

Review

# Atomic Layer Deposition of High-k Insulators on Epitaxial Graphene: A Review

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**Featured Application:** Graphene-based electronics and sensing.

**Abstract:** Due to its excellent physical properties and availability directly on a semiconductor substrate, epitaxial graphene (EG) grown on the (0001) face of hexagonal silicon carbide is a material of choice for advanced applications in electronics, metrology and sensing. The deposition of ultrathin high-k insulators on its surface is a key requirement for the fabrication of EG-based devices, and, in this context, atomic layer deposition (ALD) is the most suitable candidate to achieve uniform coating with nanometric thickness control. This paper presents an overview of the research on ALD of high-k insulators on EG, with a special emphasis on the role played by the peculiar electrical/structural properties of the EG/SiC (0001) interface in the nucleation step of the ALD process. The direct deposition of Al<sub>2</sub>O<sub>3</sub> thin films on the pristine EG surface will be first discussed, demonstrating the critical role of monolayer EG uniformity to achieve a homogeneous Al<sub>2</sub>O<sub>3</sub> coverage. Furthermore, the ALD of several high-k materials on EG coated with different seeding layers (oxidized metal films, directly deposited metal-oxides and self-assembled organic monolayers) or subjected to various prefunctionalization treatments (e.g., ozone or fluorine treatments) will be presented. The impact of the pretreatments and of thermal ALD growth on the defectivity and electrical properties (doping and carrier mobility) of the underlying EG will be discussed.

**Keywords:** epitaxial graphene; atomic layer deposition; high-k insulators

## 1. Introduction

Graphene, the two-dimensional (2D) sp<sup>2</sup> allotropic form of carbon, has been the object of continuously increasing scientific and technological interest, starting from its first isolation in 2004 [1]. Among the different types of graphene materials considered so far, the epitaxial graphene (EG) grown by controlled high temperature graphitization of the (0001) face of hexagonal silicon carbide (6H- or 4H-SiC) [2–4] is a material of choice for advanced applications in electronics [5,6], high precision metrology [7] and environmental sensing [8]. The main advantage of this growth method over other commonly used approaches (such as chemical vapor deposition, CVD, on catalytic metals [9]) is the availability of high quality graphene directly on a semiconducting or semi-insulating substrate, i.e., ready for electronic devices fabrication, without the need of transfer processes [10,11] typically responsible for contaminations and damages [12,13].

Deposition of uniform ultra-thin insulators (especially high-k dielectrics) on graphene is a key step for the fabrication of graphene-based electronic devices [6,14–17]. In this context, the atomic layer

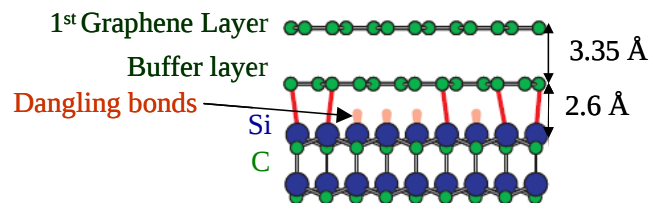
deposition (ALD), owing to its sequential layer-by-layer growth mechanism [18], is the most suitable candidate to achieve a conformal growth with subnanometric control on the thickness. However, the lack of out-of-plane bonds or surface groups in the  $sp^2$  lattice of graphene typically represents the main obstacle to films nucleation in the early stage of the ALD growth. This typically results in an inhomogeneous coverage of graphene surface, although the quality of the deposited films strongly depends on the graphene synthesis method, the graphene substrate and eventual transfer processes of graphene from the native substrate to foreign ones. As an example, for defect-free graphene flakes exfoliated from graphite, ALD growth was found to occur preferentially at the edges of the flakes [19], whereas, in the case of polycrystalline graphene grown by CVD on metals and transferred to insulating substrates, the ALD nucleation typically occurs at the grain boundaries and on wrinkles [20]. Interestingly, in the specific case of EG grown by thermal decomposition of SiC (0001), uniform ALD coverage has been observed on the monolayer (1 L) EG areas, whereas inhomogeneous growth has been found on the bilayer (2 L) or few layer regions [21]. These ALD nucleation issues common to all the graphene materials are typically circumvented by adopting surface preparation protocols, consisting of chemical prefunctionalization of graphene surface to introduce reactive ( $sp^3$ ) sites, or by the predeposition of seed layers [22–32]. However, proper optimization of these processes is necessary in order to avoid structural damages and a degradation of graphene electronic properties.

Although the research on ALD for graphene devices integration has been recently the object of comprehensive review articles [33], to the best of our knowledge, a focused paper reviewing ALD of high-k insulators on the EG/SiC(0001) system is currently missing. This article aims to provide an overview on this topic, highlighting the specific approaches adopted to achieve uniform ALD growth in the case of EG. Section 2 provides an introduction to the peculiar structural and electrical properties of EG and its interface with the (0001) SiC substrate. Section 3 presents recent results on the direct deposition of  $Al_2O_3$  thin films on the pristine EG, elucidating the key role played by the  $sp^3$  hybridized buffer layer to obtain a homogeneous  $Al_2O_3$  coverage on monolayer EG. Furthermore, the ALD on EG coated with different seeding layers, including oxidized metal films [34], high-k metal oxide thin films [35], self-assembled organic monolayers [36] or spin coated graphene oxide [37], will be presented in Section 4. Different prefunctionalization treatments of EG surface by exposure to reactive gases such as ozone [38] or  $XeF_2$  [39] will be described in the Section 5. The impact of these surface preparation processes and of thermal ALD growth on the defectivity and electrical properties of the underlying graphene will be discussed. Finally, open research issues and perspectives in the field of ALD on graphene are presented in the Section 6.

## 2. Morphology and Interface Structure of Epitaxial Graphene on SiC (0001)

Graphene growth by thermal decomposition of hexagonal SiC relies on the interplay of three mechanisms: (i) the preferential Si sublimation from the topmost SiC layers, leaving an excess of carbon, (ii) the diffusion of these C atoms on the SiC surface and (iii) their reorganization in the 2D hexagonal graphene lattice. These mechanisms depend both on the annealing conditions (sample temperature and gas partial pressures in the chamber) and on the SiC surface termination. To date most of the studies on graphene growth have been carried out on the Si terminated (0001) face [40–43] and on the C terminated (000-1) face [40–43], due to the availability of large area SiC substrates with these orientations. Some experiments on the non-polar faces (1-100) and (11-20) have been recently reported as well [44]. Graphene films with very different structural and electronic properties (defectivity, thickness homogeneity, doping and mobility) have been obtained on these different crystal orientations, as a result of the different surface reconstructions during thermal decomposition. Multilayers of graphene rotationally disordered to each other and with respect to the substrate are typically obtained on the (000-1) face. On the contrary, monolayer or Bernal stacked few layers of graphene showing single crystalline epitaxial alignment with the SiC substrate are normally achieved on the (0001) face. This is due to the specific growth mechanism, mediated by the formation of an interfacial carbon layer, the so-called buffer layer (BL), with partial  $sp^3$  hybridization with the Si face [45]. Figure 1

schematically depicts the structure of the BL, which is covalently bonded to Si atoms of the substrate with a large density of dangling bonds, and to the topmost monolayer of graphene with Van der Waals forces. This peculiar interface structure makes EG compressively strained, and the electrostatic interaction with the dangling bonds at the BL/SiC interface is responsible for a high n-type doping (approx.  $10^{13} \text{ cm}^{-2}$ ) of the overlying EG [46,47].



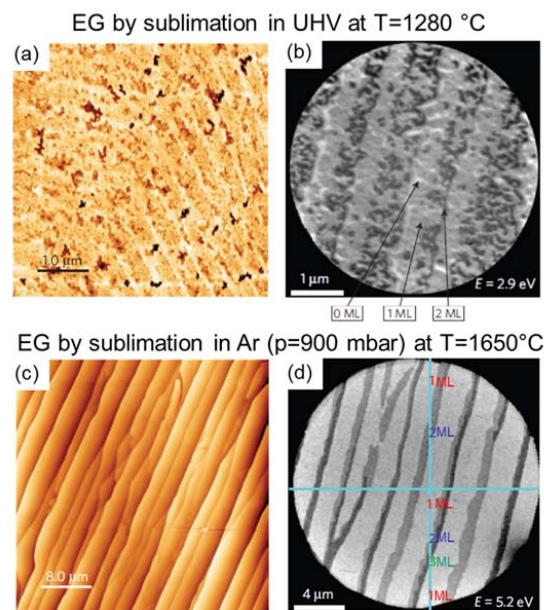
**Figure 1.** Illustration of the structure of monolayer EG grown on SiC (0001), showing the buffer layer partially bond to the Si face, with unsaturated dangling bonds at the interface.

