

Review

Substrate-Driven Atomic Layer Deposition of High- κ Dielectrics on 2D Materials

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Abstract: Atomic layer deposition (ALD) of high- κ dielectrics on two-dimensional (2D) materials (including graphene and transition metal dichalcogenides) still represents a challenge due to the lack of out-of-plane bonds on the pristine surfaces of 2D materials, thus making the nucleation process highly disadvantaged. The typical methods to promote the nucleation (i.e., the predeposition of seed layers or the surface activation via chemical treatments) certainly improve the ALD growth but can affect, to some extent, the electronic properties of 2D materials and the interface with high- κ dielectrics. Hence, direct ALD on 2D materials without seed and functionalization layers remains highly desirable. In this context, a crucial role can be played by the interaction with the substrate supporting the 2D membrane. In particular, metallic substrates such as copper or gold have been found to enhance the ALD nucleation of Al_2O_3 and HfO_2 both on monolayer (1 L) graphene and MoS_2 . Similarly, uniform ALD growth of Al_2O_3 on the surface of 1 L epitaxial graphene (EG) on SiC (0001) has been ascribed to the peculiar EG/SiC interface properties. This review provides a detailed discussion of the substrate-driven ALD growth of high- κ dielectrics on 2D materials, mainly on graphene and MoS_2 . The nucleation mechanism and the influence of the ALD parameters (namely the ALD temperature and cycle number) on the coverage as well as the structural and electrical properties of the deposited high- κ thin films are described. Finally, the open challenges for applications are discussed.

Keywords: ALD; high- κ ; 2D materials; graphene; MoS_2 ; substrate effect



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1. Introduction

Two-dimensional (2D) materials such as semi-metallic graphene and the semiconducting transition metal dichalcogenides (TMDs) have been the object of intensive research investigations in the last 15 years due to their wide range of potential applications in electronics, optoelectronics, and sensing. As an example, the excellent carrier mobility (10^3 – 10^5 cm^2/Vs) [1] and micrometer electron mean free path [2] of graphene have been exploited in the demonstration of high-frequency (100–300 GHz) transistors [3,4], for which the low on/off current ratio (due to the lack of an energy bandgap) represents a minor issue. On the other hand, semiconducting TMDs (including MoS_2 , WS_2 , MoSe_2 , and WSe_2) are currently regarded as the most suitable channel materials for ultra-thin body field effect transistors to be employed in next-generation logic or switching applications [5,6]. As an example, transistors with high on/off current ratios (10^6 – 10^8) and low subthreshold swings ($\text{SS} \approx 70$ meV/decade) [7,8] have been fabricated using monolayer (1 L) MoS_2 (with a direct bandgap of 1.8 eV) or multilayer MoS_2 (with an indirect bandgap of 1.2 eV) [9,10].

Practical implementation of electronic devices based on 2D materials requires their combination with high- κ dielectrics, such as Al_2O_3 , HfO_2 , and ZrO_2 . In the case of top-gated field effect transistors with graphene or MoS_2 channels, high- κ gate insulators are necessary for efficient electrostatic control of the lateral source-to-drain current while minimizing the gate leakage phenomena [11–13]. Furthermore, the encapsulation of the monolayer or multilayers of MoS_2 with high- κ dielectrics has been demonstrated to be

highly beneficial in the improvement of the field effect mobility up to $200\text{--}500\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ due to the efficient reduction of charged impurity scattering [7,8,14]. Obviously, with the scaling down process which invests the electronic field, most of these applications require high- κ dielectrics in the form of uniform and ultra-thin layers. Aside from conventional field effect transistor structures, novel device concepts and architectures also require the integration of high-quality and ultra-thin insulators on the surfaces of 2D materials [15,16]. As an example, the recently investigated graphene-base hot electron transistors (GBHETs) for THz electronics require the integration of an ultra-thin insulator on graphene working as a base collector tunnel barrier for vertical transport [17–19]. Furthermore, graphene sensors may involve high- κ deposition on graphene as a functional layer toward specific chemical and biological molecules [20].

In this context, the atomic layer deposition (ALD) is the most appropriate technique for the growth of ultra-thin layers, with accurate control of the thickness and surface coverage. However, the surface of pristine 2D materials is chemically inert toward the chemical reactions involved in the ALD process, typically resulting in inhomogeneous coverage by the deposited films. To overcome this inherent issue, several approaches have been investigated in order to promote ALD growth on 2D crystals, including the predeposition of seed layers and surface activation via chemical treatments. As a matter of fact, these methods present advantages and disadvantages, ultimately affecting the final performance of graphene or MoS_2 devices. Hence, the direct (i.e., pre-functionalization and seed layer-free) ALD growth of high- κ dielectrics on the pristine surface of 2D materials still remains highly desirable and has been the object of investigation in recent years. As an alternative to surface pretreatments of 2D materials, some research groups recently considered the possibility of exploiting their peculiar interaction with the underlying substrate as a way to enhance the ALD nucleation process. As an example, Dlubak et al. [21] demonstrated the direct ALD growth of uniform Al_2O_3 layers on 1 L graphene as grown by CVD on metal substrates (Cu and Ni-Au). More recently, Schilirò et al. [22] showed the deposition of highly homogeneous and ultra-thin Al_2O_3 films by direct thermal ALD on 1 L MoS_2 supported by a gold (Au) substrate. In both cases, the high-quality ALD growth was explained by the enhanced adsorption of the ALD precursor molecules on 1 L graphene or MoS_2 surfaces during the nucleation stage. This was ascribed, in part, to the action of electrostatic fields induced by charges at the interface with the metal substrate [23,24], as well as the partial transparency of the atomically thin 2D materials to the electric fields [25]. Such a beneficial role of 2D material and substrate interaction on the high- κ nucleation in ALD processes is not limited to the case of metal substrates. In fact, the direct ALD growth of uniform Al_2O_3 films has also been recently reported for 1 L epitaxial graphene on SiC (0001), and it has been ascribed to the electrostatic effect of positively charged dangling bonds related to the buffer layer at the graphene/SiC interface [26,27].

While the state of the art of ALD on 2D materials has been the object of different comprehensive review papers in recent years [28–30], a dedicated review article on the direct ALD growth of high dielectrics driven by the 2D material and substrate interaction is still missing. The aim of the present work is to provide an overview in this research topic. After a discussion on the advantages and disadvantages of the conventional approaches (seed layer and pre-functionalization treatments) used to promote ALD growth on graphene and TMDs, this paper will focus on the direct thermal ALD of high- κ dielectrics (mainly Al_2O_3 and HfO_2) on CVD graphene on Cu (or Ni), on epitaxial graphene on 4H-SiC (0001), and on exfoliated MoS_2 on gold. The role of the interaction with the underlying substrate and the relevant process parameters (i.e., the ALD temperature and number of cycles) on the coverage will be discussed. Furthermore, the morphological and electrical properties of the grown high- κ layers will be illustrated. Finally, the current status and open challenges for applications of the high- κ /2D material systems will be critically examined.

2. Atomic Layer Deposition on 2D Materials

The ALD is the most suitable deposition technique for the growth of ultra-thin and conformal dielectric layers on a substrate. The key strength of ALD is related to its peculiar deposition mechanism. It is based on sequential and self-limited chemical reactions between the properly selected chemical precursors and the active sites of the substrate surface, which results in the so-called layer-by-layer growth mode (see Figure 1a). This characteristic principle of growth allows for obtaining uniform, conformal, and pinhole-free depositions with angstrom-level control of the thickness in a large area [31]. However, ALD implementation on a pristine surface of graphene and other 2D materials is a difficult task due to the lack of dangling bonds working as active sites or functional groups for the adsorption of ALD precursors (as depicted in Figure 1b). The main consequence of this feature is a lack of deposition or the formation of inhomogeneous films (e.g., see the image of ALD- Al_2O_3 on the pristine MoS_2 surface in Figure 1c).

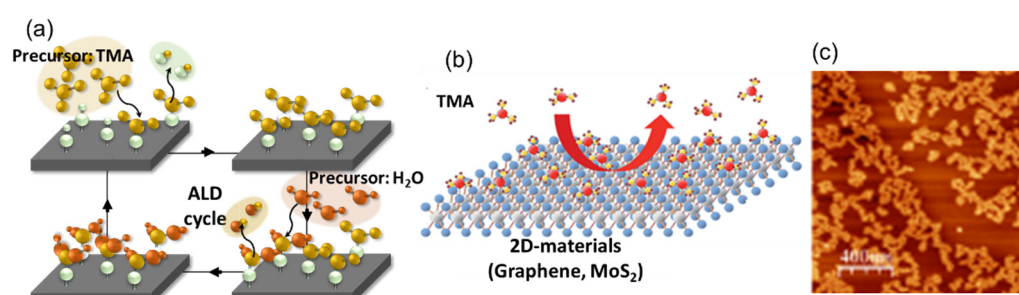


Figure 1. (a) Schematic of a typical cycle in ALD growth. (b) Schematic diagram showing the adsorption and desorption processes of a TMA precursor during the ALD deposition of Al_2O_3 on the 2D materials [32]. (c) AFM image of the ALD- Al_2O_3 layer deposited on a pristine MoS_2 surface [33].

2.1. Methods to Promote ALD Growth on 2D Materials

To date, a wide variety of processes has been reported to promote ALD nucleation on 2D layered materials, which finally results in the deposition of uniform dielectric layers. Table 1 reports a selection of the literature results for different types of 2D materials, with the indication of the used surface activation for ALD, the deposited high- κ insulator, its thickness and uniformity, and eventual damage introduced in the 2D material by the ALD process.

Table 1. ALD deposition of high- κ dielectrics on 2D materials.

Ref	2D Material	ALD Process				
		ALD Activation	T _{ALD} (°C)	High-κ Type	Uniformity	2D Damage
Seed layer deposition						
[34]	CVD-graphene on SiO ₂	3,4,9,10-perylene tetracarboxylic acid (PTCA)	100 °C	Al ₂ O ₃ , ~2 nm	High	Not
[35]	CVD-graphene on SiO ₂	Poly(4-vinylphenol) (PVP)	—	Al ₂ O ₃ , 20 nm	High	Not
[36]	CVD-MoS ₂ and CVD-WS ₂	Perylene bisimide	80 °C	Al ₂ O ₃ , ~3 nm	High	Not
[37]	Exfoliated graphene	Evaporated Al	250 °C	Al ₂ O ₃ , ~3 nm	High for seed layer > 1.2 nm	Not
[38,39]	CVD-MoS ₂	Al	150 °C	ZrO ₂ , ~15 nm		Not
[40]	MoS ₂ by sulfurization of Mo	SiO ₂ nanoparticles	300 °C	Al ₂ O ₃ , 5.7 nm HfO ₂ , 2.8 nm	High	Not
[41]	Exfoliated graphene	Seed layer of H ₂ O-assisted dielectric at low temperature (100 °C)	100 °C	Al ₂ O ₃ , ~11 nm	High	Not
[42]	Transferred CVD-graphene on SiO ₂	Seed layer of H ₂ O-assisted dielectric at low temperature (100 °C)	250 °C	Al ₂ O ₃ , ~22 nm	High	Not
[43]	Exfoliated MoS ₂	Seed layer of H ₂ O-assisted dielectric at low temperature (80 °C)	180 °C	Al ₂ O ₃ , <10 nm	High	Not
[44]	Exfoliated WS ₂	Evaporated Al	95 °C	HfO ₂ , ~20 nm	High	Not

Table 1. Cont.

