Nucleation engineering for atomic layer deposition of uniform sub-10 nm high-K dielectrics on MoTe\textsubscript{2}

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\textbf{ABSTRACT}

Continuous, uniform, and sub-10 nm Al\textsubscript{2}O\textsubscript{3} high-K dielectrics on two-dimensional exfoliated multilayer MoTe\textsubscript{2} are realized by atomic layer deposition (ALD) based on a nucleation layer (NL) prepared by the ozone-based process, interfacial AlN, and low-temperature (low-T) physical adsorption. The NLS gives rise to significant reduction of the leakage current in the sub-10 nm Al\textsubscript{2}O\textsubscript{3} high-K dielectrics as shown by conductive atomic force microscopy. For the ozone-based NL, X-ray photoelectron spectroscopy (XPS) reveals the oxidation of MoTe\textsubscript{2} which is detrimental to the electrical properties of MoTe\textsubscript{2}. For the AlN NL, XPS reveals that Mo-N bonds were formed without Mo-O bonds and no chemical shift appeared in Te-3d XPS spectrum, indicating the AlN NL did not result in the MoTe\textsubscript{2} oxidation but instead the formation of an MoN layer. For the low-T NL, the XPS spectra of MoTe\textsubscript{2} are the same as those of the as-exfoliated MoTe\textsubscript{2} flake, consistent with the absence of chemical reactions during low-T physical adsorption. The result demonstrates that the NLS prepared by the low-T physical adsorption and the interfacial AlN are effective and favorable for nucleating high-quality high-K gate dielectrics on MoTe\textsubscript{2} transistors.

\section{1. Introduction}

Owing to the atomic thickness and suitable bandgap of two-dimensional transition metal dichalcogenides (TMDs) [1], TMDs have been widely explored as promising candidates for channel materials as the scaling of Si field-effect transistors approaches the physical limit [2–8]. The chemical formula of TMDs is MX\textsubscript{2}, where M represents a transition metal including Mo, W, and Hf, and X is a chalcogen element such as S, Se, or Te. Among numerous TMDs, molybdenum ditelluride (α-MoTe\textsubscript{2}) is worthy of attention because of its attractive properties. Bandgap energies of monolayer and bulk MoTe\textsubscript{2} are 1.10 eV (direct) and 0.85–1.0 eV (indirect), respectively [9–11]. Density functional theory predicts a high electron mobility for MoTe\textsubscript{2} [12]. In addition, the ambipolar conductivity in MoTe\textsubscript{2} field effect transistors has been reported [13–17].

The interface quality between high-K dielectrics and semiconductor channels plays an important role in the performance of TMDs transistors. However, it is difficult to deposit high-quality high-K dielectrics on TMDs by atomic layer deposition (ALD) because islands or clusters are usually formed on pristine TMDs due to the lack of dangling bonds [18,19]. In order to overcome the challenges from the chemical inertness of TMDs, investigations have been conducted upon nucleation engineering on TMD surfaces [20–24]. For example, continuous high-K high-K dielectrics prepared by ozone-based ALD have been achieved without detectable oxidation states on MoS\textsubscript{2} [22]. The “NanoFog ALD” technique also produces a uniform layer of high-quality Al\textsubscript{2}O\textsubscript{3} on 2D materials without surface chemical reactions based on low-temperature (low-T) physical adsorption [24–26]. An AlN nucleation layer (NL) has been proposed to realize uniform deposition of high-quality Al\textsubscript{2}O\textsubscript{3} on MoS\textsubscript{2}, and the electrical stability of TMDs transistors was greatly improved as a result of the low border trap density [27]. Although these techniques work well on MoS\textsubscript{2} surfaces, extension of these methods to other TMDs may be challenges because of the difference in surface properties. For example, as compared with MoS\textsubscript{2}, selenium-based TMDs suffer from surface oxidation during the oxygen functionalization due to the favorable oxidation thermochemistry [28].

In this paper, the nucleation engineering for ALD of high-quality high-K dielectrics on exfoliated MoTe\textsubscript{2} is investigated using the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition. An ultrathin NL was prepared to provide nucleation sites for the subsequent deposition of an high-K layer, as shown schematically in Fig. 1. X-ray photoelectron spectroscopy (XPS) and conductive atomic force microscopy (CAFМ) were used to characterize the chemical states and the leakage current of high-K dielectrics on MoTe\textsubscript{2}. Continuous and uniform high-K high-K dielectrics on MoTe\textsubscript{2} are realized by atomic layer deposition (ALD) based on a nucleation layer (NL) prepared by the ozone-based process, interfacial AlN, and low-temperature (low-T) physical adsorption. The NLS gives rise to significant reduction of the leakage current in the sub-10 nm Al\textsubscript{2}O\textsubscript{3} high-K dielectrics as shown by conductive atomic force microscopy.
uniform Al₂O₃ high-K dielectrics can be deposited on MoTe₂ with the NL prepared by the three techniques. However, the ozone-based process results in the oxidation of MoTe₂, which will degrade the electrical performance of MoTe₂. No noticeable oxidation was observed with the NL formed by the low-T physical adsorption or interfacial AlN, indicating the high-quality nucleation engineering for ALD of continuous, uniform, low-leakage, and sub-10 nm high-K dielectrics on MoTe₂.