Although thermal decomposition of the (0001) face allows a good control of the number of layers, achieving uniform 1 L graphene coverage on the entire SiC surface remains one of the main challenges in this research field. Besides having an impact on the EG electronic properties, thickness inhomogeneities of EG have also a critical impact on the nucleation of insulating films grown by ALD, as discussed in the Section 3.

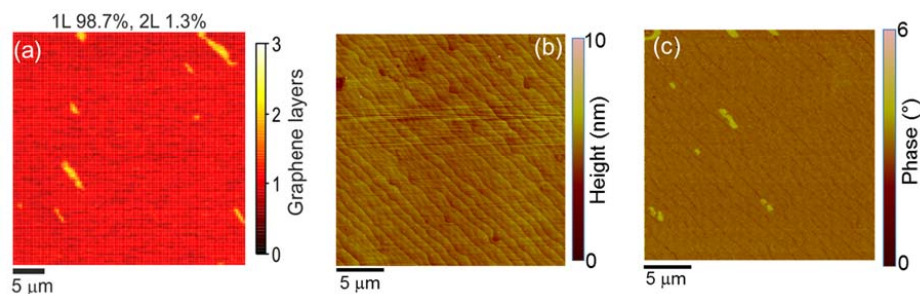
The EG thickness uniformity on the (0001) face depends on the growth conditions (temperature and pressure) and on the substrate morphology, in particular the miscut angle, with better uniformity achieved for low miscut angle (nominally “on-axis”) SiC. Under the ultra-high-vacuum (UHV) condition, EG formation has been achieved at temperatures as low as 1280 °C [3], but the topography and thickness distribution of the EG film was typically very inhomogeneous (composed of submicrometer 0 L, 1 L and 2 L patches) as shown by the atomic force microscopy (AFM) and low energy electron microscopy (LEEM) maps in Figure 2a,b. On the other hand, growth in inert gas (Ar) ambient at atmospheric pressure (approx. 900 mbar) allows it to greatly reduce the Si sublimation rate, raising the EG formation temperature at values as high as  $T = 1650 \text{ °C}$  [3]. As shown in Figure 2c,d, the EG grown on “nominally” on-axis SiC(0001) is commonly composed of 1 L domains on the planar (0001) SiC terraces, separated by long and narrow 2 L or 3 L EG stripes at SiC step edges. Such steps are inherent of SiC crystal and their spacing is related to the miscut angle [48]. The preferential formation of 2 L and 3 L EG at their edges is related to the enhanced Si-desorption from these locations due to the weaker bonding in the SiC matrix. Although the EG grown under these atmospheric pressure/high temperature conditions is more homogeneous than EG grown under UHV, the presence of nanometric steps in the substrate morphology and of 1 L/2 L lateral junctions localized at these steps have been shown to cause a reduction of local electrical conductivity of EG [49,50].

Further improvement in the EG thickness homogeneity have been achieved by performing thermal decomposition of nominally on-axis 4H-SiC (0001) at a temperature of 2000 °C in inert gas (Ar) at atmospheric pressure in a radio frequency (RF) heated sublimation growth reactor [4]. By using specific well-controlled growth conditions (temperature distribution in the growth cell, temperature ramping up, and base pressure) monolayer EG coverage on most of the SiC surface has been obtained [21]. Figure 3a reports a reflectance map collected on a large area ( $30 \mu\text{m} \times 30 \mu\text{m}$ ) of EG grown under these optimized conditions. Reflectance mapping is a straightforward method to evaluate the number of layers distribution on large area EG samples by comparing the graphene thickness dependent reflected power with that of a bare 4H-SiC substrate [51]. Here the small yellow patches, corresponding to 2 L EG regions, covered only 1.3% surface and were surrounded by 1 L EG background on the 98.7% the area. Figure 3b,c shows the AFM morphology and the corresponding phase map on a  $30 \mu\text{m} \times 30 \mu\text{m}$  sample area. The morphological image shows the typical stepped surface of 4H-SiC (0001), and the variable contrast in the phase image provides information on the variation in the number of EG layers

at different positions. In particular, the small elongated patches with higher phase contrast in Figure 3c correspond to the 2 L regions in the reflectance maps in Figure 3a.



**Figure 2.** (a) Atomic force microscopy (AFM) morphology and (b) low energy electron microscopy (LEEM) map of EG grown on 6H-SiC(0001) by sublimation in ultra-high-vacuum (UHV) at a temperature  $T = 1280$  °C. (c) AFM morphology and (d) LEEM map of EG on 6H-SiC(0001) obtained by sublimation in Ar ambient at atmospheric pressure ( $p = 900$  mbar) and at a temperature  $T = 1650$  °C. Darker LEEM contrast corresponds to a larger number of graphene layers. Images adapted with permission from Ref. [21], Copyright Nature Publishing Group 2009.



**Figure 3.** (a) Reflectance map of as-grown EG collected on a  $30 \mu\text{m} \times 30 \mu\text{m}$  sample area. The red contrast background is associated with 1 L graphene (98.7% of the total area) and the yellow elongated patches to 2 L graphene (1.3% of the total area). (b) AFM morphology and (c) phase contrast map on a  $30 \mu\text{m} \times 30 \mu\text{m}$  sample area. The small elongated patches with higher phase contrast correspond to 2 L EG. Images adapted with permission from Ref. [21], copyright Wiley 2019.

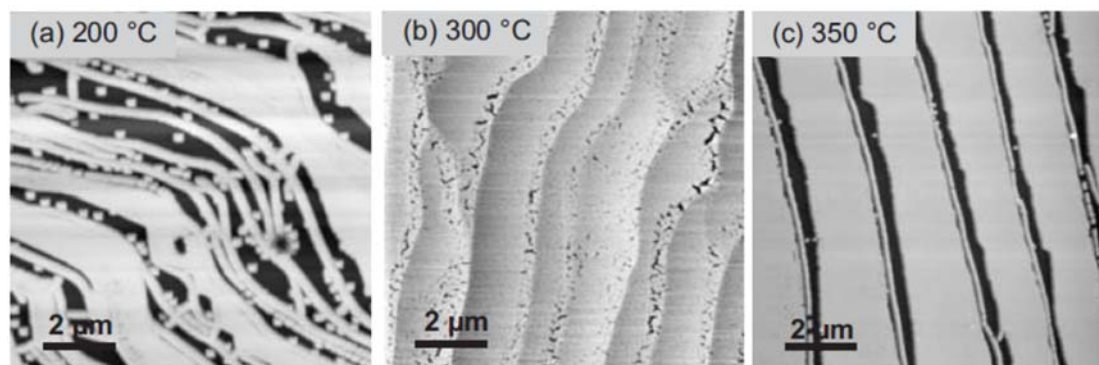
After introducing the peculiar structural and morphological properties of EG/SiC(0001), an overview of recent literature results in the ALD of high-k insulators on this material system would be provided in the next sections. Table 1 is a synoptic table including data from selected reference papers, including the specs of the EG material, the type of EG surface preparation adopted for the subsequent ALD process, the ALD growth details (precursors, temperature and number of cycles), the properties of the deposited dielectric material (thickness and uniformity), as well as the effect of the surface preparation/ALD process on the structural properties of EG.

**Table 1.** Overview of literature reports on atomic layer deposition (ALD) of dielectric materials on EG. Listed are the specs on EG growth process and number of graphene layers, the type of EG surface preparation used to achieve uniform ALD, the used ALD precursors and deposition temperatures, the thickness and uniformity of the deposited dielectric material, and whether EG was damaged by the surface preparation and/or the ALD process.

