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Uniform Growth of Sub-5-Nanometer High- κ Dielectrics on MoS₂ Using Plasma-Enhanced Atomic Layer Deposition

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S Supporting Information

ABSTRACT: Regardless of the application, MoS_2 requires encapsulation or passivation with a high-quality dielectric, whether as an integral aspect of the device (as with top-gated field-effect transistors (FETs)) or for protection from ambient conditions. However, the chemically inert surface of MoS_2 prevents uniform growth of a dielectric film using atomic layer deposition (ALD)—the most controlled synthesis technique. In this work, we show that a plasma-enhanced ALD (PEALD) process, compared to traditional thermal ALD, substantially improves nucleation on MoS_2 without hampering its electrical



performance, and enables uniform growth of high- κ dielectrics to sub-5 nm thicknesses. Substrate-gated MoS₂ FETs were studied before/after ALD and PEALD of Al₂O₃ and HfO₂, indicating the impact of various growth conditions on MoS₂ properties, with PEALD of HfO₂ proving to be most favorable. Top-gated FETs with high- κ films as thin as ~3.5 nm yielded robust performance with low leakage current and strong gate control. Mechanisms for the dramatic nucleation improvement and impact of PEALD on the MoS₂ crystal structure were explored by X-ray photoelectron spectroscopy (XPS). In addition to providing a detailed analysis of the benefits of PEALD versus ALD on MoS₂, this work reveals a straightforward approach for realizing ultrathin films of device-quality high- κ dielectrics on 2D crystals without the use of additional nucleation layers or damage to the electrical performance.

KEYWORDS: ALD, PEALD, MoS₂, ultrathin dielectric, nucleation, 2D crystals

 \mathbf{N} anomaterials have the potential to enable an entirely new era of electronic and enterly the interval of the second enterly the second ente era of electronic and optoelectronic applications. In addition to being near-atomically thin, nanomaterials offer advantages in electrical properties, mechanical robustness, unique quantum confinement behavior, and substrate independence.^{1,2} One prominent class of nanomaterials under extensive consideration is transition metal dichalcogenides (TMDs). TMDs have the chemical formula MX₂ with M being any transition metal atom and X being a chalcogen atom. Molybdenum disulfide (MoS_2) is one of the most common semiconducting TMDs with a direct band gap of 1.9 eV as a monolayer and an indirect band gap of \sim 1.29 eV in bulk form.³ MoS₂ has shown promise for a range of applications, from photodetectors⁴⁻⁶ to scaled and low-voltage field-effect transistors (FETs).⁷⁻¹⁰ To be used in an electronic or optoelectronic device, MoS2 must be encapsulated or passivated with a high-quality dielectric layer to protect it from deleterious interactions with the ambient environment.^{5,11,12} In some cases, this dielectric layer is an integral part of the device, as with top-gated FETs, where it serves as the gate dielectric and needs to be extremely thin (sub-5-nm)

for sufficient electrostatic coupling of the gate to the semiconducting channel. In other cases, the dielectric is a protective coating to keep the MoS_2 from degrading by exposure during operation. In all cases, this dielectric layer should be uniform and not compromise the electrical performance of the MoS_2 .

The most controlled approach for obtaining high-quality, scalable growth of dielectrics is atomic layer deposition (ALD). ALD is a self-limiting reaction that requires the initial precursor to uniformly react with the sample surface.^{13,14} The chemically inert basal plane of MoS₂ presents a challenge when using ALD to grow dielectrics as nucleation predominantly occurs at defect sites or through physical adsorption of precursors onto the basal plane;^{15,16} hence, only thick films (typically >10 nm) are able to yield complete coverage.^{17–19} To use ALD to grow thinner, more scalable, high- κ dielectrics on MoS₂, various surface modification methods^{16,20–24} and buffer layers^{25–27}

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Figure 1. ALD vs PEALD reactions for Al_2O_3 on MoS_2 . (a) Schematic showing difference between ALD and PEALD of Al_2O_3 . The first step is the same, where TMA is pulsed into the chamber, however, in the second step either water vapor (thermal ALD) or O_2 plasma species (PEALD) are introduced. This difference in oxidants produces an entirely different film on MoS_2 , as evidenced by the corresponding AFM images (scale bars are 100 nm). (b) Schematic showing PEALD chamber (same chamber used for ALD) with an RF-generated O_2 plasma remote and upstream from the sample, separated by a showerhead for delivering the reactant O_2 radicals to the substrate without direct exposure to the highly energetic plasma species.