Ref	2D Material	ALD Process				
		ALD Activation	T _{ALD} (°C)	High-κ Type	Uniformity	2D Damage
		Chemical functionalization				
[45]	Exfoliated graphene	NO ₂	250 °C	Al ₂ O ₃ , ~12 nm	High	Current and mobility degradation
[46]	Exfoliated graphene	O ₃ (25–200 °C)	200 °C	Al ₂ O ₃ , ~15 nm	High	Significant defect amount during O ₃ treatment at 200 °C
[33]	Exfoliated MoS ₂	O ₃ (30°)	200 °C	Al ₂ O ₃ , ~5 nm	High	Not
[47,48]	HOPG	O ₃ (25°)	200 °C	Al ₂ O ₃ , ~10 nm	High	Damage to 2D crystal
[49]	Exfoliated MoSe ₂ , WSe ₂	UV-O ₃	200 °C	HfO ₂ , ~4 nm	High on MoSe ₂ Low on WSe ₂	Partial etching of the 2D layers
[50]	Exfoliated MoS ₂	O ₂ -plasma	250 °C	Al ₂ O ₃ , ~10 nm HfO ₂ , ~10 nm	High	MoS ₂ oxidation
[51]	Transferred CVD-graphene	O ₂ -plasma	100 °C	Al ₂ O ₃ , ~10 nm	High	Significant amount of defects
[52]	Exfoliated graphene	N ₂ -plasma	—	Al ₂ O ₃ , ~28 nm	High	Significant amount of defects and reduced conductivity
		ALD parameter tuning				
[53]	Exfoliated graphene	Low-temperature ALD process	80–150 °C	Al ₂ O ₃	High (98%) at 80 °C	Not
[32]	Exfoliated MoS ₂ , WS ₂ , WSe ₂ , h-BN	Low-temperature ALD process	150 °C	Al ₂ O ₃ , 1, 10 nm	Variable as the 2D polarizability (WSe ₂ < WS ₂ < MoS ₂ < h-BN)	Not
[54]	Exfoliated HOPG and MoS ₂	Low-temperature ALD process	50 °C	Al ₂ O ₃ , few nm	High	Not
[53]	CVD graphene on Cu	Long or multiple precursor pulses	200 °C	Al ₂ O ₃ , few nm	Variable	Not

From the historical point of view, most of these approaches have been developed for graphene [35,37,55,56], and many of them have been adapted to other layered materials, such as TMDs [36]. These processes can be grouped into two categories:

- (i) Predeposition of a seed-layer;
- (ii) Chemical pre-functionalization.

The seed layers can be of both an organic nature, such as self-assembled monolayers (SAM) [34,57] or spin-coated polymers layers [35,36,55], and an inorganic nature, such as sputtered or evaporated metal or metal oxide films [37–39,56] or SiO₂ nanoparticles [40]. They can be pre-deposited “ex situ” (i.e., outside the ALD reactor chamber) and also “in situ” (i.e., within the reactor), like in the case of low temperature H₂O-assisted dielectric seed layer growth on the surface of graphene [41,42].

The seed layer approach proved to be an efficient and widely used method to promote the subsequent ALD growth process on graphene and TMDs. Typically, the spin-coating, self-assembling, and physical deposition methods (e.g., evaporation) used to deposit seed layers result in limited damage to the 2D membranes. However, from the electrical point of view, poor interface quality between the seed layer and 2D materials can result in a high-density interface or near-interface traps, ultimately compromising the performances of the final device. On the other hand, the metal seed layer deposition has been found to be beneficial for protecting the structural and electrical properties of the 2D material from the following ALD process. In particular, recent reports on the ALD deposition of ZrO₂ on MoS₂ [38,39] demonstrated that the Al seed layer reduces the oxidation effect of the 2D material by the co-reactant (H₂O, O₃) during the ALD process, mainly for the O₃-based method. Moreover, the introduction of a seed layer limits the minimum achievable thickness of the high-κ film, and this can represent a serious concern for the downscaling of 2D material-based transistors.

Chemical pretreatments of a 2D material surface, such as exposure to NO₂ [45], O₃ [33,46–48] or O₂-plasma [50,51], and N₂-plasma [52], introduce functional groups or dangling bonds, enabling the ALD nucleation and growth of high-κ dielectrics. These approaches allow, in principle, the growth of ultra-thin insulating films, but at the same time, they can introduce defects in the 2D layer, degrading its electronic properties.

Aside from the seeding layer and chemical pretreatments, the ALD process conditions (e.g., the deposition temperature and the pulse and purge times) can play a key role in achieving uniform coverage of a 2D material’s surface. ALD depositions of Al₂O₃ or HfO₂

are typically carried out in a temperature window from 200 to 300 °C, which ensures the optimal reaction of the precursors. However, lower deposition temperatures allow higher physisorption of the precursors on the graphene or TMD surface, improving ALD nucleation [32,41,53]. As an example, Aria et al. [53] demonstrated improved coverage and uniformity of deposited films on graphene within a temperature window of 80–100 °C for both Al₂O₃ and HfO₂ materials. In particular, optimized ALD coverage (up to 98%) was demonstrated using prolonged pulse times (>2 s) [53].

Recently, Park et al. [32] reported a systematic study on the thermal ALD of Al₂O₃ on the surface of multilayers of TMDs (MoS₂, WS₂, and WSe₂) using different deposition temperatures (see Figure 2). Inhomogeneous Al₂O₃ layers (with a large density of pinholes) were obtained using the conventional temperatures of 200–250 °C, whereas uniform coverage was observed when lowering T_{dep} to 150 °C. Furthermore, at the same deposition temperature, better uniformity of the deposited Al₂O₃ (~10 nm) films was observed on WSe₂ and on WS₂ than on MoS₂. This was ascribed to the larger polarizability of the W- and Se-based TMDs, giving rise to a higher adsorption energy of the TMA precursor due to electrostatic interaction.

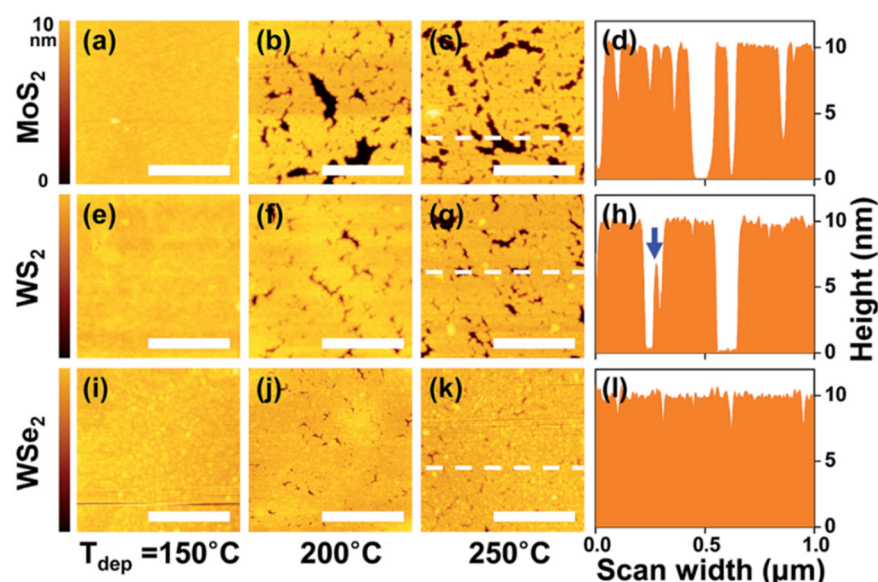


Figure 2. AFM images and height line profiles of ALD Al₂O₃ films deposited on (a–d) MoS₂, (e–h) WS₂, and (i–l) WSe₂ multilayer samples at different temperatures (150, 200, and 250 °C). Images adapted with permission from [32], copyright the Royal Society of Chemistry, 2017.

A two-step ALD process with early low-temperature (80 °C) deposition of an ultra-thin AlO_x layer and a following deposition at a higher temperature (180 °C) was also recently employed to obtain a homogeneous Al₂O₃ film with a <10 nm total thickness on MoS₂ [43]. The low temperature, however, can be responsible for the degradation of the dielectric quality due to the reduced reactivity of the ALD precursor. In these conditions, the insulating films are generally characterized by a lower density and, consequently, by a lower dielectric constant [58].

2.2. Electrical Behavior and Interface Quality of High-κ Dielectrics by ALD on 2D Materials

The quality of grown high-κ dielectrics and of their interface with the 2D material strongly influences the electrical performances of the final devices. The seed layer deposition, typically carried out ex situ, can introduce impurities and particles, which act as charge traps compromising the reliability of the high-κ dielectrics subsequently grown by ALD. Fallahzad et al. explained that the HfO₂ deposited on graphene by the evaporated Al seed layer presents a relatively low permittivity ($\epsilon = 5.5$) and a low-quality interface, which is characterized by impurities and defects responsible for mobility degradation [37,59].

Alternatively, a method based on the in situ deposition of a metal oxide H₂O-assisted seed layer has been proposed [41,42]. This approach involves the physical adsorption (by Van Der Waals interactions) of a continuous layer of H₂O molecules, which acts as a site of nucleation for a seed layer of high- κ dielectrics at a low temperature (100 °C), followed by conventional deposition at 200–250 °C. Fisichella et al. [42] demonstrated that this approach ensures the optimal electrical features of the deposited dielectric on graphene, with a favorable permittivity ($\epsilon = 7.45$) and breakdown field ($E_{BD} = 7.4$ MV/cm). On the other hand, significant charge trapping at the Al₂O₃/graphene interface has been observed during the operation of top-gated field effect transistors (Figure 3a). In particular, the density of negative trapped charges up to $\sim 4 \times 10^{12}$ cm⁻² was evaluated by capacitance voltage (C-V_{TG}) measurements when increasing the forward and backward gate bias sweeps (Figure 3b,c).

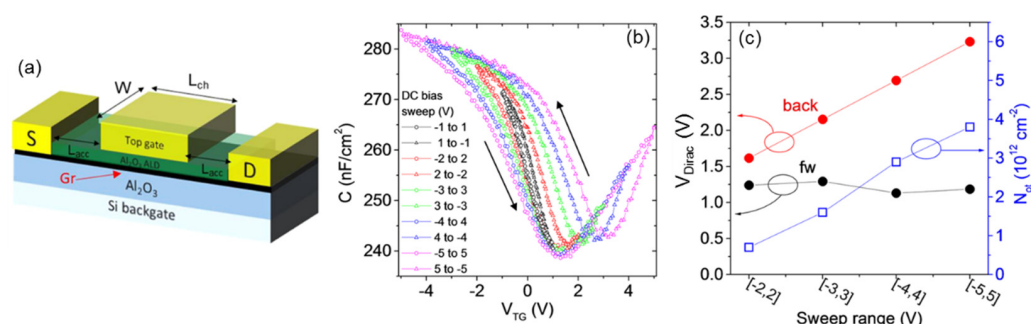


Figure 3. (a) Schematic of a top-gated graphene transistor with an ALD Al₂O₃ gate dielectric. (b) Capacitance voltage (C-V_{TG}) measurements performed by sweeping V_{TG} from negative to positive values and back using a progressively increasing sweep range. (c) Dirac point position (left axis) as a function of the bias sweep range for the forward and backward sweep and the evaluated density N_{ot} of the trapped negative charges by near-interface oxide traps (right axis). Images adapted with permission from [42], copyright American Chemical Society, 2017.

