than that of the TMA/H_2O film, consistent with the average film thicknesses of ~1.9 nm (TMA/O_3) and ~1.1 nm (TMA/H_2O) derived from attenuations of the Mo 3d core-level peak intensity. Note that the average film thicknesses calculated from XPS measurements are considered to be underestimated because of two reasons: Mo signal intensity could be enhanced after ozone exposure which is found to remove carbon residues (~50%) adsorbed from environment after MoS_2 exfoliation; the average film thickness in XPS is derived over a relatively large area, while the AFM line profiles show only the relative film thickness with respect to the underlying layer. Figure 4d shows the O 1s core levels for both samples, deconvoluted into two main components. The lower binding energy peak at ~531.5 eV, close to the O 1s peak of sapphire at ~531.1 eV,[30] is associated with Al–O bonds. The higher binding energy peak at ~533.1 eV is attributed to multiple intermediate species, including hydroxyl aluminum, carbonyl, formate, and methoxyl, caused by incomplete reactions of the metalorganic precursors.[31] The greater peak intensity at ~533.1 eV for the TMA/O_3-ALD film over that of the TMA/H_2O-ALD film could have been caused by carbon oxidation by ozone, contributing extra carbon to the film.

In summary, we investigated the growth of high-*k* dielectric Al_2O_3 layers on MoS_2 using ALD with TMA/H_2O and TMA/O_3 precursors. Our AFM and LEIS results indicated that using ozone greatly improved the film coverage and deposition rate because of accelerated TMA nucleation. We fabricated a conformal layer of Al_2O_3 using a thin seeding layer prior to performing high-temperature ozone-based ALD. The absence of noticeable oxidation states from the MoS_2 interface after TMA/ozone process at 200 °C suggests that MoS_2 is likely more chemically resistant to ozone etches than graphene.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for the exfoliation of MoS_2 flakes of varied thickness on SiO_2/Si surfaces and ALD deposition of Al_2O_3 films, information on the characterization techniques used for surface analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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