| Ref  | EG/SiC(0001) Specs                                                              | ALD Process                                                                      |                                                 |                       |                                                                                            |           |
|------|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------|-------------------------------------------------|-----------------------|--------------------------------------------------------------------------------------------|-----------|
|      |                                                                                 | EG Surface Prep                                                                  | Precursors                                      | T <sub>ALD</sub> (°C) | Insulator                                                                                  | EG Damage |
| [38] | EG growth at 1650 °C in Ar 1000 mbar, 1 L on SiC terraces, 2 L–3 L at SiC steps | None                                                                             | Trimethylaluminum/H <sub>2</sub> O, 500 cycles  | 200, 300, 350         | Al <sub>2</sub> O <sub>3</sub> (50 nm), not closed                                         | No        |
| [21] | EG growth at 2000 °C in Ar 900 mbar, 1 L EG (>98%) with submicron 2 L patches   | None                                                                             | Trimethylaluminum/H <sub>2</sub> O, 500 cycles  | 250                   | Al <sub>2</sub> O <sub>3</sub> (12 nm), closed on >98% surface                             | No        |
| [34] | EG growth at 1600 °C in Ar 600 Torr, 1 L to 3 L EG                              | Oxidized Al seed layer, 2 nm                                                     | Triethylaluminum/H <sub>2</sub> O               | 150, 300              | Al <sub>2</sub> O <sub>3</sub> , closed                                                    | No        |
|      |                                                                                 | Oxidized Ti seed layer, 2 nm                                                     | Titanium(IV) i-propoxide/H <sub>2</sub> O       | 120, 250              | TiO <sub>2</sub> , closed                                                                  | No        |
|      |                                                                                 | Oxidized Ta seed layer, 2 nm                                                     | Pentakis(dimethylamino)tantalum(V)              | 150, 300              | Ta <sub>2</sub> O <sub>5</sub> , closed, high roughness                                    | Yes       |
| [35] | EG growth at 1600 °C in Ar 900 mbar, Few layers EG                              | PVD Al <sub>2</sub> O <sub>3</sub> seed layer, 2 nm                              | Triethylaluminum/H <sub>2</sub> O               | 300                   | Al <sub>2</sub> O <sub>3</sub> (8 nm) + Al <sub>2</sub> O <sub>3</sub> seed (2 nm), closed | No        |
|      |                                                                                 |                                                                                  | Tetrakis(dimethylamino)hafnium/H <sub>2</sub> O | 250                   | HfO <sub>2</sub> (8 nm) + Al <sub>2</sub> O <sub>3</sub> seed (2 nm), closed               | No        |
|      |                                                                                 | PVD HfO <sub>2</sub> seed layer, 2 nm                                            | Triethylaluminum/H <sub>2</sub> O               | 300                   | Al <sub>2</sub> O <sub>3</sub> (8 nm) + HfO <sub>2</sub> seed (2 nm), closed               | No        |
|      |                                                                                 |                                                                                  | Tetrakis(dimethylamino)hafnium/H <sub>2</sub> O | 250                   | HfO <sub>2</sub> (8 nm) + HfO <sub>2</sub> seed (2 nm), closed                             | No        |
|      |                                                                                 | PVD SiO <sub>2</sub> seed layer, 2 nm                                            | Tetrakis(dimethylamino)hafnium/H <sub>2</sub> O | 250                   | HfO <sub>2</sub> (10 nm) + SiO <sub>2</sub> seed (2 nm), closed                            | No        |
| [36] | EG growth at 1350 °C in UHV, mixed 1 L–2 L EG                                   | Organic seed layer: 1 L of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) | Trimethylaluminum/H <sub>2</sub> O, 25 cycles   | 100                   | Al <sub>2</sub> O <sub>3</sub> (2.3 nm), closed                                            | No        |
|      |                                                                                 |                                                                                  | Tetrakis(diethylamido)hafnium(IV), 25 cycles    | 100                   | HfO <sub>2</sub> (2.5 nm), closed                                                          | No        |
| [38] | EG growth at 1650 °C in Ar 1000 mbar, 1 L on SiC terraces, 2 L–3 L at SiC steps | O <sub>3</sub> prefunctionalization at T = 250 °C                                | Trimethylaluminum/H <sub>2</sub> O, 500 cycles  | 250                   | Al <sub>2</sub> O <sub>3</sub> (50 nm), closed                                             | No        |
|      |                                                                                 | O <sub>3</sub> prefunctionalization at T = 350 °C                                | Trimethylaluminum/H <sub>2</sub> O, 500 cycles  | 350                   | Al <sub>2</sub> O <sub>3</sub> (50 nm), closed                                             | Yes       |
| [39] | EG growth at 1650 °C in Ar, 100 mbar                                            | Fluorine prefunctionalization by XeF <sub>2</sub> gas (from 0 to 200 s)          | Trimethylaluminum/H <sub>2</sub> O              | 225                   | Al <sub>2</sub> O <sub>3</sub> (~15 nm), closed                                            | No        |

### 3. Direct ALD on Pristine Epitaxial Graphene

Early studies on thermal ALD of high- $k$  insulators (like  $\text{Al}_2\text{O}_3$  or  $\text{HfO}_2$ ) on pristine EG samples typically resulted in a non-uniform coverage, with poor or no oxide nucleation in the vicinity of the step edges [34,38]. As an example, Speck. et al. [38] investigated direct thermal ALD of  $\text{Al}_2\text{O}_3$  on EG grown at 1650 °C in Ar ( $p = 900$  mbar) [3]. Figure 4 illustrates the morphologies of the  $\text{Al}_2\text{O}_3$  films obtained after 500 ALD cycles (corresponding to 50 nm  $\text{Al}_2\text{O}_3$ ) at different deposition temperatures of 200 °C (a), 300 °C (b) and 350 °C (c), using trimethylaluminum (TMA) as the aluminum source, and water as the oxidant.

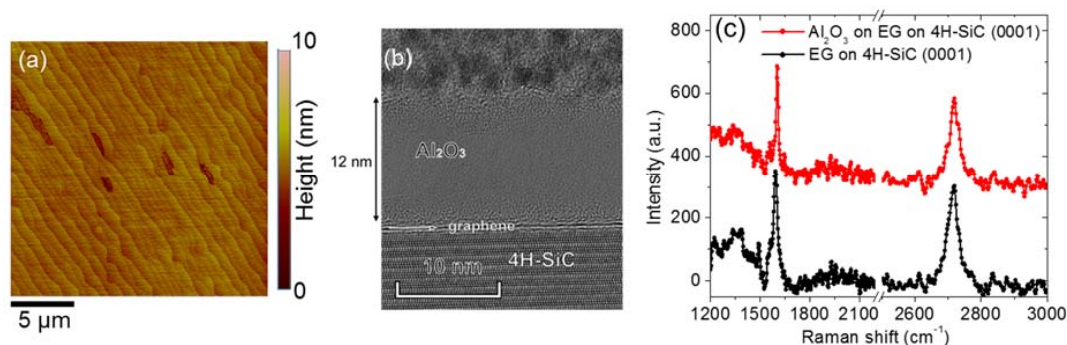


**Figure 4.** AFM images of  $\text{Al}_2\text{O}_3$  grown directly on the pristine EG surface by 500 thermal ALD cycles of TMA/water (i.e., 50 nm  $\text{Al}_2\text{O}_3$ ) at different temperatures: (a) 200 °C, (b) 300 °C and (c) 350 °C. Images adapted with permission from Ref. [38], copyright Wiley 2010.

Poor or no oxide nucleation was observed in the vicinity of the step edges. As discussed in the Section 2, samples with 1 L EG on the (0001) terraces typically exhibit 2 L or few layers EG stripes at the step edges between terraces [3]. Hence, the  $\text{Al}_2\text{O}_3$  uncovered areas were associated by the authors to the presence of 2 L or few layer EG underneath. However, no clear explanation of the different ALD nucleation and growth behavior on 1 L and 2 L EG was provided. Similarly, Robinson et al. [34] reported that the direct thermal ALD of  $\text{Ta}_2\text{O}_5$ , and  $\text{TiO}_2$  results in non-uniform coverage of EG up to a maximum deposition temperature (300 °C). More recently, Schilirò et al. [21] employed highly uniform 1 L EG samples (>98% monolayer coverage) as substrates for direct thermal ALD of  $\text{Al}_2\text{O}_3$  at a temperature of 250 °C with TMA and  $\text{H}_2\text{O}$  precursors. Figure 5 shows the morphological and structural characterization of an  $\text{Al}_2\text{O}_3$  film obtained after 190 deposition cycles, corresponding to a nominal film thickness of 15 nm, evaluated from the 0.08 nm/cycle deposition rate on a reference silicon substrate. Figure 5a depicts a representative morphological image by AFM on a  $20\ \mu\text{m} \times 20\ \mu\text{m}$  scan area. The  $\text{Al}_2\text{O}_3$  film is conformal with the topography of the EG/4H-SiC surface, except for some small depressions showing the same elongated shape of the 2L graphene patches (see, for comparison, Figure 3). A high resolution cross-sectional TEM image of the as-deposited  $\text{Al}_2\text{O}_3$  film is reported in Figure 5b, where the 1 L EG plus the underlying BL can be clearly identified, and the amorphous  $\text{Al}_2\text{O}_3$  layer shows uniform contrast, indicating a uniform  $\text{Al}_2\text{O}_3$  density. The measured  $\text{Al}_2\text{O}_3$  thickness was 12 nm, which is thinner than the nominal one and was ascribed to a lower growth rate of  $\text{Al}_2\text{O}_3$  on EG surface in the early stages of the deposition process.