Additionally, high- κ layers grown on 2D materials pre-functionalized by reactive gas species are subjected to charge trapping phenomena both at the interface and inside the dielectrics. As an example, the HfO₂ top gate dielectric grown on a MoS₂ surface after UV-O₃ treatment [60] shows significant charge trapping, which can be ascribed to impurities and defects generated during the reactive gas exposure. Additionally, O₂-plasma pretreatments have been shown to have an effect on the interfacial properties and, consequently, the performance of the dielectric [51,52]. As an example, Zhou et al. [61] demonstrated that remote O₂-plasma is effective for the ALD growth of Al₂O₃ on graphene, but on the other hand, they found the formation of a defective interfacial layer, resulting in a low breakdown field for the oxide (1.2 MV/cm). As previously discussed, the temperature used during the ALD process plays an important role in the uniformity of the dielectric coverage. In particular, as demonstrated in [32,53,54], growth temperatures lower than 150 °C allow for achieving better uniformity, but at the same time, they result in a significant increase of trapping phenomena and, consequently, a degradation of the passivation degree [60,62].

3. Substrate-Driven ALD of High- κ Dielectrics on 2D Materials

3.1. ALD on Monolayer CVD Graphene on the Native Metal Substrates

When an AD process is carried out on graphene membrane, the underlying substrate can play an important role, because it determines the wettability degree of the graphene surface. This effect has been demonstrated by Dublak et al. [21] by performing ALD deposition of Al₂O₃ on three different kinds of graphene materials: highly oriented pyrolytic graphite (HOPG), 1 L graphene grown by CVD on a copper substrate, and 1 L CVD graphene transferred on a SiO₂ substrate. Figure 4 shows the nucleation mode of the dielectric on the three systems. By performing a deposition process consisting of 100 cycles (in order to obtain a thickness lower than 10 nm) at a temperature of 80 °C, they found discontinuous coverage both on the HOPG (Figure 4a) and on 1 L graphene transferred on

a SiO_2 substrate (Figure 4b). Using the same ALD conditions, complete coverage on the entire area was instead observed in the case of 1 L graphene residing on the native metal substrate (Cu in this case) (Figure 4c). Uniform coverage was obtained even in the case of ultra-thin (~ 3 nm) deposited Al_2O_3 films, as shown in Figure 4d.

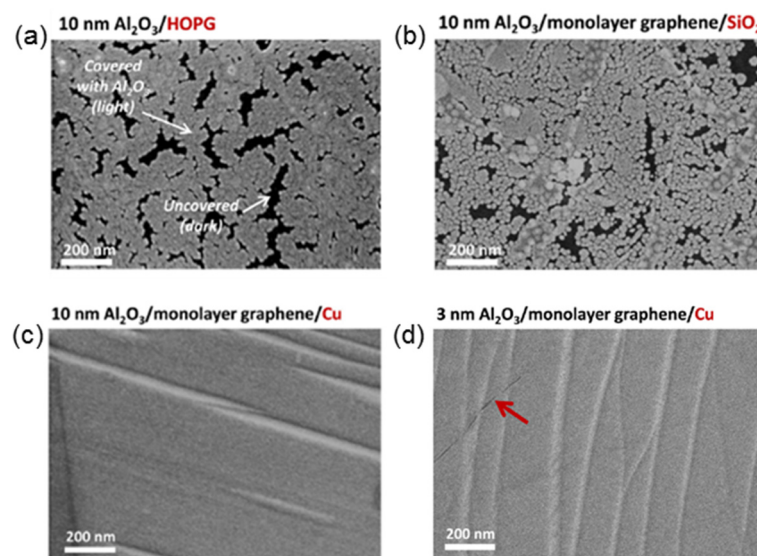


Figure 4. SEM images of 10 nm Al_2O_3 grown by ALD on HOPG (a), on monolayer CVD-graphene transferred on SiO_2 (b), and on monolayer CVD-graphene on the native metal substrate (Cu) (c), and an image of 3 nm Al_2O_3 on monolayer CVD-graphene on Cu (d). Images adapted with permission from [21], copyright the American Institute of Physics, 2012.

The authors also investigated the dependence of the Al_2O_3 coverage on the ALD deposition temperature (in the range from 80°C to 200°C) for 1 L and multilayer graphene supported by Cu or Ni-Au metal substrates, as well as for HOPG and 1 L graphene transferred onto SiO_2 (Figure 5a). While a coverage percentage $>90\%$ was obtained on the metal-supported 1 L graphene in the considered temperature range, significantly lower coverage values were found for multilayers of graphene on the same metal substrates, with a similar temperature dependence to the case of HOPG and SiO_2 -supported 1 L graphene. Aside from Al_2O_3 , other high- κ dielectrics (such as HfO_2) grown by ALD showed similar improved ALD growth on the 1 L graphene and Cu system.

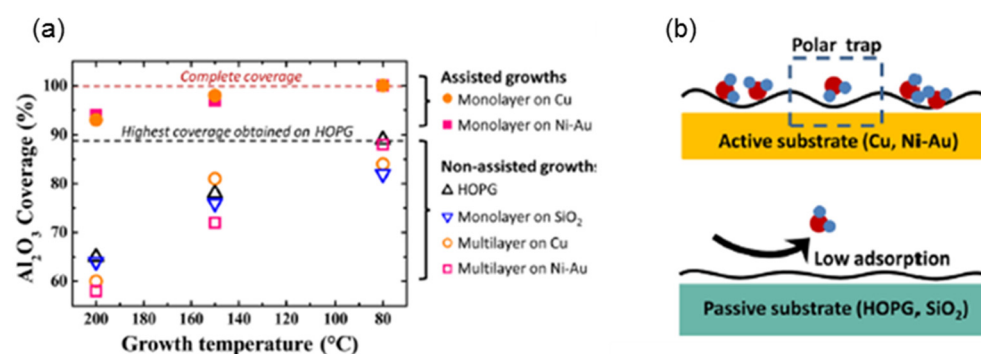


Figure 5. (a) The coverage percentage of the Al_2O_3 grown by ALD on different graphene materials as a function of the growth temperature. (b) Schematic of the precursor (H_2O) adsorption mechanism in the cases of 1 L graphene/metal and HOPG or 1 L graphene/ SiO_2 samples. Water molecules are more efficiently adsorbed on the surface of the 1 L graphene/metal system. Images adapted with permission from [21], copyright the American Institute of Physics, 2012.

This strongly improved ALD growth was due to the partial transparency of 1 L graphene to the electrostatic fields generated by the polar traps at the graphene/metal interface [23–25,63]. Such polar sites are a consequence of charge transfer phenomena between the graphene and metal due to their work function difference and also the crystal and bond distortion. The electrostatic effect of polar traps causes enhanced adsorption of the water molecules (used as a co-reactant in the thermal ALD process) on the metal-supported 1 L graphene (Figure 5b, upper panel), resulting in improved nucleation of the high- κ dielectric and, consequently, of the surface coverage. Clearly, the transparency to electrostatic fields decreases with an increasing number of graphene layers, thus explaining the poor ALD coverage on multilayer graphene on the same metal substrates. Furthermore, the lack of these polar traps at the 1 L graphene/SiO₂ interface or in HOPG results in low adsorption of the precursor molecules (as illustrated in Figure 5b, lower panel).

Using similar deposition parameters, Aria et al. [53] also reported a high coverage level of Al₂O₃ by ALD on 1 L graphene/Cu. In particular, they explored in detail the impact of the different deposition parameters (temperature, precursor pulse time, and number of ALD cycles) on the uniformity of the high- κ films. As an example, Figure 6 shows the evolution of Al₂O₃ coverage on 1 L graphene/Cu (a) with an increasing cycle number from 12 cycles (b) to 100 cycles (c) at a temperature of 200 °C.

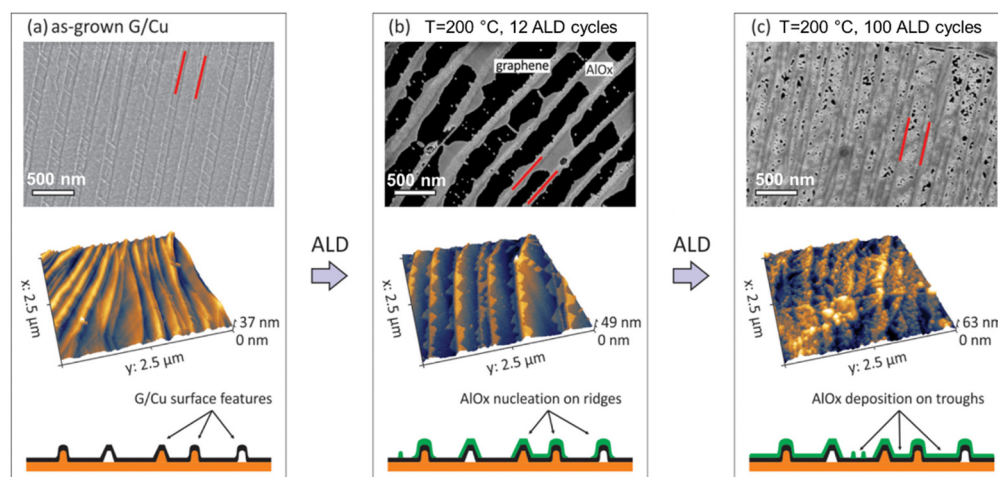


Figure 6. SEM and AFM images of the graphene/Cu system before (a) and after Al₂O₃ growth by ALD at 200 °C with 12 (b) and 100 (c) TMA/H₂O cycles. Images adapted with permission from [53], copyright the American Chemical Society, 2016.

The early-stage nucleation of high- κ dielectrics on graphene/Cu was studied by Bayer et al. [64] using scanning transmission electron microscopy (STEM) in the high-angle annular dark field (HAADF) mode. In particular, they investigated the nucleation mode of HfO₂ considering the initial 16 deposition cycles. They proposed Volmer–Weber nucleation mechanism, which involves the initial island formation and the following coalescence of the islands toward the closing of the layer. Furthermore, they found a different HfO₂ nucleation density between the 1 L and 2 L graphene regions. On the 1 L graphene, it was possible to observe by STEM the initial nuclei of the HfO₂ layer, whereas on the 2 L region, the nucleation phenomena were sparsely distributed. Such a difference further confirms the screened substrate effect in the 2 L regions.