2. Experimental

The layer structure of high-K dielectric stacks is depicted schematically in Fig. 1. First, multilayer MoTe₂ flakes were transferred onto a p-type Si (100) wafer from 2H-MoTe₂ (HQ Graphene) single crystal using mechanical exfoliation with Nitto tape. Trimethylaluminum (TMA) and ozone were used as the precursors for the ozone-based NL. Because a low temperature of 80°C was suggested in the ozone-based ALD process to prepare a NL for a continuous and thin Al₂O₃ layer on MoTe₂ [29], the deposition of ozone-based Al₂O₃ NL was conducted at 80°C with 10 ALD cycles in this work. For the deposition of the Al₂O₃ NL using low-T physical adsorption, the precursors were TMA and H₂O vapor. The H₂O-based Al₂O₃ NL was prepared at 80°C with 20 ALD cycles along with a short purge time to achieve physical adsorption of the NL [24]. For the deposition of interfacial AlN, TMA and remote N₂/H₂ plasma were used to deposit the ALD process were used to achieve physical adsorption process. Ozone-based process was used to achieve physical adsorption or interfacial AlN, in- 

<table>
<thead>
<tr>
<th>Method</th>
<th>TMA pulse time</th>
<th>TMA purge time</th>
<th>Reactant pulse time</th>
<th>Reactant purge time</th>
<th>Deposition temperature</th>
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<tr>
<td>Ozone-based process</td>
<td>0.02 s</td>
<td>15 s</td>
<td>0.02 s (ozone)</td>
<td>15 s</td>
<td>80 °C</td>
</tr>
<tr>
<td>Low-T physical adsorption</td>
<td>0.2 s</td>
<td>1 s</td>
<td>0.2 s (H₂O)</td>
<td>1 s</td>
<td>80 °C</td>
</tr>
<tr>
<td>Interfacial AlN</td>
<td>0.02 s</td>
<td>15 s</td>
<td>55 s (N₂/H₂ plasma)</td>
<td>15 s</td>
<td>200 °C</td>
</tr>
<tr>
<td>Al₂O₃ main layer</td>
<td>0.02 s</td>
<td>15 s</td>
<td>0.02 s (H₂O)</td>
<td>15 s</td>
<td>200 °C</td>
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The details of ALD recipes. The longer TMA and H₂O pulse times and the short purge times in the low-T physical adsorption process were used to achieve physical adsorption of the NL.

Results and discussion

Fig. 2(a) shows the AFM image and 3D topography of the Al₂O₃ main layer (100 ALD cycles) which was directly deposited on MoTe₂ at 200°C without any NL (Fig. 2(a)). It is seen that the nucleation proceeds in a sporadic manner, giving rise to a rough and discontinuous surface. The result can be attributed to weak adhesion of TMA and H₂O on the chemical inertness surface of TMDs [22,28]. In order to deposit a continuous high-K dielectric layer on MoTe₂, N₂/O₂ plasma was used to deposit the Al₂O₃ main layer and MoTe₂ using the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition. Figs. 2(b), (c), and (d) show AFM images and 3D topographies of the Al₂O₃ main layers, and the corresponding layer structures are depicted in Figs. 2(b′), (c′) and (d′). In contrast to Fig. 2(a), continuous and uniform surfaces of the Al₂O₃ main layers were observed in Fig. 2(b)~(d). Because ozone is easily decomposed into molecular O₂ and active O radicals in the ozone-based process, the reaction of ozone with TMDs surfaces provides nucleation sites on the dangling-bond free surfaces [22,30]. Hence the ozone-based process improves the coverage and uniformity of the Al₂O₃ layer on the MoTe₂ basal plane. On the other hand, the low-T physical adsorption technique, which relies on a low deposition temperature below 100°C and a short purge time between the precursor and reactant pulses, is also known as the "NanoFog ALD" method [25,26]. At low deposition temperatures, the thermal energy of precursors/reactants is lower than the potential well depth of physical adsorption. Thus the precursors/reactants might be trapped in the adsorption potential well [20,22,31,32]. As a result, the excess precursors/reactants are physisorbed on the MoTe₂ surface at a deposition temperature at 80°C. The physisorbed precursors/reactants do not have enough time to desorb from the MoTe₂ surface if the purge time between the TMA and H₂O pulses is short, resulting in the deposition of a Al₂O₃ NL. This Al₂O₃ NL offers nucleation sites for subsequent deposition of the high-K main layer at a higher temperature. For the interfacial AlN method, the uniform deposition of the continuous AlN/ Al₂O₃ dielectric stack on MoTe₂ may result from the preferential removal of tellurium (Te), which provides dangling bonds to form the nucleation sites. The detail is revealed in the XPS characterization in the later section.

