Direct Atomic Layer Deposition of Ultrathin Aluminum Oxide on Monolayer MoS$_2$ Exfoliated on Gold: The Role of the Substrate

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In this paper, the authors demonstrate the atomic layer deposition (ALD) of highly homogeneous and ultrathin (=3.6 nm) Al$_2$O$_3$ films with very good insulating properties (breakdown field of ≈10–12 MV cm$^{-1}$) directly onto monolayer (1L) MoS$_2$ exfoliated on gold. Differently than in the case of 1L MoS$_2$ supported by a common insulating substrate (Al$_2$O$_3$/Si), a better nucleation process of the high-$k$ film is observed on the 1L MoS$_2$/Au system. The ALD density on bilayer MoS$_2$ is found to be significantly reduced with respect to 1L MoS$_2$/Au, suggesting a role of screened interface charges with the metal substrate on the adsorption of ALD precursors. Finally, Raman and photoluminescence spectroscopy show a p-type doping and tensile strain of 1L MoS$_2$ induced by the Au underlayer can be of wide interest for electronic applications.

1. Introduction

Semiconducting transition metal dichalcogenides (TMDs), including MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, are currently widely investigated for next generation electronic and optoelectronic applications.[3–5] The deposition of high-$k$ dielectrics thin films (such as Al$_2$O$_3$ and HfO$_2$) on the TMDs surface represents a key requirement for the fabrication of electronic devices.[3–5] As an example, the deposition of a HfO$_2$ gate insulator (=30 nm thick) on top of monolayer (1L) MoS$_2$ represented the enabling step to demonstrate a field-effect transistor (FET) with excellent on/off ratio (=10$^9$), nearly ideal subthreshold swing (=70 mV dec$^{-1}$), and high room temperature electron mobility (>200 cm$^2$ V$^{-1}$ s$^{-1}$), due to the efficient reduction of charged impurities scattering because of the high-$k$ dielectric film.[6] Similarly, an Al$_2$O$_3$ top gate dielectric (=16 nm thick) was employed for the demonstration of a high mobility (=125 cm$^2$ V$^{-1}$ s$^{-1}$) multilayer MoS$_2$ transistor.[7]