The electrical insulating properties of thin high- κ dielectrics deposited on metal-supported graphene can be studied with the Conductive Atomic Force Microscopy (C-AFM) technique [65,66]. Figure 7a,b shows the surface morphologies of the as-grown 1 L graphene/Cu and after ALD of a 10-nm thick Al₂O₃ layer at a temperature of 250 °C. The high roughness of the copper substrate made it difficult to evaluate the morphology of the deposited Al₂O₃ and the coverage fraction. Figure 7c,d shows the corresponding current maps of 1 L graphene/Cu and of Al₂O₃ (10 nm)/1 L graphene/Cu, acquired

using the experimental configuration depicted in the insets of Figure 7e,f. As expected, the conductivity map of the bare graphene/Cu (Figure 7c) exhibited high current flow on the entire investigated area, even for a very low bias ($V_{\text{Tip}} = 10$ mV) applied to the tip. Conversely, the current map acquired on the Al_2O_3 deposited on the graphene/Cu showed optimal and uniform insulator behavior on the entire investigated surface up to an applied voltage of $V_{\text{Tip}} = 7$ V. No spots associated with the local current flow could be observed, and this is an indication of uniform nucleation and ALD growth of the dielectric on the 1 L graphene/Cu system. Figure 7e displays a typical current–voltage (I - V_{Tip}) characteristic measured by C-AFM on the bare 1 L graphene/Cu sample, which exhibits the expected Ohmic conduction behavior with very low resistance, whereas Figure 7f reports the local I - V_{Tip} curves acquired on the deposited 10 nm Al_2O_3 on 1 L graphene/Cu, showing negligible current flow through the insulating layer for tip bias values $V_{\text{Tip}} < 7$ V and the abrupt rise in the current, corresponding to a local dielectric breakdown at larger bias values.

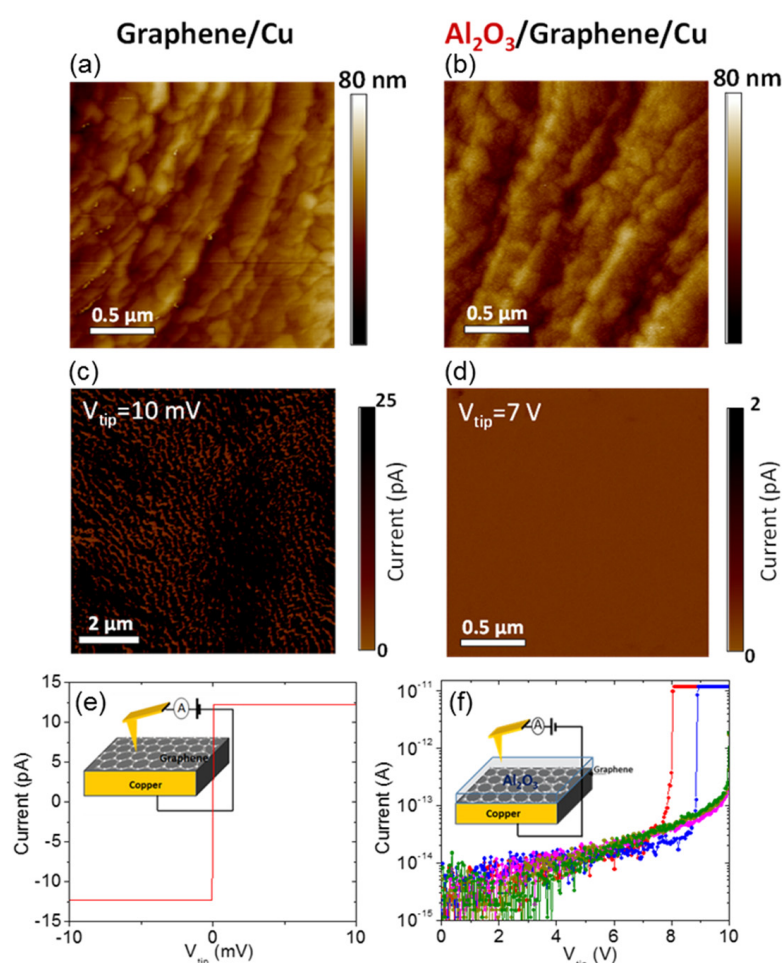


Figure 7. AFM morphology of graphene/copper without (a) and with an Al_2O_3 layer (b). Current maps (c,d) and local I - V curves (e,f) acquired on graphene/copper and Al_2O_3 /graphene/copper.

3.2. ALD on Epitaxial Graphene on SiC

Epitaxial graphene (EG) grown by high-temperature (1600–2000 $^{\circ}\text{C}$) thermal decomposition of the SiC(0001) surface typically consists of 1 L graphene on a large percentage of the surface area and 2 L or 3 L graphene regions especially localized at the step edges of the SiC surface terraces [67,68]. ALD growth of high- κ dielectrics, such as Al_2O_3 and HfO_2 , on epitaxial graphene (EG) on SiC typically results in inhomogeneous coverage [69,70], mainly on the 2 L or regions with few layers. However, by using highly homogeneous epitaxial graphene consisting of a monolayer for 98% of the surface and a bilayer for the remaining 2%, very uniform and pinhole-free Al_2O_3 layers have been obtained by direct thermal

ALD at 250 °C without any seeding layer or pre-functionalization [26]. On the other hand, very inhomogeneous ALD coverage has been observed under identical ALD conditions on monolayer graphene transferred on a pristine SiC substrate. This demonstrates that the enhanced reactivity of the epitaxial graphene towards ALD precursors is not related to the SiC substrate but rather to the peculiar EG/SiC interface. Ab initio density functional theory (DFT) calculations demonstrated enhanced adsorption energy for the water molecules (ALD precursor) on 1 L graphene, depending on the n-type doping. Thus, the high doping induced by the buffer layer (between the EG and SiC substrate) on the EG was considered a possible origin of the excellent Al_2O_3 nucleation. The effectiveness of ALD nucleation has been demonstrated following the evolution of the surface morphology, starting from the as-grown EG surface (Figure 8a) and in the early deposition cycles (10, 20, and 40 cycles) [27] as shown in Figure 8b–d. A coverage level of >80% was observed already after 10 deposition cycles and 100% after 40 deposition cycles (Figure 8e). The evolution of ALD nucleation during the first few cycles is schematically depicted in Figure 8f, which displays four consecutive steps with an increasing number of ALD cycles (from top to bottom): (1) the formation of the first nuclei on the 1 L EG surface, (2) the increase of pre-existent nuclei and the further nucleation on bare EG, (3) diffusion and coalescence of the islands, and (4) the formation of a complete layer of dielectrics on graphene.

Figure 9 shows the morphology (a) and current map (b) acquired by C-AFM on a scratch of the Al_2O_3 , demonstrating continuous ultrathin layers (~2.4 nm) of dielectrics with optimal insulator behavior (c,d). The slight fluctuations of the injected current, observable by the current map, through the ultra-thin dielectric layer are related to local changes in the surface roughness, as can be deduced from the comparison between the height and current line profiles. The obtained results have an important impact on devices exploiting epitaxial graphene.

3.3. ALD on Exfoliated MoS_2 on Gold

More recently, the direct thermal ALD of an ultra-thin and pinhole-free Al_2O_3 layer has been demonstrated on monolayer (1 L) MoS_2 residing on a gold substrate [22]. During the last few years, several research groups have investigated mechanical exfoliation on gold as an effective way to separate large-area (cm^2) 1 L MoS_2 membranes from bulk molybdenite crystals by exploiting the strong S-Au interactions [71–73]. Furthermore, the exfoliated membranes could be transferred from gold to insulating substrates, demonstrating electrical and optical properties comparable to the best-quality MoS_2 crystals [71,74]. Recently, Schilirò et al. [22] compared the thermal ALD of Al_2O_3 on 1 L MoS_2 residing on gold and on 1 L MoS_2 , transferred on an insulating Al_2O_3 substrate. Using identical ALD conditions, inhomogeneous ALD coverage by Al_2O_3 islands was obtained in the case of the 1 L $\text{MoS}_2/\text{Al}_2\text{O}_3/\text{Si}$ (see Figure 10a). In contrast, pinhole-free Al_2O_3 and a flat morphology were observed on the 1 L MoS_2/Au system (see Figure 10b). The authors illustrated the two different growth modes in Figure 10c,d for ALD- Al_2O_3 on 1 L $\text{MoS}_2/\text{Al}_2\text{O}_3/\text{Si}$ and on 1 L MoS_2/Au , respectively. They found that the ALD nucleation on 1 L MoS_2/Au was favored from the early stages of the process, with the Al_2O_3 surface coverage increasing from ~50% (after only 10 ALD cycles) to >90% (after 40 cycles). Interestingly, less uniform Al_2O_3 coverage was observed in the bilayer and multilayer MoS_2 regions. The close similarity of the observed behavior to the case of 1 L graphene/Cu suggested that the improved reactivity of Au-supported 1 L MoS_2 toward the ALD precursors could be attributed to the partial transparency of 1 L MoS_2 to the electrostatic field generated by charges at the interface with the gold substrate. Furthermore, the strong interaction between MoS_2 and Au was found to be responsible for the significant tensile strain and p-type doping of 1 L MoS_2 , which were relaxed by increasing the number of MoS_2 layers [74]. Hence, these effects of the MoS_2/Au interaction can also play a role in the enhanced nucleation in the early stages of ALD processes.