Raman spectroscopy measurements were carried out both on the virgin EG sample and after the  $\text{Al}_2\text{O}_3$  deposition, in order to evaluate the changes induced by the thermal ALD process at 250 °C on the structural quality and doping/strain of the underlying EG. Two representative Raman spectra for the two cases, respectively, are reported in Figure 5c. The characteristic G and 2D peaks of graphene exhibit single Lorentzian shape, and the FWHM of the 2D peaks in these representative spectra are consistent with the 1 L nature of EG [52]. The small changes in the positions of the G and 2D peaks after the  $\text{Al}_2\text{O}_3$  deposition indicate that the ALD process did not significantly affect the doping and strain of the EG. The features in the  $1200\text{--}1500\ \text{cm}^{-1}$  range were related to the interfacial BL, whereas

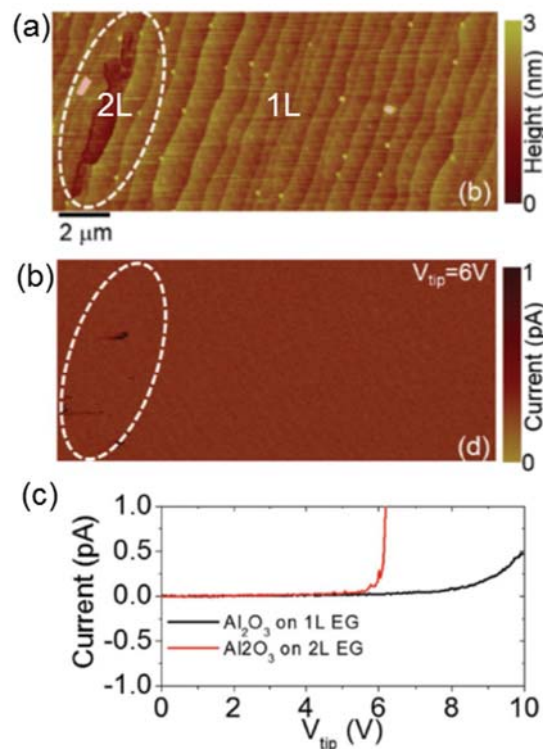
no significant increase of the the intensity of the disorder-related D peak ( $1300\text{ cm}^{-1}$ ) was observed, indicating that no defects were introduced by the ALD process.



**Figure 5.** (a) AFM morphology ( $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$  scan area) of Al<sub>2</sub>O<sub>3</sub> directly grown on 1 L EG on SiC by 190 water/TMA ALD cycles. (b) Cross-sectional TEM image of the Al<sub>2</sub>O<sub>3</sub> layer. (c) Representative Raman spectra of virgin EG and after the Al<sub>2</sub>O<sub>3</sub> deposition. Images adapted with permission from Ref. [21], copyright Wiley 2019.

The electrical quality of the insulating layer was also evaluated by conductive atomic force microscopy (C-AFM) for current mapping and local current-voltage (I-V) analyses [21]. A morphology map of the scanned area is reported in Figure 6a, which includes both uniform Al<sub>2</sub>O<sub>3</sub> on 1 L EG and Al<sub>2</sub>O<sub>3</sub> on a 2 L EG patch. Figure 6b shows a current map collected on this area with a positive value of the tip bias  $V_{\text{tip}} = 6\text{ V}$  with respect to EG. While uniform low current values were detected through the 12 nm Al<sub>2</sub>O<sub>3</sub> film onto 1 L EG, the presence of high current spots was observed in the 2 L EG region. Figure 6c illustrates two representative local current-voltage characteristics collected by the C-AFM probe on Al<sub>2</sub>O<sub>3</sub> in the 1 L and 2 L EG regions. While current smoothly increased with the bias for Al<sub>2</sub>O<sub>3</sub> on 1 L EG, an abrupt rise of current was observed for  $V_{\text{tip}} > 6\text{ V}$  in the case of Al<sub>2</sub>O<sub>3</sub> on 2 L EG. This locally enhanced conduction in the 2 L EG area was justified by the less compact Al<sub>2</sub>O<sub>3</sub> structure and the lower Al<sub>2</sub>O<sub>3</sub> thickness detected in these regions. By adopting a simplified planar capacitor model for the tip/Al<sub>2</sub>O<sub>3</sub>/EG system, a breakdown field  $> 8\text{ MV cm}^{-1}$  was estimated for the 12 nm Al<sub>2</sub>O<sub>3</sub> on 1 L EG.

The superior homogeneity of Al<sub>2</sub>O<sub>3</sub> deposition on 1 L EG areas indicates a higher reactivity of 1 L EG with respect to 2 L or few layers EG, which was explained in terms of the higher n-type doping and strain caused by the interfacial BL on a single graphene overlayer with respect to 2 L [21]. Recent experimental and theoretical investigations demonstrated that the interaction of polar water molecules with graphene depends on the Fermi level of graphene, i.e., its doping [53]. In particular, ab-initio calculations of the adsorption energy ( $E_a$ ) for water molecules (the co-reactant of the ALD growth) on 1 L graphene as a function of doping predicted an increase of  $E_a$  from 127 meV for neutral graphene to 210 meV for highly n-type doped ( $10^{13}\text{ cm}^{-2}$ ) graphene [21]. The time of residence of a water molecule on graphene at a temperature  $T$  depends on  $E_a$  as  $\exp(E_a/k_B T)$ , where  $k_B$  is the Boltzmann constant. As a result, for the ALD process temperature ( $T = 250\text{ }^\circ\text{C}$ ), the residence time of physisorbed water molecules on the highly n-type doped EG was approximately six times higher than in the case of neutral graphene. The longer residence time provides, in turns, a larger number of reactive sites for Al<sub>2</sub>O<sub>3</sub> formation during subsequent pulses of the Al precursor.



**Figure 6.** Conductive atomic force microscopy (C-AFM) local current mapping through an  $\text{Al}_2\text{O}_3$  thin film deposited onto EG on axis 4H-SiC(0001). (a) Morphology of the probed sample area, including both uniform  $\text{Al}_2\text{O}_3$  on 1 L EG and  $\text{Al}_2\text{O}_3$  on a 2 L EG patch. (b) Current map collected on this area with a tip bias  $V_{\text{tip}} = 6$  V. (c) Two representative local current-voltage characteristics collected by the C-AFM probe on  $\text{Al}_2\text{O}_3$  in the 1 L and 2 L EG regions. Images adapted with permission from Ref. [21], copyright Wiley 2019.

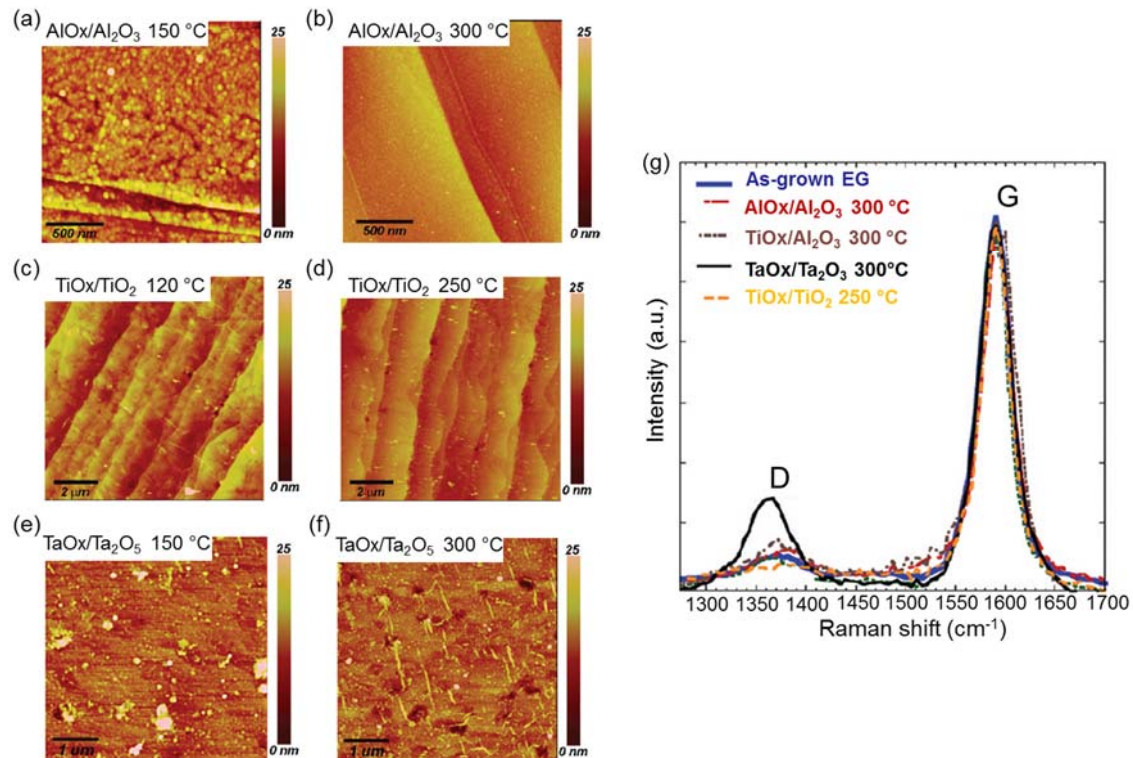
#### 4. ALD on EG With a Seeding-Layer

The above discussed literature results show that uniform and conformal high-k dielectrics could be obtained by direct ALD on monolayer EG areas. However, the availability of 100% 1 L EG coverage by thermal decomposition of SiC still represents a major challenge. For this reason, in many cases, the use of an intermediate seeding layer is the preferred solution to promote homogeneous ALD nucleation on the EG surface. In the following, the main seeding layer processes adopted so far will be presented, discussing the advantages and disadvantages in terms of their impact on the EG structural and electrical properties.