Fig. 3 shows cross-sectional HRTEM images of the high-K dielectric stacks, in which the NLs were prepared by the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition. It can be seen that the total thickness (d_{total}) of the high-K dielectric stacks is ~5.9, 9.4 and 5.2 nm, respectively, and the thickness (d_{NL}) is about 1.8 and 1.1 nm for the NLs prepared by the ozone-based process and the interfacial AlN deposition. Thus the thickness of the Al₂O₃ main layer (d_{main}) is ~4.1 nm, which can be deduced from Fig. 3(a) and (c). Accordingly, the thickness of the NL (d_{NL}) prepared by the low-T physical adsorption can be estimated to be ~5.3 nm, even though the interface between the NL and the Al₂O₃ main layer is not obvious in the TEM image (Fig. 3(b)) since the Al₂O₃ in both layers was prepared with the same H₂O-based process. Such a thick NL is attributed to precursor condensation on the MoTe₂ surface at a low deposition temperature along with a short purge time. Notice that an interface between the NL and MoTe₂ can be observed in Fig. 3(a) and the MoTe₂ lattice fringes.
are seen near the interface. Therefore, the layer underneath the NL might be a damaged MoTe₂ region with a thickness of \(\sim 1.1\) nm, resulting from high reactivity of the ozone-based process. The TEM images clearly demonstrate that continuous and uniform Al₂O₃ high-K dielectrics with a thickness below 10 nm can be achieved on MoTe₂ with the NLs prepared by the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition.

The CAFM measurement is illustrated schematically in Fig. 4, where a DC bias was applied to the \(p\)-type Si substrate and the AFM tip was scanned in the contact mode over the Al₂O₃ surface. Fig. 5 displays the mapping and the 3D CAFM topographies (Fig. 5(a)–(d)) of the leakage current through the Al₂O₃ high-K dielectrics on MoTe₂, and the statistical leakage current distributions (Fig. 5(a′)–(d′)), respectively, with the corresponding layer structure of each dielectric stack shown in Fig. 2(a′)–(d′). Fig. 5(a) shows that a large leakage current is present if Al₂O₃ was deposited directly on MoTe₂ at 200 °C without any NL, which is attributed to the island structure as shown in Fig. 2(a). The introduction of the NL between the Al₂O₃ main layer and MoTe₂ gives rise to a very low leakage current close to the noise level of CAFM, as shown in Fig. 5(b)–(d). The outcome clearly indicates that the continuous and uniform Al₂O₃ high-K dielectrics lead to a low leakage current as a result of the NLs prepared by the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition.

Because the chemical shift reveals the change in binding energies,
XPS has been extensively used for the interface characterization of TMDs. Fig. 6(a) and (b) show the Mo-3d and Te-3d XPS spectra of the as-exfoliated multilayer MoTe₂ and that covered with the high-K dielectric stack, respectively. As compared with the XPS spectra of the as-exfoliated MoTe₂, the NL prepared by the ozone-based process yields additional Mo-3d and Te-3d peaks at higher binding energies, which correspond to the Mo⁶⁺ (MoO₃) and Te⁴⁺ (TeO₂) states, respectively. The formation of MoO₃ and TeO₂ provides the nucleation sites for subsequent deposition of the continuous and uniform high-K layer [20,33]. However, MoO₃ and TeO₂ have wide bandgaps of ~3.1 eV [34] and ~3.3 eV [35], respectively, which are much higher than that of MoTe₂ [36]. Therefore, the electrical properties of MoTe₂ would be degraded by the MoTe₂ oxidation due to the band discontinuity [21].

Therefore, a NL formation process is required which prevents the oxidation of MoTe₂ during the ALD process. Please notice that the ozone-based ALD process does not result in the oxidation of MoS₂ [22], consistent with the high reactivity of MoTe₂ to oxidants. In contrast, the Mo-3d and Te-3d XPS spectra of the sample with the low-T physical adsorption NL is almost identical to those of the as-exfoliated MoTe₂. The XPS data is consistent with the absence of chemical reactions if the deposition of NL proceeds through the physical adsorption; therefore, the oxidation of molybdenum and telluride can be avoided by using the physical adsorption at low temperatures [37,38]. In the MoTe₂ sample with the AIN interfacial layer, the Mo—O peak is observed in the Mo-3d XPS spectrum, which is ~0.4 eV higher than the Mo—Te peak due to hybridization of the Mo-3d and N-2p orbitals [39–41]. In contrast to the Mo—O bond which is detrimental to the electrical characteristics of MoTe₂, previous studies have indicated that the Mo—N bonding does not cause the degradation of the electrical properties of Mo-based TMDs [27,39].