In all these cases, the high-$k$ dielectric films were grown by the atomic layer deposition (ALD) technique,[8] commonly employed in microelectronics to obtain uniform and conformal insulating films with a subnanometric control of the thickness. Ideally, layer-by-layer deposition of ultrathin films requires the presence of a sufficiently high and uniform density of dangling bonds, necessary for precursor chemisorption on the sample surface in the early stages of the ALD process.[9,10] However, the inherent lack of out-of-plane bonds in 2D layered materials represents an obstacle for an ideal ALD growth, resulting in an inhomogeneous coverage especially for very thin (<10 nm) deposited films.[11,12] In this context, relatively thick high-$k$ films were employed in the first pioneering studies on MoS$_2$ transistors to achieve a uniform coverage of MoS$_2$ surface, thus minimizing the gate leakage current. However, the real application of MoS$_2$ FETs in next generation logic devices requires an aggressive scaling of the channel length and, consequently, of the high-$k$ dielectric thickness.[3] Hence, several strategies have been investigated in the last few years to improve the ALD growth on TMDs, by tailoring the process conditions and/or by appropriate prefunctionalization treatments of the surface. Many of these approaches were inspired by ALD growth...
experiments performed on graphene.[13–15] As an example, Park et al.[16] systematically investigated thermal ALD of Al₂O₃ using trimethyl-aluminium (TMA) as the Al precursor and water (H₂O) as co-reactant, on the surface of different TMDs, that is, MoS₂, WS₂, and WSe₂ multilayers. The deposition temperature (Tdep) and the TMA adsorption energy (Eads) on the TMDs surface were demonstrated to play a crucial role on the uniformity of the deposited Al₂O₃ (~10 nm) films. In particular, Eads, which is related to the substrate polarizability, was found to be larger for W- and Se-based TMDs (e.g., WS₂ and WSe₂) than for MoS₂. Furthermore, while inhomogeneous Al₂O₃ films (with a large density of pinholes) were obtained at typical Tdep from 200 to 250 °C, the coverage uniformity was highly improved by lowering Tdep to 150 °C, that is, reducing the desorption of the metal precursors from the MoS₂ surface.[10] A two-step ALD process,[6] consisting in the low temperature (80 °C) deposition of an ultrathin AlOx layer, followed by a second ALD step at higher temperature (180 °C), was also employed to obtain a homogeneous Al₂O₃ film with <10 nm total thickness on MoS₂.[17] Although the use of a reduced temperature at the beginning or during the whole ALD process can be beneficial to improve the coverage uniformity, it may result in a lower dielectric quality due to a reduced reactivity of the ALD precursors.[18] Another strategy to improve the ALD growth on MoS₂ surface has been to replace H₂O with a more reactive co-reactant, such as ozone (O₃), which allowed to obtain uniform Al₂O₃ layers (~5 nm thick) at a temperature of 200 °C.[19] Alternatively, an O₂-plasma pretreatment of multilayer MoS₂ surface, resulting in the formation of an ultrathin Mo-oxide layer, was shown to significantly improve the uniformity of the deposited Al₂O₃ or HfO₂ films as compared to the case of pristine MoS₂.[20] More recently, water plasma pretreatments of the MoS₂ surface have been used to create hydroxyl groups for conventional thermal ALD at 200–250 °C, resulting in the deposition of uniform Al₂O₃ films with thickness down to 1.5 nm.[21] In spite of these beneficial effects, the damage and chemical modifications introduced by these plasma pretreatments can affect the electronic transport in MoS₂ devices. Besides thermal ALD, plasma-enhanced ALD (PEALD) processes have also been recently investigated to grow very thin films (<5 nm) of Al₂O₃ and HfO₂ on MoS₂ samples with different layer numbers.[22,23] In particular, electrical characterization of 1L bilayer (2L), and trilayer MoS₂ back-gated transistors before and after HfO₂ PEALD revealed the occurrence of plasma damage, resulting in significant degradation of the electronic properties especially for 1L MoS₂.[23]

In addition to these processes involving a chemical modification of MoS₂ surface, non-covalent functionalization with thin organic (e.g., perylene derivatives)[24] or inorganic (e.g., SiO₂ nanoparticles)[25] seeding layers has also been explored to promote the thermal ALD growth of thin Al₂O₃ films on MoS₂. However, the use of these interlayers ultimately limits the minimum thickness of the dielectric and may affect the electrical quality of the interface. This short overview about ALD of high-k dielectrics on TMDs indicates that the seeding layers and prefunctionalization approaches explored so far present some disadvantages, while direct thermal ALD of ultrathin films would be highly desirable. In this respect, the interaction of atomically thin MoS₂ layers with the underlying substrate is expected to play an important role in the ALD nucleation stage, similarly to what observed for IL graphene residing on some specific substrates.[26,27] As an example, Dubak et al.[28] reported an enhanced Al₂O₃ nucleation on CVD-grown 1L graphene residing on the native metal substrates (Cu, Ni), that was ascribed to an improved ALD-precursor adsorption due the electrostatic effect of polar traps located at graphene/metal interface.[28,29] More recently, the uniform growth of ultrathin (~2.4 nm) Al₂O₃ films by direct thermal ALD (at 250 °C) on IL epitaxial graphene on 4H-SiC(0001) has been ascribed to the beneficial effect of the carbon buffer layer at the interface with the substrate.[10] To the best of our knowledge, analogous substrate effects on the ALD nucleation onto IL TMDs have not been reported so far.