have been investigated. Surface treatments include O_2 plasma^{20,24} and ultraviolet ozone $(UV-O_3)$,^{21–23} where both have shown improvement of ALD nucleation on MoS₂. However, both methods have significant drawbacks. The O_2 plasma exposure reactively damages the MoS₂ surface to form an unwanted interfacial layer of molybdenum oxide (MoO₃), which disrupts the underlying crystal structure.²⁰ While the UV–O₃ does not oxidize MoS₂,^{21,22} the thinnest useable HfO₂ gate dielectric reported is 6 nm,²² likely owing to unacceptable leakage currents through the HfO₂. Further, the exposure conditions of UV–O₃ are challenging to control, such that when applied to other TMDs (e.g., MoSe₂ or WSe₂) the oxygen functionalization does lead to the undesirable oxidation of the TMDs.²³

Other methods to improve ALD nucleation on MoS₂ include the initial deposition of a buffer layer.²⁵⁻²⁷ These buffer layers have included organics, such as titanyl phthalocyanine²⁷ and metal oxides.²⁶ Unfortunately, a buffer layer adds to the overall dielectric material stack, which can be detrimental for many applications, including MoS₂ FETs where strong electrostatic gate control is imperative. There is also the possibility for more interfacial traps and carrier scattering effects introduced by the additional buffer layer; in short, the result is a more complex dielectric stack that is difficult to optimize and tune for certain applications. Among all of the above-mentioned methods, the thinnest reported ALD film deposited onto MoS₂ is 3 nm Al₂O₃ achieved by depositing (via physical vapor deposition) ~1 nm Al, followed by oxidation before performing ALD.²⁶ The resultant film was rough and the deposition of metal followed by oxidation causes strain on the MoS₂ that alters its electronic properties.^{28,29} The thinnest ALD film deposited onto MoS₂ that is demonstrated in a device (used as a gate dielectric in an

FET) is 6 nm HfO₂, achieved by exposing the MoS₂ to UV– $O_3^{\ 22}$

In this work, we demonstrate the unique benefits of plasmaenhanced ALD (PEALD) for uniformly nucleating high- κ dielectrics on MoS₂. Under appropriate conditions, HfO₂ films as thin as \sim 3.5 nm are obtained and used as the gate dielectric in top-gated FETs with low leakage current. Importantly, it is shown that the PEALD process for HfO₂ does not compromise the electrical properties of the MoS₂; in fact, back-gated MoS₂ FETs exhibit enhanced electrical performance after a capping layer of PEALD HfO₂ is formed. By comparing the impact of thermal ALD and PEALD on MoS₂ for Al₂O₃ and HfO₂, insights are gained regarding potential damage to the MoS₂ and effectiveness of the various films as gate dielectrics or passivation coatings. X-ray photoelectron spectroscopy (XPS) is used to study the nucleation behavior of the films under the myriad growth conditions, providing evidence that the PEALD process does not induce growth of a MoO₃ layer. These results show that the readily accessible PEALD approach is extremely effective for uniformly growing high-quality, scalable dielectrics on MoS₂.

To the best of our knowledge, all ALD films deposited on TMDs to date use thermal ALD processes, where reactions are driven purely by thermal energy. There are other well-established options, including plasma-enhanced ALD (PEALD), which offers many advantages, such as, lower growth temperatures, higher quality films, and shorter deposition times.³⁰ PEALD differs from thermal ALD, in the introduction of a plasma in one of the pulse steps to aid in cracking the precursor. This is illustrated in Figure 1a, where ALD is compared to PEALD for Al₂O₃ growth and the second precursor step in PEALD involves the use of oxygen (O₂) plasma instead of water vapor for ALD. In most PEALD



Figure 2. Comparison of ALD and PEALD Al_2O_3 on MoS_2 at different temperatures. Atomic force microscopy (AFM) images and line-scan height profiles after 125 cycles (~10 nm) of ALD and PEALD Al_2O_3 on MoS_2 . ALD Al_2O_3 at (a)120 °C, (b) 220 °C, and (c) 332 °C on MoS_2 . PEALD Al_2O_3 at (d) 120 °C, (e) 220 °C, and (f) 332 °C on MoS_2 . All MoS_2 flakes are nominally 6–8 nm thick. Scale bars are 100 nm.

chambers, the plasma is remote, or not in direct interaction with or proximity to the substrate, so as to minimize any substrate damage from the energetic plasma radicals. The plasma is generally sustained using the PEALD carrier gas (Ar) and then a small amount of precursor is pulsed through the plasma.