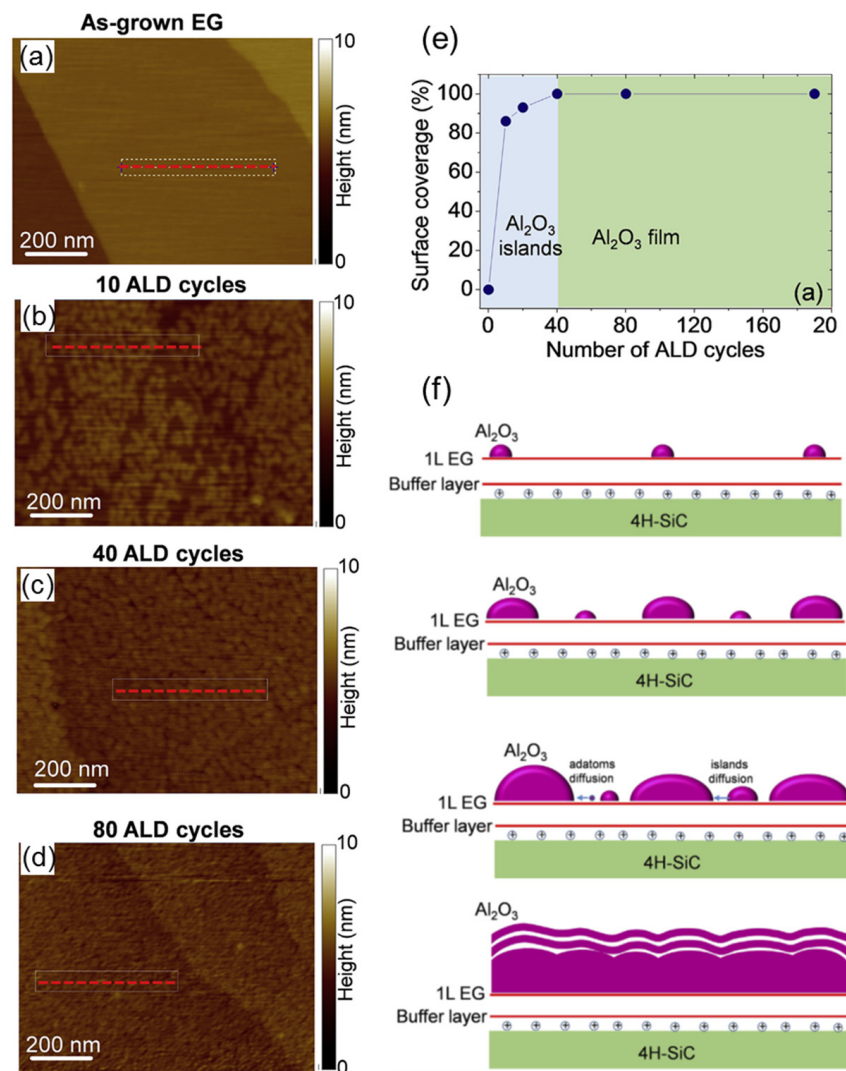


Figure 8. AFM morphology of the as-grown epitaxial graphene surface (a) and after 10 (b), 40 (c), and 80 (d) ALD cycles for Al₂O₃ deposition, as well as the percentage of the graphene surface covered by the deposited Al₂O₃ as a function of the number of ALD cycles (e). Schematic representation of the evolution of the deposited Al₂O₃ on epitaxial graphene with an increasing number of ALD cycles (f). Images adapted with permission from [27], copyright Elsevier, 2020.

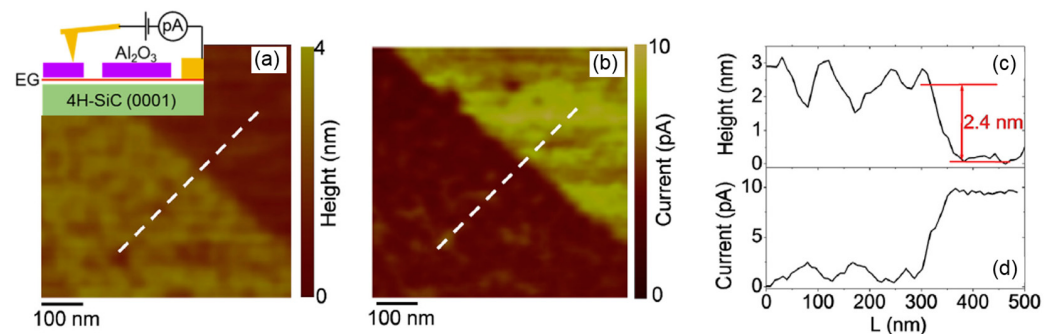


Figure 9. C-AFM morphology (a) and current map (b) acquired on a scratch of the deposited Al₂O₃ (40 cycles) on EG. Line scans of the height (c), from which the dielectric thickness of ~2.4 nm has been determined, and of the current (d), showing the insulating properties of the deposited film. Images adapted with permission from [27], copyright Elsevier, 2020.

The thickness and the insulating properties of the uniform Al_2O_3 layer on MoS_2/Au were also evaluated by C-AFM measurements according the schematic in Figure 11a. A 3.6-nm thickness of the Al_2O_3 on 1 L MoS_2 was evaluated from the morphological map (Figure 11b), whereas the good insulating behavior of the deposited high- κ material was confirmed by the current map in Figure 11c, collected at a bias of 3 V between the tip and the gold substrate. Furthermore, the current–voltage (I–V) characteristics displayed in Figure 11d show a low leakage current of up to 3 V and a rapid increase in the current at bias values in the range of 3.7–4.5 V, associated with the localized breakdown behavior. These breakdown voltage (V_{BD}) values correspond to breakdown electric fields ($E_{\text{BD}} = V_{\text{BD}}/t_{\text{ox}}$) in the range from ~ 10 to ~ 12 MV/cm. The localized behavior of the breakdown was also confirmed by the current map in Figure 11e, illustrating the changes in the leakage current spatial distribution by increasing the bias from 3 V to 4 V and then decreasing it back to 3 V. The appearance of localized breakdown spots is clearly visible in the current map region at 4 V of applied bias.

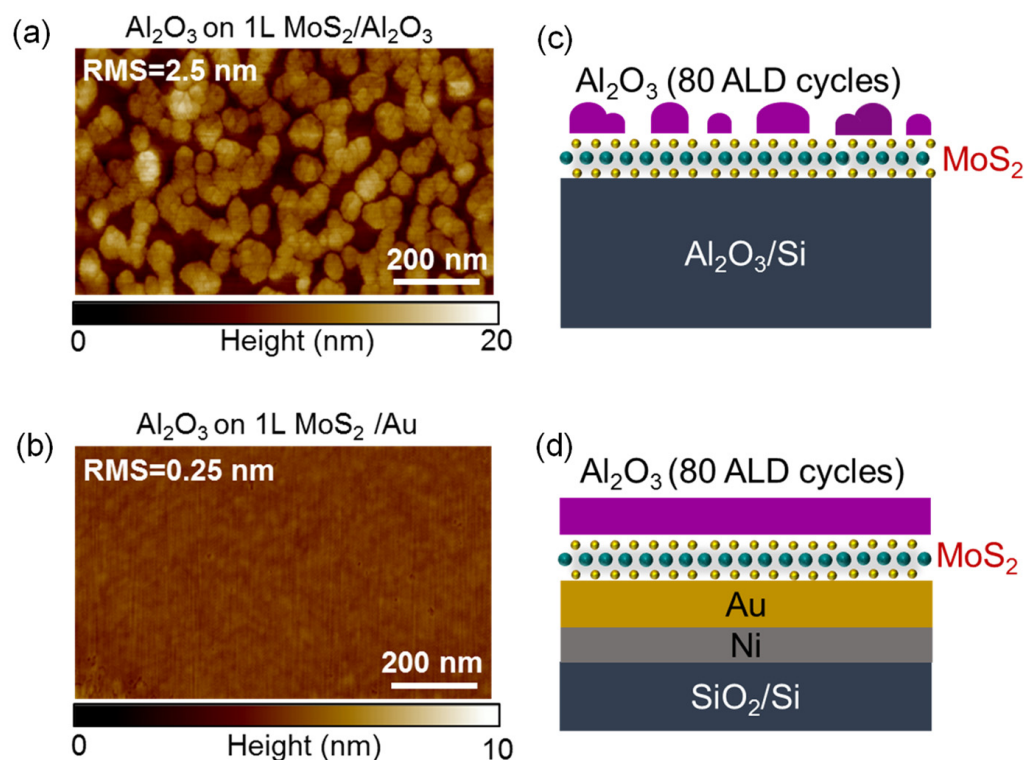


Figure 10. AFM morphologies of Al_2O_3 deposited by ALD on the 1 L $\text{MoS}_2/\text{Al}_2\text{O}_3/\text{Si}$ sample (a) and on the 1 L MoS_2/Au sample (b). The deposited Al_2O_3 on 1 L $\text{MoS}_2/\text{Al}_2\text{O}_3/\text{Si}$ and 1 L MoS_2/Au are schematically illustrated in (c,d). Images adapted with permission from [22], copyright Wiley, 2021.

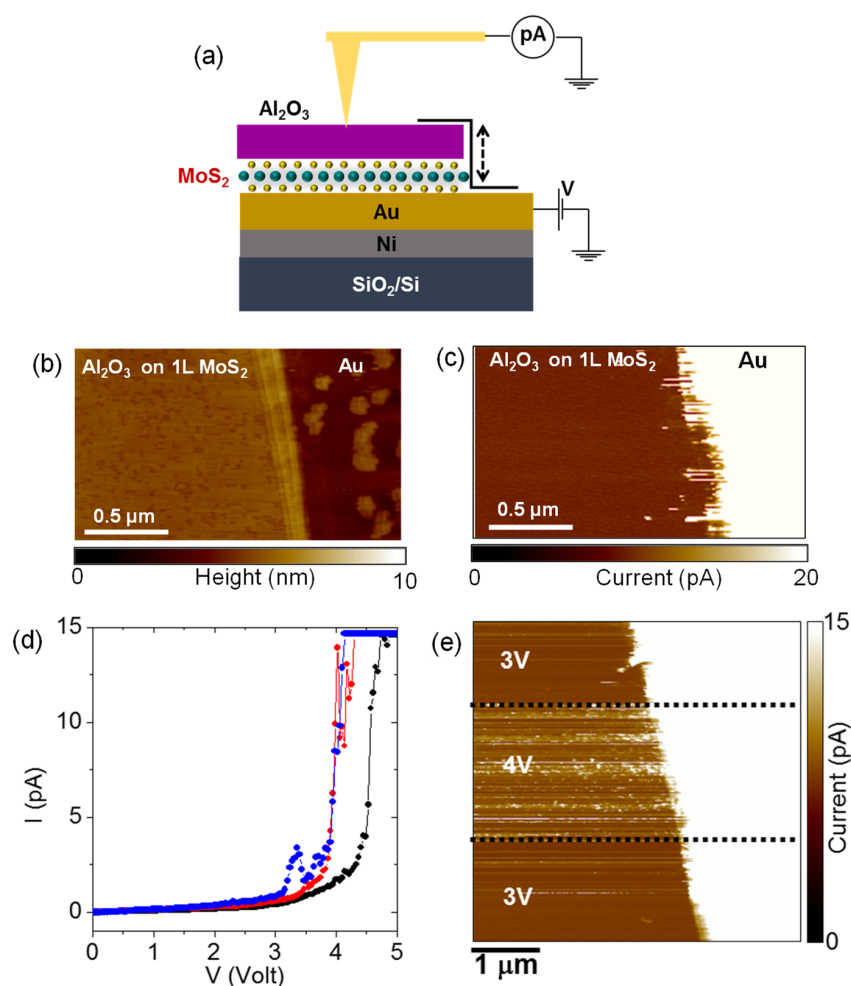


Figure 11. Schematic of the C-AFM measurement set-up (a). AFM image of a step between the Al_2O_3 /1 L MoS_2 stack and the underlying Au substrate, from which a deposited Al_2O_3 thickness of ~ 3.6 nm was estimated (b). C-AFM current map acquired with a bias $V = 3$ V (c). Local I-V characteristics collected at different positions on the Al_2O_3 / MoS_2 /Au stack, showing the current breakdown at biases between 3.7 and 4.5 V (d). C-AFM current map collected on the Al_2O_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 in the current leakage with the appearance of localized breakdown spots is observed at 4 V (e). Images adapted with permission from [22], copyright Wiley, 2021.