##### 4.1. Oxidized Metal Seed Layer

Physical vapor deposition (PVD) of ultrathin metal films followed by oxidation is one of the most straightforward ways to create a seeding layer on the graphene surface [22]. Robinson et al. [34] investigated thermal ALD of different insulators ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$ ) using oxidized metal films as seeding layers in the specific case of few layers EG/SiC(0001). Figure 7a,b shows the morphology of  $\text{Al}_2\text{O}_3$  grown at 150 and 300 °C, respectively, with an oxidized Al (AlOx) seed layer. The  $\text{Al}_2\text{O}_3$  film uniformity and coverage was found to be significantly improved by increasing the deposition temperature. Deposition of  $\text{TiO}_2$  on EG with an oxidized Ti (TiOx) seed layer resulted in conformal and continuous films both at 120 °C (Figure 7c) and 250 °C (Figure 7d). Finally, ALD grown  $\text{Ta}_2\text{O}_5$  films with an oxidized Ta (TaOx) seed layer showed a high roughness for deposition temperatures of 150 °C (Figure 7e) and 300 °C and (Figure 7f). The impact of the seeded thermal ALD on the EG structural properties (i.e., the defects density) was also qualified by Raman spectroscopy. Figure 7g shows typical Raman spectra of the D and G peaks for AlOx/ $\text{Al}_2\text{O}_3$  deposited at 300 °C, TiOx/ $\text{TiO}_2$

deposited at 250 °C, and TaOx/Ta<sub>2</sub>O<sub>5</sub> deposited at 300 °C. These results show that ALD of high-k dielectric materials with an oxidized metal seed layer generally have little impact on the structural integrity of EG, with the highest EG defectivity obtained in the case of TaOx/Ta<sub>2</sub>O<sub>5</sub>, probably generated during oxidation of the Ta seed layer.



**Figure 7.** AFM morphology of Al<sub>2</sub>O<sub>3</sub> thin films grown by ALD at 150 °C (a) and 300 °C (b) on EG/SiC with an oxidized Al seed layer. Morphology of TiO<sub>2</sub> grown by ALD at 120 °C (c) and 250 °C (d) on EG/SiC with an oxidized Ti seed layer. Morphology of Ta<sub>2</sub>O<sub>5</sub> grown by ALD at 150 °C (e) and 300 °C (f) on EG/SiC with an oxidized Ta seed layer. (g) Raman spectra of as-grown EG and after ALD deposition of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> with different seed layers. Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> deposition introduces only a small amount of disorder in EG, whereas Ta<sub>2</sub>O<sub>5</sub> deposition appears to significantly degrade the quality of the underlying EG. Images adapted with permission from Ref. [34], Copyright American Chemical Society 2010.

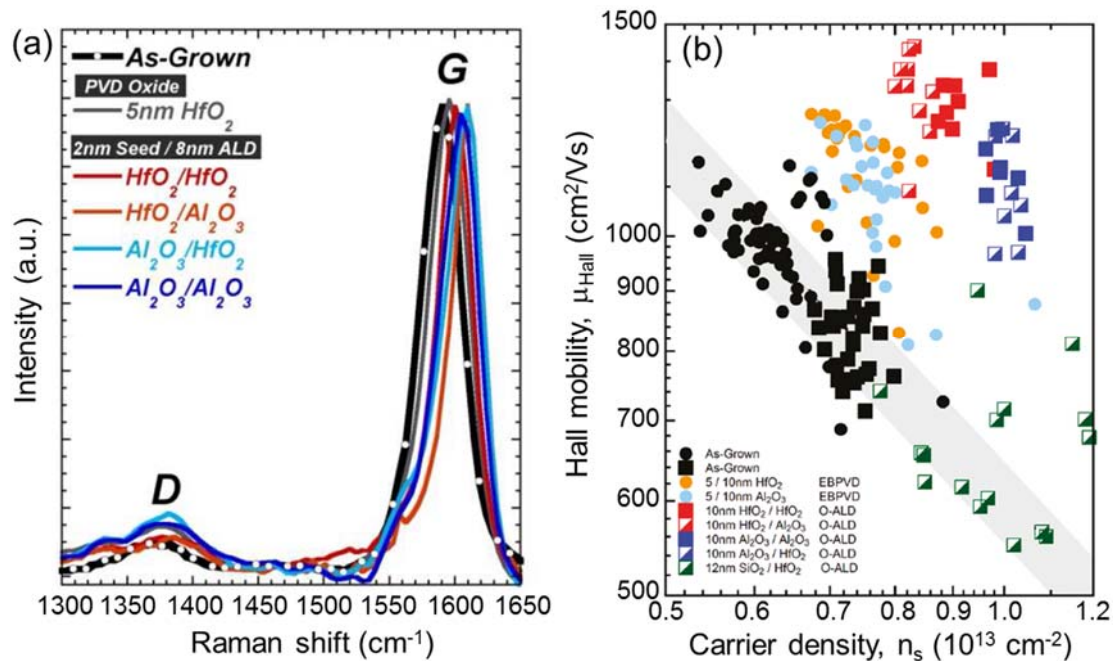
In spite of the limited increase in the EG defectivity, a reduction of the electron mobility has been reported in most of the cases after ALD of high-k dielectrics seeded by an oxidized metal [34]. This was ascribed to the poor structural quality and substoichiometric composition of the seed layer (typically due to an incomplete oxidation), leading to charge trapping phenomena and increased electron scattering by charged impurities.

#### 4.2. Deposited High-k Metal-Oxide Seed Layers

As discussed above, the metal to metal-oxide phase transition occurring in the case of the oxidized metal seeding layers can be a source of mobility degradation in EG. To avoid these issues, the deposition of the seed-layer directly on EG from a high-purity oxide source has been also considered.

As an example, Hollander et al. [35] employed 2–3 nm seed layers of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or HfO<sub>2</sub> deposited via nonreactive electron beam physical vapor deposition (EBPVD) at a pressure <10<sup>−6</sup> Torr. Immediately following the seed-layer evaporation, 8–10 nm of Al<sub>2</sub>O<sub>3</sub> or HfO<sub>2</sub> were deposited by ALD to complete the dielectric stack.

Figure 8a shows Raman spectra acquired on as-grown EG samples, after EBPVD oxide deposition and after the complete oxide-seeded ALD process. Minimal changes in the D/G ratio were observed among the different samples, whereas the blue-shift of the G peak after seed-layer and ALD was ascribed to an increase of EG doping.



**Figure 8.** (a) Raman spectra of as-grown EG, after physical vapor deposition (PVD) of 5 nm HfO<sub>2</sub> and after HfO<sub>2</sub>-seeded (or Al<sub>2</sub>O<sub>3</sub>-seeded) ALD of HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. (b) Hall mobility  $\mu_{Hall}$  vs. carrier density  $n_s$  measured on as-grown EG, after electron beam physical vapor deposition (EBPVD) of oxide seed-layers and the complete oxide-seeded ALD (O-ALD) process. Images adapted with permission from Ref. [35], Copyright American Chemical Society 2010.

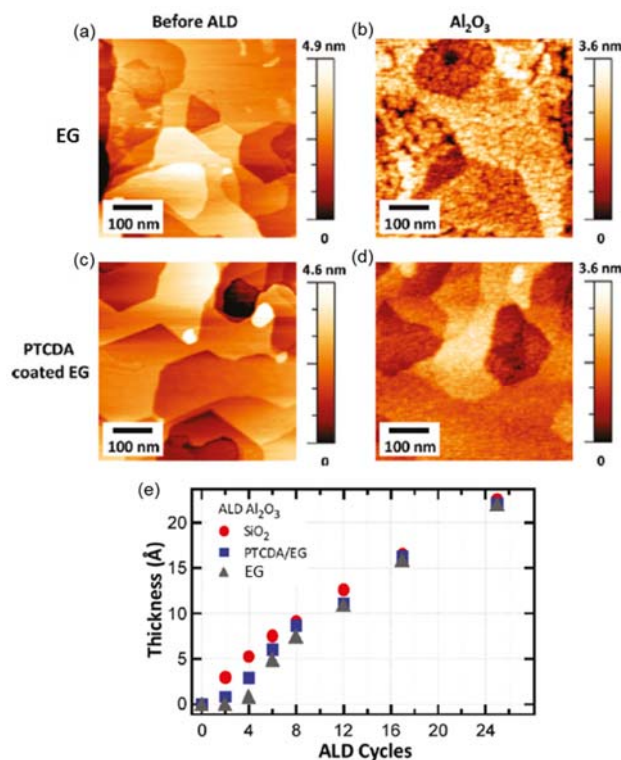
Hall effect measurements under high vacuum at 300 K were also carried out on EG prior to and following the metal-oxide seeded ALD in order to evaluate the effect of the deposited dielectrics on carrier transport properties, i.e., the carrier density ( $n_s$ ) and Hall mobility ( $\mu_{Hall}$ ) [35].