All samples used to study the ALD and PEALD growth behavior on MoS₂ flakes in this work were prepared by mechanically exfoliating MoS₂ onto thermally oxidized, pdoped silicon substrates (300 nm SiO_2). Flakes with thicknesses ranging from 6 to 8 nm were selected and characterized before and after ALD or PEALD; this MoS₂ thickness has been shown to be ideal for most FET applications.³¹ A schematic of the chamber used for this study is given in Figure 1b. The same chamber is used for both ALD and PEALD processes. Both processes used the same precursors, trimethylaluminum (TMA) and tetrakis-(ethylmethylamino)hafnium (TMDAH) for Al₂O₃ and HfO₂ films, respectively, but differed in their oxidants: water vapor for thermal ALD and oxygen plasma for PEALD. The plasma for PEALD is remote from the substrate (separated by a showerhead with holes around the perimeter to eliminate any line-of-sight interaction between plasma radicals and the substrate) and RF-generated (see Figure S1 for "to scale" schematic of PEALD chamber). Ar is used as the carrier gas throughout the system and sustains the plasma, while a small

pulse of O_2 is added to the plasma to generate the oxygen precursor radicals. Using this chamber, we first studied the difference in nucleation density between thermal ALD and PEALD processes at a range of temperatures for HfO₂ and Al₂O₃ on MoS₂ (see Supporting Information for details involving purge and pulse times).

Atomic force microscopy (AFM) was used to determine the density of nucleation and uniformity (surface roughness) of the resultant films. A summary of the results comparing ALD and PEALD of Al_2O_3 on MoS_2 at different temperatures is shown in the AFM images of Figure 2. The thermal ALD process consisted of 125 cycles of Al₂O₃ or 115 cycles of HfO₂ onto MoS₂ at 120 °C, 220 °C, and 332 °C. These numbers of cycles were chosen to yield a similar film thickness of ~10 nm based on the growth per cycle (GPC) rates, which are shown in Table S1. Note that the GPC is measured for growth on SiO_2 and it is hypothesized that the GPC on MoS₂ is approximately the same as on SiO₂. To validate this hypothesis, AFM images of MoS₂ before and after 28 cycles of PEALD HfO2 at 120 °C were obtained as shown in Figure S3; these images clearly indicate that the MoS₂ flake thickness is the same before and after the PEALD process (within the resolution of the AFM), indicating that the HfO₂ film grew at approximately the same rate on both surfaces. For comparison, on a separate set of samples, PEALD was used to deposit the same number of cycles of each film over the same range of temperatures as used for the ALD process.

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Figure 3. Scaling down of PEALD Al_2O_3 and HfO_2 on MOS_2 . AFM images and line-scan height profiles of PEALD Al_2O_3 for (a) 125, (b) 62, and (c) 31 cycles (~3.4 nm) and PEALD HfO_2 for (d) 115, (e) 57, and (f) 28 cycles (~3.5 nm). Scale bars are 100 nm.

AFM images of the thermal ALD Al_2O_3 (Figure 2a-c) show the expected island growth, lack of complete surface coverage, uniform growth along the edges (where the edge states provide reaction sites for nucleating growth), and temperature dependence on nucleation density.^{13,16} In contrast, the PEALD Al₂O₃ shows significant improvement in nucleation uniformity at all temperatures (Figures 2d-f), with surface roughness decreasing under increasing deposition temperature (see Figure S4 for RMS values). It is interesting to note that this temperature dependence for PEALD is opposite that of the ALD. Recall that ALD film growth is driven by the physical adsorption of precursors onto the basal plane of MoS₂, thus the nucleation density decreases at higher temperatures when the precursors are easily desorbed.¹⁵ The difference in temperature dependence suggests that for PEALD film growth, the physical adsorption of precursors on MoS₂ is no longer the leading mechanism for nucleation. A similar comparison between ALD and PEALD of HfO₂ on MoS₂ was also carried out (see Figure S5) and showed dramatic improvement in nucleation density and film smoothness using PEALD (see Figure S6 for RMS values). In the HfO₂ case, lower PEALD temperatures yielded smoother films. This is consistent with other observations involving ALD HfO₂, where the films were amorphous when grown at temperatures <150 °C and polycrystalline at higher growth temperatures, leading to potentially higher surface roughness.