In this paper, we investigated the ALD growth of ultrathin (3.6 nm) Al₂O₃ films on 1L MoS₂ produced by gold-assisted mechanical exfoliation from bulk crystals.[31–34] This method exploits the strong Au–S interaction to exfoliate large-area (cm²) MoS₂ membranes, predominantly formed by monolayers, on a gold substrate. These high crystalline quality membranes can be subsequently transferred on insulating substrates.[33,34]

Using identical ALD conditions on 1L MoS₂ membranes supported by gold (MoS₂/Au) or by Al₂O₃(100 nm)/Si substrate (MoS₂/Al₂O₃/Si), the typical inhomogeneous coverage by Al₂O₃ islands was observed in the case of the 1L MoS₂/Al₂O₃/Si system, whereas the formation of a highly uniform Al₂O₃ film (~3.6 nm thick) with very good insulating properties (breakdown field of 10–12 MV cm⁻¹) was observed on the 1L MoS₂/Au sample. This excellent uniformity is the result of an enhanced ALD nucleation on MoS₂ surface due to the interaction with Au substrate, giving rise to ~50% Al₂O₃ surface coverage after only 10 ALD cycles, and >90% coverage after 40 cycles. Further analysis by micro-Raman and micro-photoluminescence (PL) spectroscopy provided an insight on the substrate-related doping and strain of MoS₂/Au and MoS₂/Al₂O₃ samples, as well as on the effect of the ALD process on the vibrational and optical emission properties.

2. Results and Discussion

Figure 1a,b shows two representative atomic force microscopy (AFM) images of the Au/Ni/SiO₂ and Al₂O₃/Si starting substrates. A smooth surface morphology is observed in both cases, with similar root mean square roughness (RMS) values of 0.18 and 0.23 nm, respectively. Figure 1c,d shows two AFM images collected after exfoliation and transfer of MoS₂ on the Au/Ni/SiO₂ and Al₂O₃/Si substrates, respectively. For both samples, a region where the MoS₂ membrane was partially covering the substrate is shown, and the ~0.7 nm step height in the line profiles (insets of Figure 1c,d) confirms 1L MoS₂ thickness. Finally, two higher resolution morphological images of 1L MoS₂/Au and 1L MoS₂/Al₂O₃ are reported in Figures 1e and 1f, respectively, from which similar RMS values (0.17 and 0.18 nm) to those measured on the bare substrates were obtained.

Figure 2 shows the comparison between the AFM surface morphologies of Al₂O₃ simultaneously deposited at 250 °C by 80 ALD cycles on the surface of the 1L MoS₂/Al₂O₃/Si sample (a) and of the 1L MoS₂/Au sample (b), respectively. A high RMS roughness of 2.5 nm was observed for Al₂O₃ deposited on 1L MoS₂ supported by the Al₂O₃/Si substrate. This RMS value
is much larger than the ones of the original Al₂O₃ substrate (≈0.23 nm) and of 1L MoS₂ on Al₂O₃ (≈0.18 nm), indicating a very inhomogeneous coverage of 1L MoS₂ by the ALD grown Al₂O₃. This scenario, schematically depicted in Figure 2c, is consistent with the commonly reported island growth during direct thermal ALD on MoS₂ surface. In order to evaluate the Al₂O₃ coverage, the histogram of height distribution has been reported in Figure 2e. This histogram shows two components, related to bare and Al₂O₃-covered MoS₂ areas, from which >70% coverage and an average Al₂O₃ islands height of ≈4 nm were deduced. Differently, for 1L MoS₂ supported by the Au substrate (Figure 2b), a pinhole-free Al₂O₃ layer with a very flat morphology is observed after 80 ALD cycles. The deposited film exhibits a very narrow height distribution (Figure 2f) and low surface roughness (RMS = 0.25 nm), only slightly higher than the one measured on bare 1L MoS₂ on Au (RMS = 0.17 nm). Such morphological results suggest that, under identical process conditions, an enhanced Al₂O₃ nucleation occurs on the surface of 1L MoS₂ in contact with gold, resulting in the formation of a continuous Al₂O₃ film, as schematically depicted in Figure 2d.