Figure 8b shows the correlation between  $\mu_{Hall}$  and  $n_s$  measured on as-grown EG, after EBPVD of oxides and the complete oxide-seeded ALD (O-ALD). As-grown EG samples presented  $\mu_{Hall}$  values of 700–1100 cm<sup>2</sup>V<sup>−1</sup>s<sup>−1</sup> and  $n_s$  values of  $(5\text{--}8) \times 10^{12}$  cm<sup>−2</sup> (n-type), typical of Si-face EG. Figure 8 demonstrates that the high-k seeded dielectrics deposited by PVD and O-ALD resulted in an increase in  $n_s$  and an increase in  $\mu_{Hall}$ . Conversely, HfO<sub>2</sub> seeded by a low-k insulator (SiO<sub>2</sub>) resulted in a decrease of  $\mu_{Hall}$  and the increase in  $n_s$ . The measured increase of  $\mu_{Hall}$  with deposition of high-k seed was attributed to dielectric screening, i.e., a reduction in scattering by remote charged impurities [54]. In particular, HfO<sub>2</sub> seeded O-ALD dielectrics enhance carrier mobility by an estimated 57%–73%, while Al<sub>2</sub>O<sub>3</sub> seeded O-ALD dielectrics increase mobility by 43%–52%.

#### 4.3. Self-Assembled Organic Monolayer

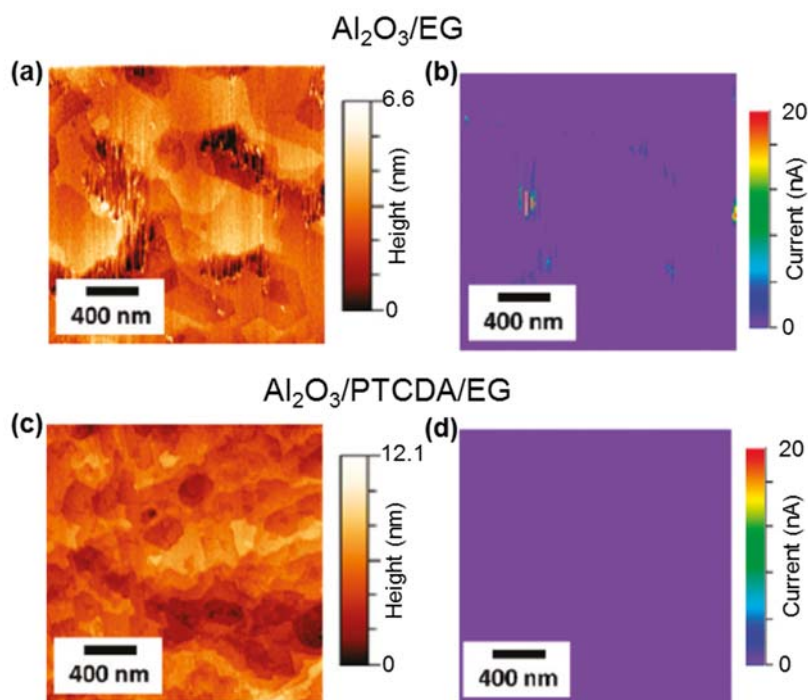
Alaboson et al. [36] demonstrated an alternative ALD seeding layer based on organic monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). EG on SiC(0001) grown by sublimation in UHV conditions at 1350 °C was used in this study. PTCDA was deposited on the EG surface via gas-phase sublimation in ultrahigh vacuum (UHV), resulting in a highly uniform and ordered self-assembled monolayer. Two typical AFM images of the bare EG and PTCDA/EG surfaces are presented in Figure 9a,c, respectively, showing nearly identical roughness. Figure 9b,d shows two representative AFM images of Al<sub>2</sub>O<sub>3</sub> deposited on the bare EG (b) and on PTCDA/EG (d) using

25 cycles of TMA and H<sub>2</sub>O at a temperature of 100 °C. While a discontinuous Al<sub>2</sub>O<sub>3</sub> film was observed on the bare EG, the use of the PTCDA seeding layer resulted in a uniform Al<sub>2</sub>O<sub>3</sub> film, conformal with the underlying terraces of the EG surface. Figure 9e shows the evolution of the Al<sub>2</sub>O<sub>3</sub> film thickness as a function of ALD growth cycle evaluated by spectroscopic ellipsometry on the bare EG, on PTCDA/EG and on a reference SiO<sub>2</sub> surface. The Al<sub>2</sub>O<sub>3</sub> ALD on the bare EG surface was initially inhibited for 3–4 ALD cycles, indicating a lack of reactive sites for the ALD precursors, as compared to the case of the SiO<sub>2</sub> surface. On the other hand, nucleation on the PTCDA-seeded EG surface was more efficient with ALD growth showing a linear behavior after only 1–2 ALD cycles, similarly to the case of the SiO<sub>2</sub> surface with a high density of reactive sites.



**Figure 9.** (a) Representative AFM image of an EG surface prepared by UHV graphitization. (b) AFM images of EG surface after ALD of 25 cycles of Al<sub>2</sub>O<sub>3</sub>. (c) AFM images of EG surface immediately after PTCDA deposition and (d) following ALD of 25 cycles of Al<sub>2</sub>O<sub>3</sub>. (e) Al<sub>2</sub>O<sub>3</sub> film thickness as a function of ALD growth cycle evaluated by spectroscopic ellipsometry on the bare EG, on PTCDA/EG and on a reference SiO<sub>2</sub> surface. Images adapted with permission from Ref. [36], Copyright American Chemical Society 2011.

To probe the adhesion and the insulating properties of the deposited ALD films, C-AFM imaging was employed. The morphology and current maps in Figure 10a,b show that for a thin Al<sub>2</sub>O<sub>3</sub> film (25 ALD cycles) on bare EG, conductive defects were produced after only one C-AFM scan in contact mode (contact force 20 nN, tip/sample voltage V = 0.3 V), resulting in localized conduction spots in the current map. This defect density was further increased after multiple C-AFM scans. Figure 10c,d shows the C-AFM morphology and current maps acquired under the same measurement conditions on the Al<sub>2</sub>O<sub>3</sub> film grown using the same number of ALD cycles on PTCDA/EG. These maps demonstrate the excellent morphological and uniform insulating properties of Al<sub>2</sub>O<sub>3</sub> on PTCDA seeded EG, which are maintained even after multiple C-AFM scans.



**Figure 10.** C-AFM morphology (a) and current map (b) of  $\text{Al}_2\text{O}_3$  deposited by 25 ALD cycles on the bare EG surface. Morphology (c) and current map (d) of  $\text{Al}_2\text{O}_3$  deposited with the same number of cycles on the PTCDA/EG surface. Images adapted with permission from Ref. [36], copyright American Chemical Society 2011.

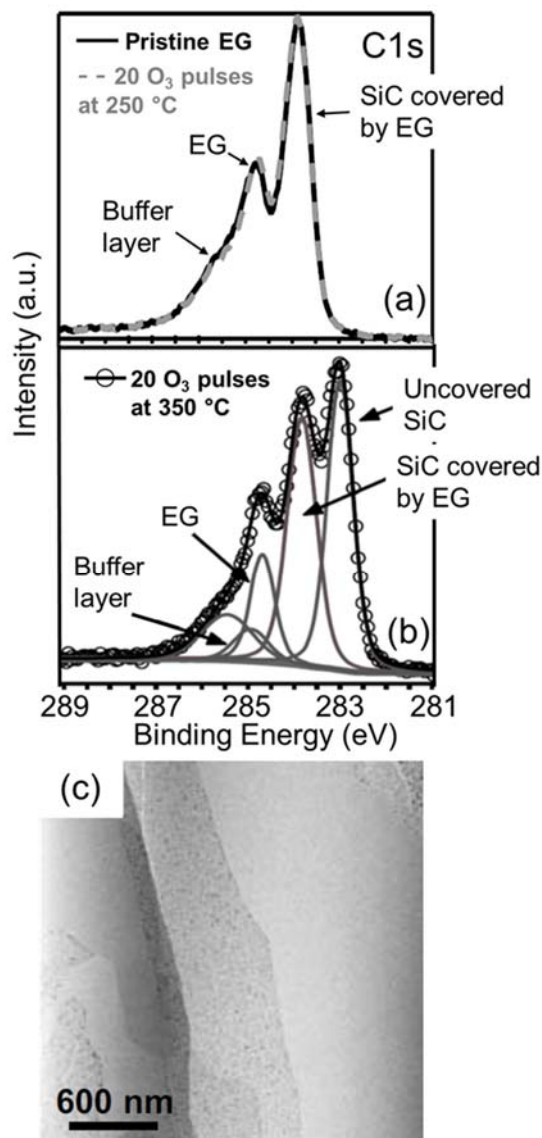
## 5. ALD on Prefunctionalized EG

Different prefunctionalization processes of the EG surface by direct exposure to reactive gas species have been reported so far.