Having established the benefits of PEALD for producing uniform films on MoS_{22} the scalability of these films is now

considered. While the ~ 10 nm thick films shown in Figure 2df and Figure S2d-f are very smooth (as small as ~0.30 nm roughness), it is not entirely clear whether the nucleation density is sufficient to support aggressive downscaling in the film thickness without compromising uniformity. Hence, the number of PEALD cycles was reduced to target films that were approximately 5 and 3 nm thick to compare to the ~10 nm films. The temperature was fixed at 220 °C for Al₂O₃ and 120 °C for HfO₂—the most favorable deposition conditions for the thicker films with lowest surface roughness. AFM results for the scaling of PEALD Al₂O₃ and HfO₂ on MoS₂ are shown in Figure 3 Uniform, low surface roughness films were realized down to 31 cycles (~3.4 nm, Figure 3c) and 28 cycles (~3.5 nm, Figure 3f) for Al₂O₃ and HfO₂, respectively (see Figure S7 for RMS values). To date, these represent the thinnest, highquality, high- κ dielectric films achieved on MoS₂ with no surface treatments or buffer layers for promoting nucleation.

With evidence for uniform nucleation and film scalability using PEALD, it is critical to consider potential damage to the MoS_2 from the PEALD process. This was first studied by monitoring the MoS_2 electrical properties in back-gated fieldeffect transistors (FETs) before and after using PEALD to grow Al_2O_3 or HfO₂ on top of the MoS_2 , in this case as a passivation layer. The device structure is shown schematically in Figure 4a. MoS_2 was exfoliated onto 10 nm SiO₂/Si wafers and flakes of thickness ranging from 5 to 8 nm were selected. Electron-beam lithography (EBL) was used to define the contacts and pads. Electron-beam evaporation was carried out to deposit 25 nm Ni



Figure 4. Impact of PEALD Al₂O₃ and HfO₂ on MoS₂ electrical performance using back-gated FETs ($V_{ds} = 1$ V). (a) Schematic of back-gated MoS₂ FET before and after PEALD Al₂O₃ or HfO₂. The p-doped Si substrate is used as the back gate (V_{bg}) with the 10 nm SiO₂ as the gate dielectric and a channel length of 0.5 μ m (width = 1.8 μ m) (b, c) and 3.5 μ m (width = 1.4 μ m) (d, e). (b) Subthreshold hysteresis curves from the same device before and after PEALD Al₂O₃ showing an increase in SS but decrease in hysteresis. (c) Transfer curves (same device as in panel b) before and after PEALD Al₂O₃ show a decrease in transconductance and I_{ON} . (d) Subthreshold hysteresis curves from the same device before and after PEALD HfO₂ showing a slight decrease in SS and hysteresis. (e) Transfer curves (same device as in panel d) before and after PEALD showing an increase in transconductance and e are all shifted so that the threshold voltage (V_{T}) is 0 V for all curves in order to compare the on-state performance.

for the contacts and 2 nm Ti/20 nm Pd/20 nm Au for the pads. Back-gated characteristics (using the p-doped Si substrate as the gate and the 10 nm SiO₂ as the dielectric) of the MoS₂ FET before and after PEALD Al₂O₃ (Figure 4b and c) shows that the PEALD Al₂O₃ process causes degradation to the off- and on-state performance of the device. In the off-state (Figure 4b), an increased subthreshold swing (SS) and decreased on/off current ratio are exhibited. The hysteresis is also reduced (Figure 4b and d) because of the PEALD process removing adsorbents that cause hysteresis in MoS₂ FETs (such as water molecules), and subsequently capping the MoS₂.¹¹ Meanwhile, the on-state (Figure 4c) shows a decreased transconductance and reduced on-current (I_{ON}).