In order to evaluate the thickness and the electrical insulating quality of the uniform Al₂O₃ film deposited on 1L MoS₂/Au, conductive AFM (C-AFM) morphology and current maps were simultaneously acquired by scanning the metal tip across a step between the Al₂O₃/1L MoS₂ stack and the underlying Au substrate, as schematically depicted in Figure 3a. Figure 3b shows a morphological image collected in the proximity of a crack in the 1L MoS₂ membrane. The growth of a uniform and compact Al₂O₃ film on 1L MoS₂ and a poor ALD growth on the bare Au surface can be deduced from this image. Furthermore, the height line-profile in Figure 3c displays a total thickness of the Al₂O₃/MoS₂ stack of ≈4.3 nm, from which a deposited Al₂O₃ thickness of ≈3.6 nm can be estimated, by subtracting the thickness of 1L MoS₂ on Au (≈0.7 nm).[34] The slightly increased height observed at the step edge can be ascribed to the folding of the broken 1L MoS₂ membrane. The electrical insulating properties of the 3.6 nm Al₂O₃ film deposited onto 1L MoS₂ on Au are demonstrated by the current map in Figure 3d, acquired by applying a bias of 3 V between the tip and the gold substrate. In particular, the line-profile in Figure 3e shows very low current values in the Al₂O₃/1L MoS₂ region, whereas the saturation value of the current sensor was reached on Au region. The current conduction in the region close to the step edge suggests lower insulating properties of Al₂O₃ deposited on the locally folded MoS₂ membrane.

To get further insight on the electrical insulating quality of the 3.6 nm Al₂O₃ film, local current–voltage (I–V) characteristics were acquired by the C-AFM tip on the Al₂O₃/1L MoS₂/Au stack. Figure 4a shows three representative I–V curves measured at different positions on the Al₂O₃ surface by ramping the bias from 0 to 5 V. While very low leakage current values are observed up to 3 V, an abrupt rise of current up to the compliance level (indicating a localized dielectric breakdown) occurs at bias values in the range from 3.7 to 4.5 V, depending on the local I–V curve. For the Al₂O₃ film thickness t_{ox} = 3.6 nm, these breakdown voltage (V_{BD}) values correspond to breakdown electric fields (E_{BD} = V_{BD}/t_{ox}) of ≈10–12 MV cm⁻¹. These values are comparable to those reported for the state-of-the-art high-k dielectrics with similar equivalent oxide thickness deposited by ALD on MoS₂.[35] The localized nature of the breakdown events is further confirmed by the current map in Figure 4b, acquired on the surface of the Al₂O₃/1L MoS₂/Au stack while changing the bias from 3 V (in the upper part of the image) to 4 V (in the middle part) and then back to 3 V (bottom part). An increase of the leakage current level is observed when increasing the bias from 3 to 4 V, with the appearance of conduction instability and some localized breakdown spots. After reducing the bias down to 3 V (bottom part of the image), the current level becomes identical to the one in the upper part, confirming the localized character of the breakdown behavior.

After demonstrating the formation of a compact ≈3.6 nm Al₂O₃ insulating film on top of 1L MoS₂/Au by 80 ALD cycles at 250 °C, we investigated the film nucleation and growth stages by AFM analyses performed after a reduced number of ALD cycles at the same temperature. Figure 5a,d shows the tapping mode morphological images acquired on 1L MoS₂/Au samples after 10 and 40 ALD cycles, respectively. The AFM analysis of the sample after 80 ALD cycles is also reported in Figure 5g for comparison.
particular, after ten cycles, a very irregular and ultrathin coating can be deduced from the morphological image, resulting in a \( \text{RMS} \approx 0.4 \) nm, slightly higher than the \( \approx 0.17 \) nm value measured on the bare 1L MoS\(_2\)/Au sample. On the other hand, a grain-shaped morphology (\( \text{RMS} \approx 0.6 \) nm) of the deposited Al\(_2\)O\(_3\) film can be clearly observed after 40 ALD cycles (see Figure 5d), suggesting the occurrence of 3D growth of Al\(_2\)O\(_3\) islands on top of the inhomogeneous nucleation layer formed at lower number of cycles. Finally, a flat surface morphology (\( \text{RMS} \approx 0.25 \) nm) is observed after 80 ALD cycles (Figure 5g). A quantification of the coverage percentage is very difficult from these morphological images. On the other hand, the Al\(_2\)O\(_3\)-coated and uncoated 1L MoS\(_2\) areas can be clearly distinguished in the corresponding AFM phase maps (Figure 5b,e,h), as the phase signal is known to be very sensitive to the surface properties of materials. In particular, the red and black contrast in these three images corresponds to the Al\(_2\)O\(_3\)-covered and