4. Challenges for Applications

The above-discussed substrate-enhanced ALD provides a unique way to obtain uniform and compact films of high- κ dielectrics with very good insulating properties directly on the pristine surface of 1 L graphene or MoS_2 . However, some challenges need to be faced for the application of the obtained high- κ /2D material stacks in electronic devices. Firstly, the substrate-enhanced ALD growth is observed especially on the monolayers of these 2D materials, whereas less uniform and compact films are typically obtained on the bilayer of the multilayers. Although graphene CVD on copper and the sublimation growth of epitaxial graphene on SiC(0001) have been widely investigated in the last decade, but obtaining uniform 1 L graphene on a large area still remains a challenge. In fact, a small percentage (1–2%) of the copper or SiC surface, typically corresponding to surface defects in the crystals, is covered by 2 L or a few layers of graphene. In the case of MoS_2 exfoliated from the bulk crystal on a gold substrate, the obtained membrane is mostly composed of monolayers, with a significant fraction being 2 L or multilayer regions. As a matter of fact, even the presence of few percent of areas with poor-quality high- κ films

represents a critical point for some device applications, such as field effect transistors or vertical hot electron transistors. Hence, further optimization of graphene and MoS₂ synthesis methods to achieve full monolayer coverage will be crucial to take full benefit of the substrate-enhanced ALD growth.

A second key challenge to be addressed will be the development of reliable procedures for the integration of the high- κ /2D material stacks in electronic devices. In fact, while the ALD-grown dielectrics on EG/SiC(0001) can be immediately employed for the fabrication of top-gated field effect transistors, the transfer of the high- κ /2D material stacks to an insulating or semiconductor substrate is required in the case of metal-supported 2D materials.

Recently, Cabrero-Vilatela et al. [75] also adopted the transfer procedure typically used for CVD-grown graphene on copper in the case of graphene coated by ALD-deposited Al₂O₃. As schematically illustrated in Figure 12, after direct ALD of the oxide on 1 L graphene/Cu, a poly-methyl methacrylate (PMMA) film was spin-coated on the oxide surface in order to protect the stack during the handling process. Therefore, the copper layer was removed by an etching solution and, after a series of rinses in DI water, the PMMA/Al₂O₃/graphene was transferred on the final substrate (SiO₂/Si). The polymer support was finally removed by solvents.

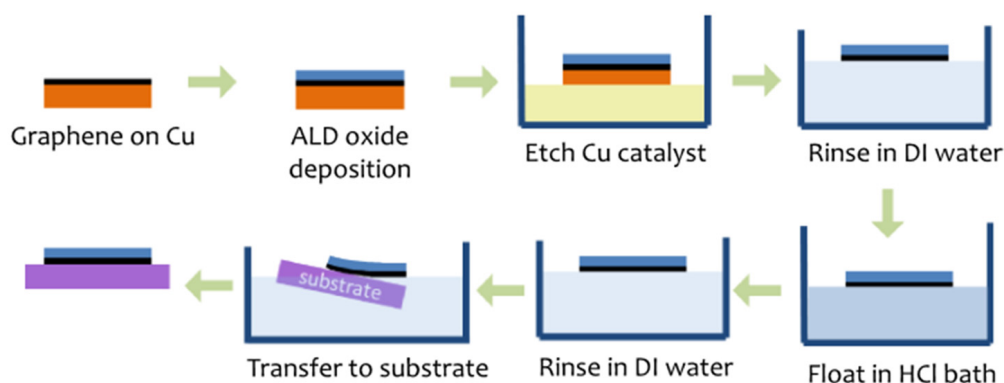


Figure 12. Schematic representation of the transfer process from copper to the required substrate of the dielectric/graphene stack. Image adapted with permission from [75], copyright IOP, 2017.

The same authors demonstrated a beneficial effect of the Al₂O₃ encapsulation of 1 L graphene/Cu on the final electrical performance of the graphene devices. Figure 13 shows the comparison of the transfer characteristics (I_D - V_G) of three different kinds of back-gated field effect transistors on a SiO₂/Si substrate, fabricated using (1) graphene monolayers without Al₂O₃ on top (no Al₂O₃), (2) graphene monolayers with Al₂O₃ deposited after being transferred onto SiO₂ (Al₂O₃ ALD after transfer), and (3) graphene monolayers with Al₂O₃ deposited before the transfer (Al₂O₃ ALD before transfer). It is noteworthy that the third approach guarantees both very low doping of graphene (i.e., a charge neutrality point very close to $V_G = 0$ V) and reduced hysteresis of the characteristics, which are attributable to the significantly reduced charges at the interface. These improved electrical performances have been correlated to the reduced contaminations at the Al₂O₃/graphene interface, since the direct contact between graphene and PMMA is avoided in this case. In this regard, a double application of the Al₂O₃ layer deposited by ALD on the graphene on copper prior to the transfer process to SiO₂ substrates has been proposed.

Aside from working as a protective layer for graphene during the transfer from copper and for passivation of the back-gated graphene transistors, the deposited high- κ films can be exploited as active layers (e.g., as dielectrics of top-gated field transistors or as a base collector barrier in graphene base hot electron transistors (GBHETs)). In this respect, the most crucial issue is the optimization of handling procedures to avoid damage or cracking of the high- κ /graphene stack during the transfer.

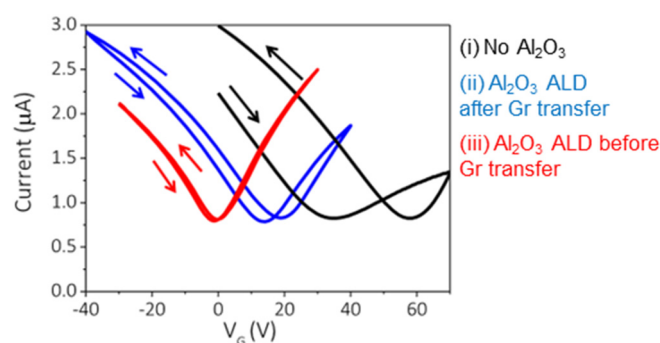


Figure 13. Electrical characteristics (I_D - V_G) of back-gated field effect transistors fabricated using (i) 1 L graphene without Al_2O_3 on top (no Al_2O_3), (ii) 1 L graphene with Al_2O_3 deposited after being transferred onto SiO_2 (Al_2O_3 ALD after Gr transfer), and (iii) 1 L graphene with Al_2O_3 deposited before the transfer (Al_2O_3 ALD before Gr transfer). Image adapted with permission from [75], copyright IOP, 2017.

Similarly, the transfer of the dielectric/ MoS_2 stack from Au to an insulating substrate is mandatory for the field effect transistor applications of this system. To date, several authors demonstrated the transfer of large-area 1 L MoS_2 exfoliated on Au to insulating substrates (using very similar methods to those used for CVD-grown graphene on copper), and excellent electronic and optical quality has been shown for the transferred 1 L MoS_2 membranes [72,76]. However, the transfer of Al_2O_3 -coated 1 L MoS_2 from Au to other substrates has not been reported so far. The transfer from the metal substrate is not required for other recently investigated devices, such as MoS_2 memristors [77], exploiting the properties of Au-supported 1 L MoS_2 membranes for non-volatile memory applications.

5. Conclusions

The integration of uniform and ultra-thin high- κ dielectrics on 2D materials is a challenge for future electronic and sensing applications in these systems. In fact, the seed layer and pre-functionalization approaches typically employed to promote ALD nucleation on 2D materials presents both advantages and disadvantages, and direct ALD growth remains highly desirable. This paper provided a detailed review of the literature reports on the direct ALD of uniform high- κ dielectric films on monolayer graphene and MoS_2 , driven by the interaction with the underlying substrates. In the case of CVD 1 L graphene on copper, the enhancement of ALD nucleation was correlated with the electrostatic effect of polar traps (at the graphene/metal interface) on the adsorption of the water precursor. For 1 L epitaxial graphene on $\text{SiC}(0001)$, a similar electrostatic effect happens due to the positive charges at the interface between the buffer layer and the substrate, which cause n-type doping of the graphene and its enhanced reactivity toward ALD precursors. Finally, in the case of 1 L MoS_2 exfoliated on gold substrate, the improvement in ALD growth is explained by the combined effect of electrostatic charges at the interface and of the tensile strain induced on the 2D material by the gold. Hence, opportunely choosing the substrate, excellent ALD coverage, and optimal structural and insulating properties of the high- κ layers can be obtained on 2D materials. For all these systems, the electrical insulating properties of the grown high- κ dielectrics have been examined. Finally, the open issues and challenges for applications of these high- κ /2D material systems have been thoroughly discussed.