To determine if the degradation in the back-gated MoS₂ FET after PEALD Al_2O_3 is due to damage of the MoS₂, two important factors must be considered: (1) how the PEALD process temperature affects the Ni-MoS₂ contact interface and (2) what impact the presence of the Al_2O_3 has on the transport in the MoS₂. Since the PEALD process is performed after the metal contacts to the MoS₂ are established, the elevated temperature of the PEALD process environment will serve as a thermal anneal to the Ni-MoS₂ contact interface, which has been shown to increase contact resistance in some cases.³² To determine the impact of the annealing effect, devices were fabricated and tested before and after undergoing the same thermal exposure but without the PEALD Al₂O₃ process (the substrate was loaded into the same PEALD chamber, brought up to the process temperature, 220 °C, and held for approximately the same amount of time as the PEALD process, which is ~ 1 h). The result, shown in Figure S8, indicates the annealing step does result in degradation of I_{ON} by an average of ~27%. The degradation in I_{ON} was determined by shifting the threshold voltage (V_T) to 0 V for the before and after annealing curves, and then extracting the I_{ON} at an overdrive voltage $(V_{ov} = V_{bg} - V_T)$ of 1.0 V; this accounts for any V_T shift from the annealing treatment.

There is a possibility that the presence of the Al_2O_3 layer on the MoS₂ will cause degradation in the transport through the MoS₂, such as by introducing more phonon modes for scattering. To determine this potential impact, and thus isolate it from the impact of the PEALD nucleation process, backgated MoS₂ FETs were characterized before and after the thermal ALD deposition of 250 cycles of Al₂O₃, a thick layer was needed to ensure that the MoS₂ was entirely covered, at 220 °C (Figure S9). The back-gate characteristics after the \sim 20 nm Al₂O₃ deposition exhibit a slight decrease in SS, decreased hysteresis, and ~7% reduction in $I_{\rm ON}$. The ~7% reduction in $I_{\rm ON}$ is remarkable considering the expected >27% reduction in I_{ON} from the contact annealing effect described above. The lower than expected reduction in I_{ON} clearly indicates that the presence of the thermal ALD Al₂O₃ layer is partially offsetting the degradation in $I_{\rm ON}$ that occurs from the thermal annealing effect on the contacts.

Taking into account the two factors discussed above, the impact of the contacts being annealed by the PEALD process and the presence of Al_2O_3 on the MoS_2 , we now consider whether the PEALD Al_2O_3 process is damaging the MoS_2 . After 62 cycles (~5 nm) of PEALD Al_2O_3 was deposited, the backgated MoS_2 FET shown in Figure 4b experiences a ~51% degradation in I_{ON} . Part of this degradation is due to the



Figure 5. Impact of ALD and PEALD of Al_2O_3 and HfO_2 on MoS_2 crystal structure. XPS spectra showing the Mo 3d and S 2s core energy levels for (a) ALD and (b) PEALD Al_2O_3 and (c) ALD and (d) PEALD HfO_2 after the indicated number of ALD or PEALD cycles.

thermal annealing effect on the Ni–MoS₂ contacts, which accounts for a ~27% drop. Recall that the addition of a thermal ALD Al₂O₃ layer on MoS₂ actually mitigated some of the damage resulting from the heat treatment. However, this healing effect is not seen in the PEALD Al₂O₃ case, indicating that the PEALD process is damaging the electrical performance of the MoS₂ structure, causing the remaining reduction in $I_{\rm ON}$.

While the PEALD of Al₂O₃ does lead to degradation of the MoS_2 , the same is not true for PEALD of HfO_2 . An important finding in this study is that the PEALD HfO₂ process yields an overall enhancement in the back-gated MoS₂ FET performance (Figure 4d and e). The effects of deposition temperature and the presence of the HfO₂ passivation layer on the back-gated electrical properties are taken into consideration in a fashion similar to that of PEALD Al₂O₃. The deposition temperature for the PEALD HfO2 is 100 °C lower than that of the PEALD Al_2O_3 , resulting in a lower average reduction of ~14% in I_{ON} $(V_{ov} = 1.5 \text{ V})$ due to contact annealing (Figure S10). Remarkably, there is still an overall increase in I_{ON} after the PEALD HfO₂ process (Figure 4e) of 136% (2.36× increase), signifying that the process mitigates the deleterious effects of the thermal annealing on the Ni-MoS₂ contact interfaces while providing a more favorable, passivated interface for carrier transport through the MoS₂ channel.