Figure 2. AFM morphologies of Al\(_2\)O\(_3\) simultaneously deposited at 250 °C by 80 ALD cycles on the surface of the a) 1L MoS\(_2\)/Al\(_2\)O\(_3\)/Si sample and of the b) 1L MoS\(_2\)/Au sample. The root mean square (RMS) roughness values of the two samples are indicated. c,d) Schematic illustrations of the configurations of the deposited Al\(_2\)O\(_3\) on 1L MoS\(_2\)/Al\(_2\)O\(_3\)/Si and 1L MoS\(_2\)/Au. e) Histogram of the height distribution obtained from the AFM map of Al\(_2\)O\(_3\) on 1L MoS\(_2\)/Al\(_2\)O\(_3\)/Si, from which \( \approx 70\% \) Al\(_2\)O\(_3\) coverage and an average height of \( \approx 4 \) nm of Al\(_2\)O\(_3\) islands were evaluated. f) Histogram of the height distribution for Al\(_2\)O\(_3\) on 1L MoS\(_2\)/Au.

Figure 3. a) Schematic of the step between the Al\(_2\)O\(_3\)/1L MoS\(_2\) stack and the underlying Au substrate and of the circuit used for C-AFM measurements. b) AFM image and c) height line-profile of the step, from which a deposited Al\(_2\)O\(_3\) with thickness of \( \approx 3.6 \) nm was estimated, after subtracting 1L MoS\(_2\) thickness (~0.7 nm). d) C-AFM current map simultaneously acquired with a bias \( V = 3 \) V and e) current profile, demonstrating a good insulating quality of the deposited Al\(_2\)O\(_3\) film onto 1L MoS\(_2\) on Au.

Figure 4. a) Local current–voltage (I–V) characteristics collected at different positions on the Al\(_2\)O\(_3\)/MoS\(_2\)/Au stack, showing current breakdown at biases between 3.7 and 4.5 V. b) C-AFM current map collected on the Al\(_2\)O\(_3\)/MoS\(_2\)/Au stack at bias values of 3 V (upper region), 4 V (middle region), and 3 V (bottom region). A significant increase of the current leakage, with the appearance of localized breakdown spots is observed at 4 V.
uncovered 1L MoS₂, respectively. Furthermore, the histograms of the phase distribution extracted from the three maps are reported in Figure 5c,f,i, from which an Al₂O₃ coverage percentage of 50%, 93%, and 100% were evaluated after 10, 40, and 80 ALD cycles, respectively. The very high coverage after only 40 ALD cycles, corresponding to \( \approx 1.4 \) nm Al₂O₃ thickness (measured by an AFM step-height analysis as in Figure 3b), demonstrates a very good nucleation on Au supported 1L MoS₂.

Interestingly, the coverage degree of ALD grown Al₂O₃ was found to be strongly dependent on the number of MoS₂ layers. Figure 6a,b shows typical AFM morphology and phase maps measured on the as-exfoliated MoS₂/Au sample including 1L and 2L MoS₂ regions. The two regions exhibit similar surface roughness and the same uniform phase signal. Figure 6c,d shows the morphology (c) and phase images (d) collected in a 1L/2L area of the MoS₂/Au sample after 40 ALD cycles. A very different Al₂O₃ coverage can be clearly observed (especially in the phase image) on 1L and 2L MoS₂, with a much denser Al₂O₃ nucleation on 1L than on the 2L MoS₂.