### 5.1. Ozone Prefunctionalization

Speck et al. [38] evaluated the effect of in-situ ozone ( $\text{O}_3$ ) pretreatment on the uniformity of ALD grown  $\text{Al}_2\text{O}_3$  onto EG. Firstly, a preliminary study of the influence of different  $\text{O}_3$  dosing conditions (i.e., number of  $\text{O}_3$  pulses and temperature) on the structural properties of EG was carried out. Figure 11a shows the comparison between two C1s core level X-ray photoelectron spectroscopy (XPS) measurements on as-grown EG and after exposure to 20  $\text{O}_3$  pulses at a temperature of 250 °C, respectively. The two spectra show two prominent peaks associated to the EG and to the SiC substrate (covered by EG), respectively, and a shoulder associated to the interfacial BL. The two spectra are almost perfectly overlapped, indicating a negligible effect of the  $\text{O}_3$  treatment at 250 °C on EG structural and chemical properties. Figure 11b shows a C1s core level spectrum acquired on EG after 20  $\text{O}_3$  pulses at a higher temperature of 350 °C, with a deconvolution of the different spectral contributions, associated to the SiC substrate, to EG and to the BL. In addition to the components present in the pristine EG sample and in the  $\text{O}_3$ -functionalized one at 250 °C (Figure 11a), another peak at lower binding energy, associated to SiC uncovered by EG, was observed in the EG sample subjected to the 20  $\text{O}_3$  pulses at 350 °C. From the XPS peaks intensity ratio, these bare SiC regions due to partial etching of EG by  $\text{O}_3$ , were found to correspond to 45% of EG surface. The degradation of the structural integrity of EG after this  $\text{O}_3$  pretreatment (20 pulses at 350 °C) was also confirmed by Raman spectroscopy, showing a strong increase of the defects-related D peak and a large broadening of the G peak. Noteworthy, further experiments showed that EG damage can be mitigated by properly reducing the number of  $\text{O}_3$  pulses [38]. As an example, the percentage of etched EG at 350 °C was found to be reduced to 2.5% by using only 2  $\text{O}_3$  pulses. Figure 11c shows a representative AFM image of a 50 nm thick  $\text{Al}_2\text{O}_3$  film

obtained by 500 TMA/water cycles on the EG sample prefunctionalized using 20 O<sub>3</sub> pulses at 250 °C, i.e., the non-destructive conditions illustrated in Figure 11a. Although a uniform Al<sub>2</sub>O<sub>3</sub> coating was obtained on the entire EG surface, the higher roughness of the oxide film in the 2 L EG region close to the SiC steps indicated a limit for further reduction of O<sub>3</sub> exposure and temperature.

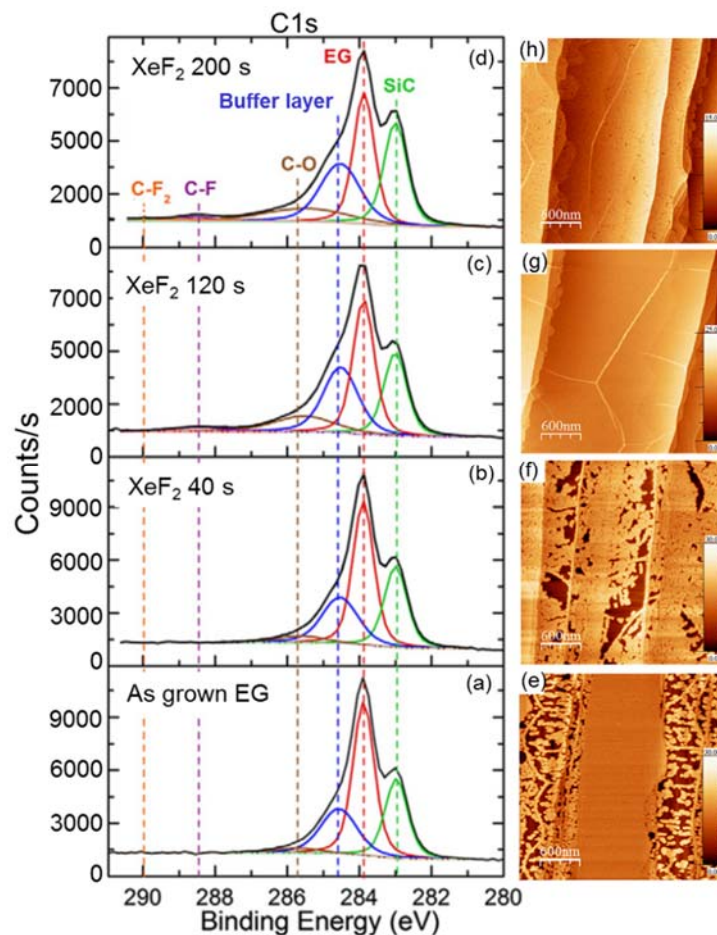


**Figure 11.** (a) XPS spectra from C1s core-level for pristine EG on SiC(0001) (solid line) and after 20 O<sub>3</sub> pulses at 250 °C. The two spectra are overlapped indicating negligible etching of graphene by the O<sub>3</sub> treatment. (b) C 1s core level spectrum of EG after 20 O<sub>3</sub> pulses at 350 °C, showing the appearance of an additional peak associated to uncovered SiC, which indicates partial etching of EG. (c) AFM image of a 50 nm thick Al<sub>2</sub>O<sub>3</sub> film grown by 500 TMA/water cycles on EG pretreated with 20 O<sub>3</sub> pulses at 250 °C. Figures adapted with permission from Ref [38], copyright Wiley 2010.

## 5.2. Fluorine Prefunctionalization

Wheeler et al. [39] investigated fluorine prefunctionalization of EG for uniform deposition of thin high-k dielectrics. Due to its high electronegativity (4.0) and its ability to adhere to carbon surfaces [55], fluorine is a suitable reactive species to enhance graphene surface reactions with ALD precursors. Fluorination of the EG grown onto on-axis 6H-SiC (0001) was carried out at room temperature exposing the EG surface to XeF<sub>2</sub> gas pulses, with the total fluorine dosing time varied in the range from 0 to

200 s. Core level XPS was used to preliminary determine the bonding characteristics of fluorine with the EG surface with increasing  $\text{XeF}_2$  exposure time. Figure 12a,d shows the C1s XPS spectra acquired on as-grown EG (a) and on EG subjected to 40 s (b), 120 s (c) and 200 s (d)  $\text{XeF}_2$  exposure times. For as-grown EG (a), the contributions associated to the SiC substrate, to EG and to the interfacial buffer layer were visible. A very similar XPS spectrum was found after 40 s  $\text{XeF}_2$  exposure (b), whereas the appearance of a feature at 288.5 eV, associated to C–F bonds, could be observed after 120 s (c) and 200 s (d)  $\text{XeF}_2$  exposure times. Such bonds are created by breaking the  $\text{sp}^2$  symmetry of the EG lattice resulting in carbon  $\text{sp}^3$  bonds with fluorine. A decrease in the EG peak intensity was observed corresponding to the appearance of C–F bonds, which further supports the transition from  $\text{sp}^2$  to  $\text{sp}^3$  bonded carbon on the surface. For the largest exposure time (d), an additional small peak associated to C–F<sub>2</sub> bonds was detected at 290 eV. The formation of C–F<sub>2</sub> was accompanied by a significant deformation of the EG lattice, leading to a degradation of EG electrical properties. Hence, it was chosen to work in a fluorination regime where C–F bonding only occurred. The C–F  $\text{sp}^3$  bond configuration was found to provide additional reaction sites of oxide nucleation and growth during the subsequent ALD process. After the initial assessment of the effect of  $\text{XeF}_2$  exposure on EG chemical properties,  $\text{Al}_2\text{O}_3$  films (15 nm thickness) were deposited by thermal ALD at 225 °C using TMA/ $\text{H}_2\text{O}$  precursors.



