Atomic Layer Deposition of a High-k Dielectric on MoS$_2$ Using Trimethylaluminum and Ozone

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ABSTRACT: We present an Al$_2$O$_3$ 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$_2$O$_3$ layers, in contrast to the incomplete coverage we observe when using TMA/H$_2$O 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, 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 (~$1 \times 10^3$). To fabricate high-performance devices based on MoS$_2$, high-k dielectrics such as HfO$_2$ or Al$_2$O$_3$ 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. 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$_2$O$_3$ (~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$_2$O$_3$ 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$_2$O$_3$ films on room temperature UV-ozone functionalized MoS$_2$ surface using TMA/H$_2$O-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$_2$. 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,
uniform Al2O3 layers with thicknesses of 5 nm or less without noticeable oxidation of the MoS2 interface. Ozone, compared with H2O and oxygen plasma as oxidant precursors, has well-recognized advantages, such as higher reactivity,18 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 states12,17 in the resulting ALD films. The present letter studies the reaction behavior of ozone with the MoS2 surface and the feasibility of depositing high-k dielectrics using ozone-based ALD.

Figure 1a shows a representative AFM topographic image of an ALD-Al2O3 layer deposited on a MoS2 flake with 30 cycles of TMA/H2O at 200 °C. The thickness of the Al2O3 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 Al2O3 layer deposited at 200 °C by Liu et al.,2 the Al2O3 layer reported in the present letter exhibits less than 40% coverage, revealed by the formation of dispersed Al2O3 clusters resembling the Al2O3-ALD film on a MoS2 surface, as reported by Yang1 and Azcatl13 et al. When using TMA/H2O, we observed more rapid Al2O3 growth along the step edge of the MoS2 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 Al2O3 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/H2O-ALD process, using ozone enhances the Al2O3 film coverage and uniformity on both the MoS2 step edges and basal planes, suggesting that the ozone facilitates initial TMA precursor nucleation on the MoS2 by increasing the number of activation sites.19 It is believed that the differing growth behavior at 200 °C when using TMA/O3 is associated with the distinct interaction mechanisms of ozone with the MoS2 surface. Different than water, ozone readily decomposes into molecular O2 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 Al2O3 film, leading to higher surface roughness.17,19

In an attempt to deposit a uniform, thin Al2O3 layer on MoS2, we deposited five cycles of TMA/O3 at 30 °C as a seeding layer prior to sequential ALD at 200 °C. Figure 1c shows an AFM image of the conformal Al2O3 layer after 45 cycles of TMA/O3 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 Al2O3 layer grown on H-terminated Si. In contrast to the film shown in Figure 1b, this Al2O3 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 MoS2). 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/O3-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 surface elemental compositions show only O (404 eV) and Al (573 eV) peaks, originating from the Al2O3 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 MoS2 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/H2O-ALD, clear evidence of incomplete film coverage. Because the Mo scattering cross-section is four times larger than that of S.
atoms,\textsuperscript{25} 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\textsubscript{2}. These LEIS results, which complement our AFM images, suggest that ozone-based ALD more effectively deposits uniform dielectric layers on MoS\textsubscript{2}.