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References

1. Du, X.; Skachko, I.; Barker, A.; Aandrei, E.Y. Approaching ballistic transport in suspended graphene. *Nat. Nanotechnol.* **2008**, *3*, 491. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Giannazzo, F.; Sonde, S.; Lo Nigro, R.; Rimini, E.; Raineri, V. Mapping the Density of Scattering Centers Limiting the Electron Mean Free Path in Graphene. *Nano Lett.* **2011**, *11*, 4612–4618. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Lin, Y.-M.; Dimitrakopoulos, C.; Jenkins, K.A.; Farmer, D.B.; Chiu, H.-Y.; Grill, A.; Avouris, P. 100-GHz Transistors from Wafer-Scale Epitaxial Graphene. *Science* **2010**, *327*, 662. [\[CrossRef\]](#)
4. Moon, J.S.; Curtis, D.; Hu, M.; Wong, D.; McGuire, C.; Campbell, P.M.; Jernigan, G.; Tedesco, J.L.; VanMil, B.; Myers-Ward, R.; et al. Epitaxial-Graphene RF Field-Effect Transistors on Si-Face 6H-SiC Substrates. *IEEE Electron Device Lett.* **2009**, *30*, 650–652. [\[CrossRef\]](#)
5. Liu, H.; Neal, A.T.; Ye, P.D. Channel Length Scaling of MoS₂ MOSFETs. *ACS Nano* **2012**, *6*, 8563–8569. [\[CrossRef\]](#)
6. Liu, Y.; Guo, J.; Wu, Y.; Zhu, E.; Weiss, N.O.; He, Q.; Wu, H.; Cheng, H.-C.; Xu, Y.; Shakir, I.; et al. Pushing the Performance Limit of Sub-100 nm Molybdenum Disulfide Transistors. *Nano Lett.* **2016**, *16*, 6337–6342. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150. [\[CrossRef\]](#)
8. Kim, S.; Konar, A.; Hwang, W.S.; Lee, J.H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.B.; Choi, J.Y.; et al. High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals. *Nat. Commun.* **2012**, *3*, 1011. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805. [\[CrossRef\]](#)
10. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Reddy, D.; Register, L.F.; Carpenter, G.D.; Banerjee, S.K. Graphene Field-Effect Transistors. *J. Phys. D Appl. Phys.* **2011**, *45*, 019501. [\[CrossRef\]](#)
12. Echtermeyer, T.J.; Lemme, M.C.; Baus, M.; Szafrank, B.N.; Geim, A.K.; Kurz, H. Non-volatile switching in graphene field effect devices. *IEEE Electron Device Lett.* **2008**, *29*, 29952–29954. [\[CrossRef\]](#)
13. Fisichella, G.; Lo Verso, S.; Di Marco, S.; Vinciguerra, V.; Schilirò, E.; Di Franco, S.; Lo Nigro, R.; Roccaforte, F.; Zurutuza, A.; Centeno, A.; et al. Advances in the fabrication of graphene transistors on flexible substrates. *Beilstein J. Nanotechnol.* **2017**, *8*, 467–474. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Liu, H.; Ye, P.D. MoS₂ Dual-Gate MOSFET With Atomic-Layer-Deposited Al₂O₃ as Top-Gate Dielectric. *IEEE Electron Device Lett.* **2011**, *33*, 546–548. [\[CrossRef\]](#)
15. Giannazzo, F.; Greco, G.; Roccaforte, F.; Sonde, S.S. Vertical Transistors Based on 2D Materials: Status and Prospects. *Crystals* **2018**, *8*, 70. [\[CrossRef\]](#)
16. Giannazzo, F. Engineering 2D heterojunctions with dielectrics. *Nat. Electron.* **2019**, *2*, 54. [\[CrossRef\]](#)
17. Giannazzo, F.; Fisichella, G.; Greco, G.; Schilirò, E.; Deretzi, I.; Lo Nigro, R.; La Magna, A.; Roccaforte, F.; Iucolano, F.; Lo Verso, S.; et al. Cordier, Fabrication and Characterization of Graphene Heterostructures with Nitride semiconductors for High Frequency Vertical Transistors. *Phys. Status Solidi* **2017**, *215*, 1700653. [\[CrossRef\]](#)
18. Giannazzo, F.; Greco, G.; Schilirò, E.; Lo Nigro, R.; Deretzi, I.; La Magna, A.; Roccaforte, F.; Iucolano, F.; Ravesi, S.; Frayssinet, E.; et al. High-performance graphene/AlGaIn/GaN schottky junctions for hot electron transistors. *ACS Appl. Electron. Mater.* **2019**, *1*, 2342–2354. [\[CrossRef\]](#)
19. Mehr, W.; Dabrowski, J.; Scheytt, J.C.; Lippert, G.; Xie, Y.H.; Lemme, M.C.; Ostling, M.; Lupina, G. Vertical Graphene Base Transistor. *IEEE Electron Device Lett.* **2012**, *33*, 691–693. [\[CrossRef\]](#)
20. Bae, T.-E.; Kim, H.; Jung, J.; Cho, W.-J. Fabrication of high-performance graphene field-effect transistor with solution-processed Al₂O₃ sensing membrane. *Appl. Phys. Lett.* **2014**, *104*, 153506. [\[CrossRef\]](#)
21. Dlubak, B.; Kidambi, P.R.; Weatherup, R.S.; Hofmann, S.; Robertson, J. Substrate-assisted nucleation of ultra-thin dielectric layers on graphene by atomic layer deposition. *Appl. Phys. Lett.* **2012**, *100*, 173113. [\[CrossRef\]](#)

22. Schilirò, E.; Lo Nigro, R.; Panasci, S.E.; Agnello, S.; Cannas, M.; Gelardi, F.M.; Roccaforte, F.; Giannazzo, F. Direct Atomic Layer Deposition of Ultrathin Aluminum Oxide on Monolayer MoS₂ Exfoliated on Gold: The Role of the Substrate. *Adv. Mater. Interfaces* **2021**, *8*, 2101117. [\[CrossRef\]](#)
23. Pollard, A.J.; Perkins, E.W.; Smith, N.A.; Saywell, A.; Goretzki, G.; Phillips, A.G.; Argent, S.P.; Sachdev, H.; Müller, F.; Hüfner, S.; et al. Supramolecular Assemblies Formed on an Epitaxial Graphene Superstructure. *Angew. Chem. Int. Ed.* **2010**, *49*, 1794. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Zhang, H.; Sun, J.; Low, T.; Zhang, L.; Pan, Y.; Liu, Q.; Mao, J.; Zhou, H.; Guo, H.; Du, S.; et al. Assembly of iron phthalocyanine and pentacene molecules on a graphene monolayer grown on Ru(0001). *Phys. Rev. B* **2011**, *84*, 245436. [\[CrossRef\]](#)
25. Rafiee, J.; Mi, X.; Gullapalli, H.; Thomas, A.V.; Yavari, F.; Shi, Y.; Ajayan, P.M.; Koratkar, N.A. Wetting transparency of graphene. *Nat. Mater.* **2012**, *11*, 217–222. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Schilirò, E.; Lo Nigro, R.; Roccaforte, F.; Deretzi, I.; La Magna, A.; Armano, A.; Agnello, S.; Pecz, B.; Ivanov, I.G.; Yakimova, R.; et al. Seed-Layer-Free Atomic Layer Deposition of Highly Uniform Al₂O₃ Thin Films onto Monolayer Epitaxial Graphene on Silicon Carbide. *Adv. Mater. Interfaces* **2019**, *6*, 1900097. [\[CrossRef\]](#)
27. Schilirò, E.; Lo Nigro, R.; Panasci, S.E.; Gelardi, F.M.; Agnello, S.; Yakimova, R.; Roccaforte, F.; Giannazzo, F. Aluminum oxide nucleation in the early stages of atomic layer deposition on epitaxial graphene. *Carbon* **2020**, *169*, 172–181. [\[CrossRef\]](#)
28. Vervuurt, R.H.J.; Kessels, W.M.M.; Bol, A.A. Atomic Layer Deposition for Graphene Device Integration. *Adv. Mater. Interfaces* **2017**, *4*, 1700232. [\[CrossRef\]](#)
29. Kim, H.G.; Lee, H.-B.-R. Atomic Layer Deposition on 2D Materials. *Chem. Mater.* **2017**, *29*, 3809–3826. [\[CrossRef\]](#)
30. Giannazzo, F.; Schilirò, E.; Lo Nigro, R.; Roccaforte, F.; Yakimova, R. Atomic Layer Deposition of High-k Insulators on Epitaxial Graphene: A Review. *Appl. Sci.* **2020**, *10*, 2440. [\[CrossRef\]](#)
31. Oviroh, P.O.; Akbarzadeh, R.; Pan, D.; Coetzee, R.A.M.; Jen, T.-C. New development of atomic layer deposition: Processes, methods and applications. *Sci. Technol. Adv. Mater.* **2019**, *20*, 465–496. [\[CrossRef\]](#)
32. Park, T.; Kim, H.; Leem, M.; Ahn, W.; Choi, S.; Kim, J.; Uh, J.; Kwon, K.; Jeong, S.-J.; Park, S.; et al. Atomic layer deposition of Al₂O₃ on MoS₂, WS₂, WSe₂, and h-BN: Surface coverage and adsorption energy. *RSC Adv.* **2017**, *7*, 884–889. [\[CrossRef\]](#)
33. Cheng, L.; Qin, X.; Lucero, A.T.; Azcatl, A.; Huang, J.; Wallace, R.M.; Cho, K.; Kim, J. Atomic Layer Deposition of a High-k Dielectric on MoS₂ Using Trimethylaluminum and Ozone. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11834–11838. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Wang, X.; Tabakman, S.M.; Dai, H. Atomic Layer Deposition of Metal Oxides on Pristine and Functionalized Graphene. *J. Am. Chem. Soc.* **2008**, *130*, 8152. [\[CrossRef\]](#)
35. Shin, W.C.; Kim, T.Y.; Sul, O.; Cho, B.J. Seeding atomic layer deposition of high-k dielectric on graphene with ultrathin poly(4-vinylphenol) layer for enhanced device performance and reliability. *Appl. Phys. Lett.* **2012**, *101*, 033507. [\[CrossRef\]](#)
36. Wirtz, C.; Hallam, T.; Cullen, C.P.; Berner, N.C.; O'Brien, M.; Marcia, M.; Hirsch, A.; Duesberg, G.S. Atomic layer deposition on 2D transition metal chalcogenides: Layer dependent reactivity and seeding with organic ad-layers. *Chem. Commun.* **2015**, *51*, 16553. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Fallahazad, B.; Lee, K.; Lian, G.; Kim, S.; Corbet, C.; Ferrer, D.; Colombo, L.; Tutuc, E. Scaling of Al₂O₃ dielectric for graphene field-effect transistors. *Appl. Phys. Lett.* **2012**, *100*, 093112. [\[CrossRef\]](#)
38. Guo, T.; Wu, H.; Su, X.; Guo, B.; Liu, C. Surface functionalization toward top-gated monolayer MoS₂ field-effect transistors with ZrO₂/Al₂O₃ as composite dielectrics. *J. Alloy. Compd.* **2021**, *871*, 159116. [\[CrossRef\]](#)
39. Woo, W.J.; Oh, I.K.; Park, B.E.; Kim, Y.; Park, J.; Seo, S.; Song, J.-G.; Jung, H.; Kim, D.; Lim, J.H.; et al. Bi-layer high-k dielectrics of Al₂O₃/ZrO₂ to reduce damage to MoS₂ channel layers during atomic layer deposition. *2D Mater.* **2019**, *6*, 015019. [\[CrossRef\]](#)
40. Haodong, Z.; Arutchelvan, G.; Meersschart, J.; Gaur, A.; Conard, T.; Bender, H.; Lin, D.; Asselberghs, I.; Heyns, M.; Radu, I.; et al. MoS₂ Functionalization with a Sub-nm Thin SiO₂ Layer for Atomic Layer Deposition of High-κ Dielectrics. *Chem. Mater.* **2017**, *29*, 6772–6780.
41. Zhang, Y.; Qiu, Z.; Cheng, X.; Xie, H.; Wang, H.; Xie, X.; Yu, Y.; Liu, R. Direct growth of high-quality Al₂O₃ dielectric on graphene layers by low-temperature H₂O-based ALD. *J. Phys. D Appl. Phys.* **2014**, *47*, 055106. [\[CrossRef\]](#)
42. Fisichella, G.; Schilirò, E.; Di Franco, S.; Fiorenza, P.; Lo Nigro, R.; Roccaforte, F.; Ravesi, S.; Giannazzo, F. Interface Electrical Properties of Al₂O₃ Thin Films on Graphene Obtained by Atomic Layer Deposition with an in Situ Seedlike Layer. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7761–7771. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Lin, Y.-S.; Cheng, P.-H.; Huang, K.-W.; Lin, H.-C.; Chen, M.-J. Atomic layer deposition of sub-10 nm high-K gate dielectrics on top-gated MoS₂ transistors without surface functionalization. *Appl. Surf. Sci.* **2018**, *443*, 421–428. [\[CrossRef\]](#)
44. Gong, F.; Luo, W.; Wang, J.; Wang, P.; Fang, H.; Zheng, D.; Guo, N.; Wang, J.; Luo, M.; Ho, J.C.; et al. High-Sensitivity Floating-Gate Phototransistors Based on WS₂ and MoS₂. *Adv. Funct. Mater.* **2016**, *26*, 6084–6090. [\[CrossRef\]](#)
45. Lin, Y.M.; Jenkins, K.A.; Valdes-Garcia, A.; Small, J.P.; Farmer, D.B.; Avouris, P. Operation of Graphene Transistors at Gigahertz Frequencies. *Nano Lett.* **2009**, *9*, 422. [\[CrossRef\]](#)
46. Lee, B.; Mordí, G.; Kim, M.J.; Chabal, Y.J.; Vogel, E.M.; Wallace, R.M.; Cho, K.J.; Colombo, L.; Kim, J. Characteristics of high-k Al₂O₃ dielectric using ozone-based atomic layer deposition for dual-gated graphene devices. *J. Appl. Phys. Lett.* **2010**, *97*, 043107. [\[CrossRef\]](#)
47. Lee, J.; Lee, B.; Kim, J.; Cho, K. Ozone Adsorption on Graphene: Ab Initio Study and Experimental Validation. *J. Phys. Chem. C* **2009**, *113*, 14225. [\[CrossRef\]](#)