**Figure 12.** XPS C1s spectra on as-grown EG (a) and after  $\text{XeF}_2$  exposure for 40 s (b), 120 s (c) and 200 s (d). AFM images of  $\text{Al}_2\text{O}_3$  morphology for samples treated with varying amounts of fluorine: (e) no pretreatment and (f) 40 s  $\text{XeF}_2$  exposure results in large areas of no oxide deposition; (g) 120 s  $\text{XeF}_2$  exposure yields a conformal, uniform film and (h) 200 s  $\text{XeF}_2$  exposure shows pinholes throughout the oxide. Figures adapted with permission from Ref. [39], Copyright Elsevier 2012.

AFM characterization of the  $\text{Al}_2\text{O}_3$  uniformity was carried out for all the fluorine prefunctionalization conditions. Figure 12e,h shows four representative AFM images of  $\text{Al}_2\text{O}_3$  deposited on pristine EG (c) and after fluorine prefunctionalization at 40 s (f), 120 s (g) and 200 s (h), respectively. An inhomogeneous  $\text{Al}_2\text{O}_3$  coverage, especially close to the SiC step edges, was observed on the untreated EG (e) and after 40 s  $\text{XeF}_2$  exposure (f). Highly uniform and conformal coverage by the 15 nm  $\text{Al}_2\text{O}_3$  film was obtained on the fluorine prefunctionalized sample by 120 s  $\text{XeF}_2$  exposure, as shown in Figure 12g. This indicated the need of C–F bonding, as observed by XPS (Figure 12c) to promote adhesion of the ALD oxide to the EG film. A slight degradation of  $\text{Al}_2\text{O}_3$  uniformity with the appearance of small pinholes in the oxide was observed in the sample prefunctionalized by 200 s  $\text{XeF}_2$  exposure (Figure 12h). Hence, based on morphological characterization, an optimal window of  $\text{XeF}_2$  exposure times from 60 to 180 s was identified to functionalize the EG surface with C–F bonds, resulting in uniform ALD of high-k dielectric films. Noteworthy, an almost unchanged surface roughness was observed comparing the morphology of EG before and after the prefunctionalization under these optimal conditions, indicating that the formation of C–F bonds does not substantially disrupt the EG lattice and planarity. Raman spectroscopy was also performed after the  $\text{XeF}_2$  pretreatment and ALD to evaluate the effect of these processes on the underlying EG. In spite of the formation of  $\text{sp}^3$  C–F bonds due to the  $\text{XeF}_2$  pretreatment, no significant increase in the D/G peaks intensity ratio was observed with increasing the  $\text{XeF}_2$  exposure time (i.e., the fluorine percentage on EG surface), suggesting the EG lattice was relatively unperturbed throughout the  $\text{XeF}_2$  and ALD process.

## 6. Open Research Issues and Perspectives

Deposition of ultra-thin and conformal insulators represents a key requirement for the fabrication of devices based on different kinds of graphene. Besides ALD, also physical deposition methods (e.g., evaporation or sputtering) have been explored to this purpose. Although the presence of active sites on graphene surface is not required for these approaches, physical deposition of insulators typically results in graphene damage and/or a reduction of the carrier mobility [56,57]. For this reason, ALD became the preferred approach for insulators deposition on graphene, in spite of the nucleation issues.

Thermal ALD of high-k dielectrics on EG presents some peculiar aspects related to the unique electrical/structural properties of the EG/SiC(0001) system, i.e., the presence of the  $\text{sp}^3$  hybridized interfacial BL, responsible for a high n-type doping and compressive strain of the overlying graphene. These properties were shown to be beneficial in enhancing the  $\text{Al}_2\text{O}_3$  nucleation on 1 L EG, whereas a poorer nucleation was observed on 2 L or few layers EG. Hence, the availability of 100% 1L EG coverage by thermal decomposition of SiC still represents a major challenge for direct ALD on EG.

CVD grown graphene on catalytic metals is another type of graphene widely used for electronics/optoelectronic applications. Typically, this material is transferred on insulating substrate and subsequently processed for devices fabrication. As the thermal ALD process commonly results in an inhomogeneous coverage, seeding layers or prefunctionalization treatments with reactive gas species are commonly employed to promote the ALD growth. However, these processes need to be carefully optimized to minimize structural damage and/or a degradation of the electrical properties (doping and mobility) of underlying graphene.

Recently, Dlubak et al. [58] demonstrated the direct thermal ALD of uniform  $\text{Al}_2\text{O}_3$  films on monolayer CVD graphene laying on the native metal substrates (Cu and Ni-Au). The enhanced nucleation was ascribed to the wetting transparency of monolayer graphene [59] and to the presence of peculiar polar traps at the graphene/metal interface, which promote the adsorption of water molecules (i.e., the oxygen precursor for the ALD process) on the graphene surface. Clearly, the number of graphene layers is a crucial aspect for this growth mechanism. In fact, the strength of the electrostatic interaction between the water precursor and the polar traps is weakened for multilayer graphene due to a decreased transparency, resulting in an inhomogeneous  $\text{Al}_2\text{O}_3$  coverage [58]. The direct growth of  $\text{Al}_2\text{O}_3$  or  $\text{HfO}_2$  on CVD graphene residing on the native metal substrate has the advantage of providing a protective layer for graphene, avoiding the direct contact of Gr with the polymeric films typically

used for the transfer process [60]. Furthermore, after transfer to an insulating substrate, the oxide layer on graphene can work a gate dielectric for graphene field effect transistors [60]. Although the ALD grown protective layer is beneficial to solve the problems related to polymeric contaminations on graphene surface, the transfer of the oxide/graphene stack from the native metal substrate to the target substrate still remains a critical step.

Most studies reported so far for ALD on graphene concern the deposition of metal-oxides. However, the integration of ultra-thin films of other materials, such as nitrides (including  $\text{SiN}_x$ ,  $\text{AlN}$ , etc.), hexagonal boron nitride, and transition metal dichalcogenides, TMDs, (such as  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$  and  $\text{WSe}_2$ ), with graphene (and specifically with the EG/SiC(0001) system) is attracting an increasing interest for novel electronics/optoelectronics applications [61,62], and ALD can play a key role in this field. To date, MOCVD and MBE are mainly employed for the integration of nitrides with graphene. Although plasma assisted-ALD allows a superior control on the uniformity of  $\text{SiN}_x$  [63] and  $\text{AlN}$  [64] thin films, the main issue is the plasma-induced damage or doping in graphene. Optimized ALD approaches for the growth of these materials on graphene are envisaged for the next years.

Hexagonal boron nitride (h-BN) is an insulating layered material with lattice structure similar to graphite. Due to the atomically sharp interface formed between h-BN and graphene, it is considered as the ideal insulator to achieve the intrinsic graphene mobility [65]. However, due to its low dielectric constant ( $k \approx 4$ ), the h-BN interfacial layer must be combined with a high- $k$  dielectric overlayer in order to reduce the effective oxide thickness (EOT) for realistic integration in graphene field effect transistors. Recently, the direct ALD growth of a high- $k$  insulator ( $\text{Y}_2\text{O}_3$ ) on the  $\text{sp}^2$  h-BN surface has been demonstrated, and the deposition mechanism was explained by enhanced adsorption of the Y precursor on h-BN due to the polarization [66]. The challenge in this research field is the large area growth of h-BN on graphene by scalable approaches.

The growth of  $\text{MoS}_2$  and other TMDs on EG is currently explored for the realization of 2D materials Van-der Waals heterojunctions on large area [67]. In this context, ALD can represent a valid alternative to the most employed CVD approaches. Dedicated studies on the selection of the precursors and on ALD deposition conditions are expected in the forthcoming years in this emerging research field.

## 7. Conclusions

In conclusion, the research on ALD of high- $k$  insulators on EG was reviewed, with a focus on the role played by the peculiar electrical/structural properties of the EG/SiC(0001) interface in the nucleation step of the ALD process. Direct thermal ALD of uniform  $\text{Al}_2\text{O}_3$  thin films on monolayer EG areas was demonstrated to be possible, but achieving monolayer graphene on the entire SiC surface still remains a major challenge. An overview of seeding layers approaches (oxidized metal films, directly deposited metal-oxides and self-assembled organic monolayers) and prefunctionalization treatments (e.g., ozone or fluorine treatments) for the ALD of different high- $k$  materials on EG was provided, considering the impact of these surface preparation processes on the defectivity and electrical properties (doping and carrier mobility) of the underlying EG. Finally, the open scientific issues and the perspectives for ALD growth of alternative insulator/semiconductor films (including  $\text{AlN}$ ,  $\text{SiN}$ , h-BN and TMDs) on graphene were discussed.

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