The above-illustrated experimental phenomena, that is, the enhanced Al₂O₃ nucleation on 1L MoS₂ supported by Au and its reduction on 2L regions, exhibit close similarities to reported ALD growth on CVD graphene on metals (Ni and Cu)[26] and on epitaxial graphene on 4H-SiC. In the first case, the optimal Al₂O₃ nucleation on 1L graphene during thermal ALD with H₂O and TMA precursors was ascribed to the enhanced adsorption of the polar H₂O molecules due to the electrostatic field generated by charged dipoles located at graphene/metal interface.[26] In the case of epitaxial graphene on 4H-SiC, the electrostatic field due to charges at buffer layer/SiC interface was found to play a similar role.[27] In both cases, the intensity of this electrostatic field was drastically reduced in 2L graphene, due to the screening effect, resulting in a less homogeneous Al₂O₃ growth. A similar mechanism can be considered in the present case to explain the Al₂O₃ nucleation on 1L and 2L MoS₂ supported by Au. Furthermore, the significant tensile strain experienced by the 1L MoS₂ membrane exfoliated on Au can also play an important role, as discussed in the following.
Micro-Raman spectroscopy analyses have been performed to investigate the strain and doping status of 1L MoS₂ residing on Au and Al₂O₃ substrates before and after the ALD growth. Figure 7 reports two representative Raman spectra for as-exfoliated 1L MoS₂ on Au (reference) and after 80 TMA/H₂O ALD cycles, resulting in the homogeneous ≈3.6 nm Al₂O₃ film deposition shown in Figure 3b. The corresponding Raman spectra for 1L MoS₂ transferred onto the Al₂O₃/Si substrate (reference) and after the 80 ALD cycles are shown in Figure 7b. From the comparison of the reference spectra on the two substrates, a significantly higher separation Δω between the in-plane (E') and out-of-plane (A₁') vibrational peaks is observed for 1L MoS₂ on Au (Δω = 21 cm⁻¹) as compared to the case of 1L MoS₂ on Al₂O₃/Si (Δω = 18 cm⁻¹). Such a difference is due to significant red-shift of the E' peak (mostly associated to the strain) and to a slight blue-shift of the A₁' peak (mostly related to the doping) for 1L MoS₂ membrane on gold. This is a typically observed behavior originating from the strong S–Au interaction, although slightly different Δω values (Δω ≈ 20 cm⁻¹) have been reported in other literature reports, probably due to different quality of the MoS₂/Au interface.[31,32]

Interestingly, the E' peak red-shift is further increased and the A₁' peak blue-shift is slightly reduced after ALD of the uniform Al₂O₃ film on the gold-supported membrane. On the other
hand, only a slight red-shift of the A’ peak was observed after 80 ALD cycles on the Al2O3-supported IL MoS2, probably due to the inhomogeneous Al2O3 coverage (as shown in Figure 2a). In order to achieve a quantification of the strain, ε (%), and doping, n (cm⁻²), for the IL MoS2 membranes on the two different substrates before and after the ALD process, a correlation analysis of the A’ versus E’ peak frequencies has been carried out in Figure 7c, according to the procedure recently discussed in ref. [34]. The red and black lines in Figure 7c represent the theoretical behavior of the peaks’ frequencies for IL MoS2 subjected only to a biaxial strain (tensile or compressive) or to doping (n-type or p-type), respectively. The crossing point (grey square) of these lines corresponds to literature values of the E’ and A’ positions for a free-standing IL MoS2, taken as the best approximation for ideally unstrained and undoped MoS2. The spacing of the dashed lines parallel to the ideal strain and doping lines is associated with carrier density changes of 0.1 × 10¹³ cm⁻² and strain changes of 0.1%, respectively. The black point is the average value of the A’ versus E’ frequencies from several (>20) Raman spectra measured on the reference 1L MoS2/Au sample, whereas the error bars are the standard deviations from this statistical analysis. The magenta point is the average value obtained from Raman analyses on several points of the reference 1L MoS2/Al2O3 sample. For this sample, the A’ frequency exhibits a significant dispersion (indicated by the error bar), whereas the small E’ frequency dispersion is within the data point. According to the graphical analysis in Figure 7c, the reference 1L MoS2/Au sample is characterized by an average tensile strain of ε = 0.21% and p-type doping of n = −0.25 × 10¹³ cm⁻², whereas an opposite compressive strain ε = −0.25% and n-type doping n = 0.5 × 10¹³ cm⁻² are observed for 1L MoS2 transferred onto the Al2O3/Si substrate. Such n-type behavior is consistent with the unintentional doping type commonly reported for exfoliated or CVD-grown MoS2, which has been associated to the presence of defects (e.g., sulfur vacancies) or to other impurities in the MoS2 lattice.[36,37] In the case of 1L MoS2 on Au, a strong electron transfer to the substrate is guessed, which overcompensates the native n-type doping, resulting in a net p-type behavior.[34,38] This is consistent with several literature reports showing a transition from n- to p-type doping for MoS2 layers functionalized with an AuCl₄ solution.[38] single Au atoms,[40] Au thin films,[41] as well as for MoS2 deposited by gold nanoparticles-assisted CVD.[42]