Figure 3a, b show the ex situ Raman spectra of a monolayer-thick MoS\textsubscript{2} flake exposed to ozone at 30 or 200 °C for 10 s; we assessed the thickness of the flake by interpreting the \(\sim 18.2\ \text{cm}^{-1}\) separation between the two peaks present. Raman spectroscopy has been widely used to study the 2D crystalline structure of MoS\textsubscript{2} because of its ability to detect its characteristic phonon modes.\textsuperscript{21} The prominent peak observed at low Raman shifts of \(\sim 384\ \text{cm}^{-1}\) is attributed to S–Mo–S in-plane motion (E\textsubscript{2g} mode), whereas the peak at \(\sim 402\ \text{cm}^{-1}\) is assigned to out-of-plane motion (A\textsubscript{1g} mode).\textsuperscript{22} These two Raman active modes have been reported to shift with changes in thickness,\textsuperscript{23} strain,\textsuperscript{24} temperature,\textsuperscript{25} and doping;\textsuperscript{26} therefore, they are considered a signature of the stoichiometric MoS\textsubscript{2} lattice structure. Figure 3a shows that exposing MoS\textsubscript{2} to ozone at 30 °C for 10 s (\(\sim 380\ \text{g/Nm}^3\), P\[O\textsubscript{3}\]=\(\sim 150\ \text{Torr}\)) 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\textsubscript{1g} mode at \(\sim 402\ \text{cm}^{-1}\) shifts down by \(\sim 0.6\ \text{cm}^{-1}\) and broadens by \(\sim 0.3\ \text{cm}^{-1}\). 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\textsubscript{2} transistors,\textsuperscript{26} in which electron doping caused the A\textsubscript{1g} mode to red-shift and broaden, but did not affect the E\textsubscript{2g} peak. In the present letter, the absence of noticeable alterations to the MoS\textsubscript{2} Raman active modes and the lack of the MoO\textsubscript{3} frequency at \(\sim 820\ \text{cm}^{-1}\) suggests that exposing the MoS\textsubscript{2} to ozone did not significantly disorder its lattice. Reports have shown that MoS\textsubscript{2} is relatively stable in oxygen-rich environments at temperatures up to \(370\ \text{°C}\)\textsuperscript{27} because of its high Mo–S dissociation binding energy (\(\sim 368\ \text{kJ/mol}\)).\textsuperscript{28} Therefore, our Raman analysis of monolayer MoS\textsubscript{2} suggests that the improved coverage of the Al\textsubscript{2}O\textsubscript{3} film when using TMA/O\textsubscript{3} as precursors can be traced to the relatively weak interaction between the oxygen species and MoS\textsubscript{2}; the sulfur and oxygen interactions that do occur are not strong enough to alter the MoS\textsubscript{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\textsubscript{2} against ozone etching, which can degrade device characteristics,\textsuperscript{20} we used ex situ XPS to examine the binding energies of Mo 3d, S 2s, and S 2p core states for MoS\textsubscript{2} after 30 ALD cycles at 200 °C using TMA/O\textsubscript{3} or TMA/H\textsubscript{2}O, and compared them with those of an as-exfoliated MoS\textsubscript{2} crystal. Shown in Figure 4a, b, we assign the binding energies at \(\sim 232.96\) and \(\sim 229.83\ \text{eV}\) to the Mo 3d\textsubscript{3/2} and Mo 2d\textsubscript{3/2} chemical states, whereas we assign the peaks at \(\sim 227.05\) and \(\sim 162.7\ \text{eV}\) to the S 2s and S 2p core levels, which originate from the corresponding Mo(IV) and S(II) chemical states in the MoS\textsubscript{2} crystal.\textsuperscript{11} For both samples, depositing Al\textsubscript{2}O\textsubscript{3} on MoS\textsubscript{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 \(\sim 162.7\ \text{eV}\). The good overlap of the Mo 3d and S 2p peaks over those of as-exfoliated MoS\textsubscript{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\textsubscript{2} demonstrates better chemical stability against ozone treatment compared with that of graphene, in which ozone exposure at \(200\ \text{°C}\) leads to graphene surface damage arising from ozone etches\textsuperscript{19,20} but no apparent evidence of MoS\textsubscript{2} interface structure changes is seen in our Raman and XPS investigations. Compared to pretreating MoS\textsubscript{2} with oxygen plasma,\textsuperscript{27} 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\textsubscript{2}O\textsubscript{3} layers deposited by ALD at 200 °C with TMA/O\textsubscript{3} and TMA/H\textsubscript{2}O precursors, respectively. For both samples, the Al 2p peaks are composed of a predominant chemical state centered at \(\sim 74.9\ \text{eV}\); we measured the binding energy difference between Al–O to be \(\sim 456.6\ \text{eV}\), which agrees well with the previously reported binding energies of Al 2p for O–Al–O in fully oxidized Al\textsubscript{2}O\textsubscript{3} films.\textsuperscript{29} The peak intensity of the
Al 2p state in the TMA/O3 film is ~50% greater than that of the TMA/H2O film, consistent with the average film thicknesses of ~1.9 nm (TMA/O3) and ~1.1 nm (TMA/H2O) 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 MoS2 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, 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/O3-ALD film over that of the TMA/H2O-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 Al2O3 layers on MoS2 using ALD with TMA/H2O and TMA/O3 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 Al2O3 using a thin seeding layer prior to performing high-temperature ozone-based ALD. The absence of noticeable oxidation states from the MoS2 interface after TMA/ozone process at 200 °C suggests that MoS2 is likely more chemically resistant to ozone etches than graphene.

**ASSOCIATED CONTENT**

Supporting information for the exfoliation of MoS2 flakes of varied thickness on SiO2/Si surfaces and ALD deposition of Al2O3 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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