Table 2 lists the atomic ratio of Te to Mo (MoTex) of the as-exfoliated multilayer MoTe₂ and that covered with the high-K dielectric stack, which were obtained from the analysis of XPS spectra shown in Fig. 6. The tellurium content in MoTe₂ decreases significantly if the NLs are deposited by the ozone-based process and the interfacial AIN deposition, suggesting that tellurium might be removed by oxygen and nitrogen. Note that the tellurium content of the sample with the NL prepared by the low-T physical adsorption is the same as that of the as-exfoliated MoTe₂. The result is consistent with the inference from the XPS spectra, revealing the lack of chemical reactions at the MoTe₂ surface as the NL is deposited by the low-T physical adsorption.

Since Raman spectroscopy is a versatile tool to characterize TMDs structures [42–44], Raman spectra were measured for the as-exfoliated MoTe₂ and that covered with the NLs prepared by the ozone-based process, the low-T physical adsorption, and the interfacial AIN deposition, respectively (Fig. 7). The Raman peaks at ~235 cm⁻¹ and ~174 cm⁻¹ are associated with the $E_{2g}^1$ and $A_{1g}$ modes of bulk MoTe₂ [45]. As compared with exfoliated MoTe₂, no detectable variation in
the Raman peaks was observed as the NL was prepared by the low-T physical adsorption. It should be noted that even the MoTe2 and the ozone-based processes, which result in surface oxidation and nitridation as shown in the XPS spectra (Fig. 6), do not give rise to any obvious change in the Raman spectra. This result can be ascribed to the fact that both oxidation and nitridation occur only at the region close to the MoTe2 surface. Because the probed depth of Raman scattering (> ~1000 nm) is much deeper than that of XPS (~5 nm), XPS characterization is more sensitive to the surface oxidation and nitridation than Raman spectroscopy.

A comparison of the low-T physical adsorption method, which was performed on MoTe2 and MoS2, is provided and discussed as follows. Fig. S1 (a)(b) in Supplementary Materials display the AFM images and 3D topographies of the Al2O3 main layers together with the corresponding layer structures as schematically illustrated in Figs. S1 (a’)(b’), in which the NLs were prepared with the purge time of 1 and 2 s, respectively, on MoTe2. A decrease of the purge time from 2 to 1 s leads to a dramatic transformation of the Al2O3 main layer from a sporadic/pinhole-like structure (with a large RMS roughness of 2.65 nm) to a continuous film (with a low RMS roughness of 0.39 nm). A shorter purge time results in more residues of precursors/reactants on the MoTe2 surface, resulting in more physical adsorption of precursors/reactants. The precursors/reactants adsorbed on the TMD surface provide the nucleation sites for the subsequent Al2O3 deposition. Therefore, the shorter purge time, the more residues of precursors/reactants and nucleation sites, which lead to the formation of a continuous Al2O3 main layer. Fig. S2 (a)(b) and (a’)(b’) in Supplementary Materials show the AFM images and 3D topographies of the Al2O3 main layers and their layer structures on MoTe2 and MoS2, respectively. For the formation of a continuous Al2O3 main layer as shown in Figs. S2 (a) and (b), the required purge time (1 s) for the NL deposited on MoTe2 is shorter than that on MoS2 (5 s). If the precursors/reactants are difficult to adsorb on the TMD surface, a shorter purge time is needed to increase the residues of precursors/reactants. Therefore, Fig. S2 suggests that the physical adsorption of precursors/reactants on MoTe2 is more difficult than that on MoS2. The result indicates that the purge time is a critical processing parameter for the NLs prepared by the low-T physical adsorption technique on different 2D materials.

3. Conclusion

Continuous, uniform, low-leakage, and sub-10 nm Al2O3 high-K dielectrics on MoTe2 are demonstrated in this study through the nucleation engineering based on the ozone-based process, the low-T physical adsorption, and the interfacial AlN deposition. The CAFM measurement demonstrates that the introduction of the NL between the Al2O3 main layer and MoTe2 leads to significant reduction of the leakage current. Nevertheless, the oxidation of MoTe2 takes place as the NL was prepared by the ozone-based process, which is unfavorable to the device characteristics of MoTe2. Conversely, the low-T physical adsorption and the interfacial AlN deposition do not result in the oxidation of MoTe2 but instead the formation of a weakly interacting interface or a MoN interface, respectively; these two interfaces may be preferable for nucleation engineering of high-quality high-K gate dielectrics on MoTe2 transistors.

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