The tensile strain for 1L MoS2 on Au can be assigned to the lattice mismatch between MoS2 and the Au surface, mostly exposing (111) orientation.[43,44] According to recent literature reports, tensile strain of 1L MoS2 is responsible of an enhanced reactivity on the basal plane, specifically at sulfur (S) vacancy sites.[45] Hence, the observed tensile strain of 1L MoS2 exfoliated on Au substrates, combined with the presence of a very high density of native S vacancies in the material,[46] can also contribute to the enhanced Al2O3 nucleation during the early stages of thermal ALD. Furthermore, recent investigations of the vibrational properties for MoS2/Au samples with variable MoS2 thickness showed a significantly reduced effect of the MoS2/Au interaction on 2L MoS2 as compared to 1L samples.[48] These results would contribute further to explain the lower reactivity of 2L MoS2/Au during the early stage of Al2O3 growth, as observed in Figure 6c.d.

Noteworthy, the blue point in Figure 7c obtained from Raman analyses after 80 ALD cycles on 1L MoS2/Au indicates a further increase of the tensile strain (ε ≈ 0.65%), as compared to the original value of 0.21%, which can be associated to the formation of a compact Al2O3 film on top of MoS2. On the other hand, no significant changes with respect to the original p-type doping value were observed after the ALD growth, confirming that the doping status of the film is strongly dominated by the strong Au–1L MoS2 interaction. Finally, the data-point for the 1L MoS2/Al2O3 sample after the 80 ALD cycles indicates no significant changes in the tensile strain, consistently with the highly inhomogeneous Al2O3 coverage, and an increase of the n-type doping to n = 0.6 × 10¹³ cm⁻². This latter can be ascribed to positively charged defects[47] at the interface between the poor quality Al2O3 film and 1L MoS2.

Raman analyses clearly show very different strain and doping properties of 1L MoS2 residing on the Au and Al2O3/Si substrates, which finally result in the growth of different quality Al2O3 films after ALD deposition.

In Figure 8, micro-PL spectra acquired on the two reference 1L MoS2 samples and after 80 cycles ALD growth are also reported, to further elucidate the impact of the substrate and of the deposition process on the optical emission properties of the direct bandgap 1L MoS2 membrane.

A prominent emission peak located at 1.84 eV can be observed for 1L MoS2 supported by Al2O3/Si, whereas a significant reduction of the PL intensity accompanied by the red-shift of the main peak position at 1.79 eV is found for the reference sample on Au. A similar quenching of the PL intensity has been reported for 1L MoS2 exfoliated on Au[34,48] and for MoS2 functionalized with Au nanoparticles.[49] This behavior can be explained in terms of a preferential transfer of photoexcited charges from MoS2 to Au. In addition, the tensile strain of 1L MoS2 in contact with Au can also play a role in the reduction of the PL yield.[49] After 80 ALD cycles, only a small reduction of the PL intensity was observed for the 1L MoS2/Al2O3 sample, which can be explained by the highly inhomogeneous Al2O3 coverage and by the small interaction of MoS2 with the dielectric substrate. On the other hand, further quenching of the PL intensity was found in the case of 1L MoS2/Au sample covered by the ~3.6 nm uniform Al2O3 film. This observation can be consistent with the increase of the tensile strain observed by Raman analyses and with the
increase of the interaction with the Au substrate due to the material added on top of MoS$_2$.