48. Lee, B.; Park, S.Y.; Kim, H.C.; Cho, K.; Vogel, E.M.; Kim, M.J.; Wallace, R.M.; Kim, J. Conformal Al₂O₃ dielectric layer deposited by atomic layer deposition for graphene-based nanoelectronics. *J. Appl. Phys. Lett.* **2008**, *92*, 203102. [\[CrossRef\]](#)
49. Azcatl, A.; Santosh, K.C.; Peng, X.; Lu, N.; McDonnell, S.; Qin, X.; de Dios, F.; Addou, R.; Kim, J.; Kim, M.J.; et al. HfO₂ on UV-O₃ Exposed Transition Metal Dichalcogenides: Interfacial Reactions Study. *2D Mater.* **2015**, *2*, 014004. [\[CrossRef\]](#)
50. Yang, J.; Kim, S.; Choi, W.; Park, S.H.; Jung, Y.; Cho, M.-H.; Kim, H. Improved Growth Behavior of Atomic-Layer-Deposited High-*k* Dielectrics on Multilayer MoS₂ by Oxygen Plasma Pretreatment. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4739–4744. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Nayfeh, O.M.; Marr, T.; Dubey, M. Impact of Plasma-Assisted Atomic-Layer-Deposited Gate Dielectric on Graphene Transistors. *IEEE Electron Device Lett.* **2011**, *32*, 473–475. [\[CrossRef\]](#)
52. Lim, T.; Kim, D.; Ju, S. Direct deposition of aluminum oxide gate dielectric on graphene channel using nitrogen plasma treatment. *Appl. Phys. Lett.* **2013**, *113*, 013107. [\[CrossRef\]](#)
53. Aria, A.I.; Nakanishi, K.; Xiao, L.; Braeuninger-Weimer, P.; Sagade, A.A.; Alexander-Webber, J.A.; Hofmann, S. Parameter Space of Atomic Layer Deposition of Ultrathin Oxides on Graphene. *ACS Appl. Mater. Interfaces* **2016**, *8*, 30564. [\[CrossRef\]](#)
54. Kwak, I.; Kavrik, M.; Park, J.H.; Grissom, L.; Fruhberger, B.; Wong, K.T.; Kang, S.; Kummel, A.C. Low interface trap density in scaled bilayer gate oxides on 2D materials via nanofog low temperature atomic layer deposition. *Appl. Surf. Sci.* **2019**, *463*, 758–766. [\[CrossRef\]](#)
55. Kitzmann, J.; Göritz, A.; Fraschke, M.; Lukosius, M.; Wenger, C.; Wolff, A.; Lupina, G. Perfluorodecyltrichlorosilane-based seed-layer for improved chemical vapour deposition of ultrathin hafnium dioxide films on graphene. *Sci. Rep.* **2016**, *6*, 29223. [\[CrossRef\]](#)
56. Farmer, D.B.; Chiu, H.-Y.; Lin, Y.-M.; Jenkins, K.A.; Xia, F.; Avouris, P. Utilization of a Buffered Dielectric to Achieve High Field-Effect Carrier Mobility in Graphene Transistors. *Nano Lett.* **2009**, *9*, 4474. [\[CrossRef\]](#)
57. Kim, S.; Nah, J.; Jo, I.; Shahrjerdi, D.; Colombo, L.; Yao, Z.; Tutuc, E.; Banerjee, S.K. Realization of a high mobility dual-gated graphene field-effect transistor with Al₂O₃ dielectric. *Appl. Phys. Lett.* **2009**, *94*, 062107. [\[CrossRef\]](#)
58. Iraiwa, A.; Matsumura, D.; Kawarada, H. Effect of atomic layer deposition temperature on current conduction in Al₂O₃ films formed using H₂O oxidant. *J. Appl. Phys.* **2016**, *120*, 084504.
59. Fallahazad, B.; Kim, S.; Colombo, L.; Tutuc, E. Dielectric Thickness Dependence of Carrier Mobility in Graphene with HfO₂ Top Dielectric. *Appl. Phys. Lett.* **2010**, *97*, 123105. [\[CrossRef\]](#)
60. Zhao, P.; Khosravi, A.; Azcatl, A.; Bolshakov, P.; Mirabelli, G.; Caruso, E.; Hinkle, C.L.; Hurley, P.K.; Wallace, R.M.; Young, C.D. Evaluation of border traps and interface traps in HfO₂/MoS₂ gate stacks by capacitance–voltage analysis. *2D Mater.* **2018**, *5*, 031002. [\[CrossRef\]](#)
61. Zhou, P.; Yang, S.; Sun, Q.; Chen, L.; Wang, P.; Ding, S.; Zhang, D.W. Direct Deposition of Uniform High-*k* Dielectrics on Graphene. *Sci. Rep.* **2014**, *4*, 6448. [\[CrossRef\]](#)
62. Dingemans, G.; van de Sanden, M.C.M.; Kessels, W.M.M. Influence of the Deposition Temperature on the c-Si Surface Passivation by Al₂O₃ Films Synthesized by ALD and PECVD. *Electrochem. Solid-State Lett.* **2010**, *13*, H76. [\[CrossRef\]](#)
63. Roos, M.; Ku^ˆnzl, D.; Uhl, B.; Huang, H.H.; Brandao, O.; Hoster, H.E.; Gross, A.; Behm, R.J. Hierarchical Interactions and Their Influence upon the Adsorption of Organic Molecules on a Graphene Film. *J. Am. Chem. Soc.* **2011**, *133*, 9208. [\[CrossRef\]](#)
64. Bayer, B.C.; Aria, A.I.; Eder, D.; Hofmann, S.; Meyer, J.C. Resolving the Nucleation Stage in Atomic Layer Deposition of Hafnium Oxide on Graphene. *arXiv* **2019**, arXiv:1909.00712.
65. Giannazzo, F.; Fisichella, G.; Greco, G.; Fiorenza, P.; Roccaforte, F. *Conductive Atomic Force Microscopy: Applications in Nanomaterials*; Lanza, M., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2017; Chapter 7; pp. 163–186.
66. Sonde, S.; Giannazzo, F.; Raineri, V.; Yakimova, R.; Huntzinger, J.-R.; Tiberj, A.; Camassel, J. Electrical properties of the graphene/4H-SiC (0001) interface probed by scanning current spectroscopy. *Phys. Rev. B* **2009**, *80*, 241406(R). [\[CrossRef\]](#)
67. Emtsev, K.V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G.L.; Ley, L.; McChesney, J.L.; Ohta, T.; Reshanov, S.A.; Reohrl, J.; et al. Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nat. Mater.* **2009**, *8*, 203–207. [\[CrossRef\]](#)
68. Giannazzo, F.; Deretzis, I.; La Magna, A.; Roccaforte, F.; Yakimova, R. Electronic transport at monolayer-bilayer junctions in epitaxial graphene on SiC. *Phys. Rev. B* **2012**, *86*, 235422. [\[CrossRef\]](#)
69. Speck, F.; Ostler, M.; Rohrl, J.; Emtsev, K.V.; Hundhausen, M.; Ley, L.; Seyller, T. Atomic layer deposited aluminum oxide films on graphite and graphene studied by XPS and AFM. *Phys. Status Solidi C* **2010**, *7*, 398. [\[CrossRef\]](#)
70. Robinson, J.A.; LaBella, M.; Trumbull, K.A.; Weng, X.; Cavelero, R.; Daniels, T.; Hughes, Z.; Hollander, M.; Fanton, M. Nucleation of Epitaxial Graphene on SiC(0001). *ACS Nano* **2010**, *4*, 2667. [\[CrossRef\]](#)
71. Desai, S.R.; Madhvapathy, S.R.; Amani, M.; Kiriya, D.; Hettick, M.; Tosun, M.; Zhou, Y.; Dubey, M.; Ager, J.W.; Chrzan, D.; et al. Gold-Mediated Exfoliation of Ultralarge Optoelectronically-Perfect Monolayers. *Adv. Mater.* **2016**, *28*, 4053–4058. [\[CrossRef\]](#)
72. Huang, Y.; Pan, Y.-H.; Yang, R.; Bao, L.-H.; Meng, L.; Luo, H.-L.; Cai, Y.-Q.; Liu, G.-D.; Zhao, W.-J.; Zhou, Z.; et al. Universal mechanical exfoliation of large-area 2D crystals. *Nature Commun.* **2020**, *11*, 2453. [\[CrossRef\]](#)
73. Panasci, S.E.; Schilirò, E.; Greco, G.; Cannas, M.; Gelardi, F.M.; Agnello, S.; Roccaforte, F.; Giannazzo, F. Strain, Doping, and Electronic Transport of Large Area Monolayer MoS₂ Exfoliated on Gold and Transferred to an Insulating Substrate. *ACS Appl. Mater. Interfaces* **2021**, *13*, 31248–31259. [\[CrossRef\]](#)

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74. Panasci, S.E.; Schilirò, E.; Migliore, F.; Cannas, M.; Gelardi, F.M.; Roccaforte, F.; Giannazzo, F.; Agnello, S. Substrate impact on the thickness dependence of vibrational and optical properties of large area MoS₂ produced by gold-assisted exfoliation. *Appl. Phys. Lett.* **2021**, *119*, 093103. [[CrossRef](#)]
 75. Cabrero-Vilatela, A.; Alexander-Webber, J.A.; Sagade, A.A.; Aria, A.I.; Braeuninger-Weimer, P.; Martin, M.-B.; Weatherup, R.S.; Hofmann, S. Atomic layer deposited oxide films as protective interface layers for integrated graphene transfer. *Nanotechnology* **2017**, *28*, 485201. [[CrossRef](#)]
 76. Magda, G.Z.; Pető, J.; Dobrik, G.; Hwang, C.; Biró, L.P.; Tapasztó, L. Exfoliation of large-area transition metal chalcogenide single layers. *Sci. Rep.* **2015**, *5*, 14714. [[CrossRef](#)]
 77. Ge, R.; Wu, X.; Kim, M.; Shi, J.; Sonde, S.; Tao, L.; Zhang, Y.; Lee, J.C.; Akinwande, D. Atomristor: Nonvolatile Resistance Switching in Atomic Sheets of Transition Metal Dichalcogenides. *Nano Lett.* **2018**, *18*, 434. [[CrossRef](#)]