Having established that PEALD HfO₂ enhances performance in back-gated MoS₂ FETs when employed as a channel passivation layer, the impact of a thermal ALD HfO₂ passivation layer is also important to evaluate (Figure S11). The thermal ALD HfO₂ layer was deposited at 120 °C, consistent with the PEALD HfO₂, however twice as many cycles (230 cycles) were deposited to ensure complete coverage of the MoS₂. While, the ALD HfO₂ shows an enhancement in the back-gated electrical performance of $\sim 3\%$, this is significantly less than the improvement seen using the PEALD HfO₂. This shows that the PEALD HfO₂ process is not degrading the MoS₂ device performance, and is actually yielding a HfO₂ film that improves the performance compared to ALD HfO₂.

To study the impact of the ALD and PEALD processes on the MoS₂ crystal structure, X-ray photoelectron spectroscopy (XPS) was carried out (Figure 5). XPS was done ex situ after 1, 2, 3, 4, 5, and 62 cycles of the ALD and PEALD Al₂O₃ and HfO₂ on chips containing a high density of MoS₂ flakes. The peaks were calibrated to the C 1s peak with a binding energy of 284.8 eV (Figure S12). A baseline of exfoliated MoS_2 was measured and showed the characteristic Mo 3d peaks at 229 and 332 eV and S 2s peak at 226 eV.²¹ For ALD of both Al_2O_3 and HfO2, the Mo 3d peak shifts by ~0.2 eV by cycle #5 (within the experimental uncertainty), indicating that the ALD process is not changing the MoS₂ structure. Previous work has shown that exposing MoS_2 to an oxygen plasma produces molybdenum oxide (MoO_3) ,^{20,24} which appears as a peak around 236 eV.³³ Neither of the PEALD XPS spectra (Figures 5c and d) exhibit the signature MoO_3 peak at 236 eV, indicating that the O₂ plasma precursor is not fully oxidizing the MoS₂; however, it is possible that some partial oxidation of the topmost MoS₂ layer is occurring that is below the XPS detection limit. Note that previous reports, using the same XPS conditions, have shown evidence for the formation of monolayer MoO₃ after exposure to oxygen radicals.^{23,34} The PEALD XPS spectra do show the MoS₂ core energy levels, Mo 3d and S 2s, shifting collectively to lower binding energies. The



Figure 6. Integration of scaled PEALD HfO₂ as gate dielectric in top-gated MoS₂ FET ($V_{ds} = 1 \text{ V}$, $V_{bg} = 8 \text{ V}$). (a) Schematic of top-gate device, which has a channel length (L_{ch}) of 1 μ m and underlap regions (L_u) of ~200 nm between the gate-source and gate-drain. (b) Cross-sectional STEM showing ~3–4 nm PEALD HfO₂ gate dielectric (covered by focused ion beam (FIB) deposited Pt for STEM preparation). (c) Subthreshold characteristics of the device showing very low gate leakage current out to -4 V of top-gate bias (V_{tg}).

PEALD Al_2O_3 has a rather large shift of ~1.2 eV, whereas, the PEALD HfO_2 has a much smaller shift of ~0.4 eV. The shift of both peaks by the same amount toward lower binding energy denotes a possible p-doping of MoS_2 rather than the formation of new chemical species, as has been demonstrated in other studies.^{35,36} The XPS data confirms the result of the back-gated FET characteristics: PEALD Al_2O_3 is modifying the underlying MoS_2 structure (~1.2 eV peak shifts) whereas the PEALD HfO_2 appears to be doing minimal, if any, modification.