3. Conclusion

In conclusion, we have demonstrated the direct thermal ALD growth at 250 °C of highly homogeneous and ultrathin (~3.6 nm) Al$_2$O$_3$ films with excellent insulating properties onto a 1L MoS$_2$ membrane exfoliated on gold. Differently from the case of 1L MoS$_2$ supported by a common insulating substrate (Al$_2$O$_3$/Si), an enhanced nucleation of the high-k films was observed on the 1L MoS$_2$/Au system since the early stages of the ALD process, with the Al$_2$O$_3$ surface coverage increasing from ≈50% (after only 10 ALD cycles) to >90% (after 40 cycles). The coverage percentage was found to be significantly reduced in the case of 2L MoS$_2$/Au, indicating a crucial role of the S–Au interaction at the interface in the observed phenomena. Raman spectroscopy and PL analyses provided an insight about the role played by the tensile strain and p-type doping of 1L MoS$_2$ induced by the gold substrate on the enhanced high-k nucleation on MoS$_2$ surface.

The demonstrated high-quality ALD growth of high-k dielectrics on large-area 1L MoS$_2$ produced by the Au-assisted exfoliation can find important device applications, including the fabrication of FETs or the passivation of non-volatile switching memory devices based on Au/1L MoS$_2$/Au junctions. The development of an optimized transfer of the Al$_2$O$_3$/1L MoS$_2$ stack from Au to insulating or semiconductor substrates will represent a key enabling step for some of these technologies.

4. Experimental Section

The gold substrate used for MoS$_2$ mechanical exfoliation was prepared by sequentially depositing a 10 nm Ni adhesion layer and a 15 nm Au film with DC magnetron sputtering on top of a SiO$_2$/Si sample. MoS$_2$ exfoliation was performed by pressing a bulk molybdenite (2H-MoS$_2$) stamp on the surface of a freshly prepared Au/Ni/SiO$_2$ sample, in order to avoid the adsorption of contaminants (e.g., adventitious carbon) on Au surface, which would reduce the 1L MoS$_2$ exfoliation yield. This process results in a large area mostly composed by 1L MoS$_2$ with some 2L regions identified by optical contrast, AFM, and Raman spectroscopy.

The Al$_2$O$_3$/Si substrate used for transferring the Au-exfoliated MoS$_2$ was prepared by DC-pulsed RF reactive sputtering of 100 nm Al$_2$O$_3$ on a Si wafer. The transfer procedure of the large-areas MoS$_2$ membranes from gold to the insulating substrate is discussed in details in ref. [34].

Thermal ALD of Al$_2$O$_3$ thin films on MoS$_2$ was carried out in a PE-ALD LL SENTECH Instruments GmbH reactor, using TMA and H$_2$O as the aluminum precursor and cocurrent, respectively. All depositions were carried out at a temperature of 250 °C and with a pressure of 10 Pa. Initially, a process consisting of 80 ALD cycles was simultaneously carried out on both 1L MoS$_2$/Au and 1L MoS$_2$/Al$_2$O$_3$/Si systems, to compare the Al$_2$O$_3$ coverage uniformity. After observing the beneficial effect of the Au substrate on the uniformity of the Al$_2$O$_3$ growth on 1L MoS$_2$, the nucleation and growth mechanisms on the 1L MoS$_2$/Au were investigated in more details, by performing shorter ALD processes (10 and 40 deposition cycles). To assess the reproducibility of the results, the ALD growth experiments were performed on several (>10) sets of MoS$_2$/Au and MoS$_2$/Al$_2$O$_3$/Si samples prepared during different runs.

The surface roughness, coverage fraction, and thickness of the deposited Al$_2$O$_3$ on MoS$_2$ were evaluated by tapping mode AFM, morphology, and phase, using a DI3100 equipment by Bruker with Nanoscope V electronics. Sharp silicon tips with a curvature radius of 5 nm were used for these measurements. Furthermore, the electrical insulating properties of the very thin Al$_2$O$_3$ films deposited on 1L MoS$_2$/Au were evaluated by C-AFM analyses using the TUNA module and Pt-coated silicon tips.

Micro-Raman spectroscopy and micro-PL measurements of MoS$_2$ on the different substrates before/after the ALD growth of Al$_2$O$_3$ were carried out using a Horiba HR-Evolution micro-Raman system with a confocal microscope (100× objective) and a laser excitation wavelength of 532 nm.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

atomic force microscopy, atomic layer deposition, conductive atomic force microscopy, MoS$_2$, photoluminescence, Raman spectroscopy

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