As the PEALD HfO₂ led to improvement of back-gated MoS₂ FET characteristics and XPS gives no evidence for significant damage to the MoS₂ crystal, it was employed as an aggressively scaled gate dielectric in a top-gated MoS₂ FET. The top-gated MoS₂ FET was fabricated with a \sim 3.5 nm HfO₂ gate dielectric grown by PEALD at 120 °C (Figure 6a). A similar process flow was used to that of the back-gated FETs with the additional formation of a metal top gate (see Figure S13 for process details). Note that the \sim 3.5 nm HfO₂ thickness is based on ex situ multiwavelength ellipsometry that provided a growth-per-cycle (GPC) rate for the PEALD conditions used to fabricate this device (see Table. S1). The HfO_2 gate dielectric thickness was further validated by obtaining a crosssectional scanning transmission electron microscopy (STEM) image of the device, as shown in Figure 6b. The STEM image confirms that the HfO2 is between 3 and 4 nm thick and uniformly nucleated on the MoS₂. Electron diffraction spectroscopy (EDS) was also performed to clearly identify the layers in the STEM image (Figure S14). The resultant device structure is shown in Figure 6a, where there is an underlap between the top gate and the metal source/drain of ~ 200 nm. The subthreshold characteristics for this device show excellent switching behavior with low gate leakage (<0.1 nA/ μ m²) even up to 4 V applied gate bias (Figure 6c). This observed low leakage current is within the range of gate leakage values previously reported for thin HfO₂ films.³⁷ This is the thinnest known gate dielectric reported to date for a top-gated MoS₂ FET. Importantly, other devices were fabricated that had the top gate misaligned and thus overlapping the source or drain contact. While these devices did not operate properly due to the misalignment, they did allow for testing of the leakage current between the top gate and metal contact and proved to be similarly robust with similarly low leakage as seen between the gate contact and MoS₂ channel.

In conclusion, we have demonstrated that PEALD yields uniform growth of high- κ dielectrics on MoS₂ without surface

preparation steps or buffer layers. The PEALD of Al₂O₃ and HfO₂ are both shown to be scalable to the sub-5 nm regime. Back-gated MoS₂ FETs tested before and after PEALD show that HfO₂ yields enhancement in the MoS₂ electrical performance, offering substantial improvement that even overcomes degradations in contact and surface scattering effects. Corresponding to these electrical results, XPS shows a large shift in the MoS₂ core energy levels in the PEALD Al₂O₃ process and a minimal shift during the PEALD HfO₂, further indicating that the PEALD Al₂O₃ process is more impactful on the MoS₂ crystal structure. XPS also shows the absence of the formation of MoO₃ for both PEALD processes. Integration of a \sim 3.5 nm PEALD HfO₂ into a top-gated MoS₂ transistor yields an impressively low leakage current and strong gate control. Importantly, these results show that the use of a commonly available growth technique, PEALD, is capable of yielding highquality, aggressively scalable high- κ dielectrics on MoS₂ and serves as a foundation for determining the reaction mechanism of the PEALD process on MoS₂.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b00538.

A "to scale" schematic of PEALD/ALD chamber; details on PEALD/ALD process and experimental setup/details on AFM, XPS, and STEM; growth per cycle for PEALD/ ALD Al₂O₃ and HfO₂; AFM of MoS₂ before and after PEALD HfO₂; AFM of PEALD HfO₂; AFM of 1 μ m² scan area on MoS₂ for PEALD/ALD Al₂O₃ and HfO₂ films; impact of thermal exposure during PEALD at 120 and 220 °C; effect of thermal ALD Al₂O₃ on back-gated characteristics; effect of thermal ALD HfO₂ on backgated characteristics; top-gate fabrication process flow; XPS of C 1s peak for PEALD/ALD Al₂O₃ and HfO₂; EDS spectra of STEM images; and CV curves for PEALD/ALD Al₂O₃ at 220 °C and ALD HfO₂ at 120 °C (PDF)

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Author Contributions

K.M.P. and A.D.F. conceived the idea and designed the experiments. K.M.P and K.E.S performed ALD/PEALD comparison on MoS_2 (AFM) and fabricated and tested the back-gated MoS_2 transistors. K.M.P performed the XPS experiments and fabricated and tested the top-gate MoS_2 transistors. F.A.M aided in MoS_2 transistor fabrication, ALD/PEALD, and ellipsometry. K.M.P., K.E.S., D.B.F., and A.D.F. analyzed and interpreted the data. K.M.P. wrote the manuscript with comments from all authors.

Notes

The authors declare no competing financial interest.

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