Atomic layer deposition of aluminum oxide films on graphene

Raul Rammula, Lauri Aarik, Arne Kasikov, Jekaterina Kozlova, Tauno Kahro, Leonard Matisen, Ahti Niilisk, Harry Alles and Jaan Aarik

Institute of Physics, University of Tartu, Tartu, 51014, Estonia

E-mail: raul.rammula@ut.ee

Abstract. Seed-layer approach was studied to initiate atomic layer deposition (ALD) of Al₂O₃ films on graphene. Low-temperature ALD and electron beam evaporation (EBE) were applied for seed-layer preparation before deposition of the dielectric at 200 °C using trimethylaluminum and water or ozone as precursors. To characterize nucleation of the films and possible influence of the ALD processes on the quality of graphene, properties of graphene and Al₂O₃ films were investigated by Raman spectroscopy, X-ray fluorescence and X-ray photoelectron spectroscopy methods. The results suggest that seed layer formation by low-temperature ALD was more efficient in the O₃-based process than in the H₂O-based one while EBE seed layer provided fastest growth of Al₂O₃ together with minimum incubation period.

1. Introduction

Studies of various graphene-containing nanostructures and related thin film materials have been progressively extended since revealing the versatile properties of graphene in 2004 [1]. Field-effect transistors and spintronic devices belong to the most attractive application areas of graphene. These applications require integration of graphene into structures that contain very thin dielectric layers as gate dielectrics and/or tunnel barriers. Atomic layer deposition (ALD) has been considered to be a promising technique for preparation of this kind of dielectrics in the case of electronic devices based on traditional materials. ALD of thin films on graphene is, however, much more complex task because there are no reactive adsorption sites on the perfect graphene surface.

For preparation of monolayer graphene on large areas, chemical vapor deposition (CVD) is widely exploited. Unfortunately, uniformity of graphene obtained by this method is not very high yet [2]. Boundary regions of independently grown graphene flakes in conjunction with step edges, wrinkles and basal plane defects, typical for CVD graphene, are nucleation centers for ALD thin films [3,4]. Furthermore, impurities from the lift-off procedure can contaminate highly reactive graphene edges. These effects together with very low sticking probability of ALD precursors on defect-free areas of graphene make the deposition of ALD films on graphene non-uniform. Thus, direct deposition of Al₂O₃ has resulted in selective growth of the dielectric on graphene edges and defects [3,4]. In order to improve the uniformity of ALD films, a physisorbed seed layer can be added between graphene and dielectric, more effective/reactive precursor chemistry can be used and/or growth temperature (T_G) can be reduced. Typical route to obtain Al₂O₃ film is to apply trimethylaluminum (TMA) and water vapor (H₂O) as precursors [5]. At low T_G (<100 °C), high concentration of hydrogen in the films is a major concern [5] that does not allow obtaining dielectric films with sufficient quality. Furthermore, purge periods that are needed to eliminate CVD like growth should be very long in the low-temperature H₂O-based ALD processes (about 180 seconds at T_G = 33 °C [5]). By replacing water to ozone (O₃),
Al₂O₃ of higher quality can be obtained [6]. However, care must be taken when graphene is treated with ozone, especially at higher temperatures [7,8]. Therefore in order to directly compare nucleation of Al₂O₃ on graphene in different cases, ALD of Al₂O₃ on CVD graphene was studied in this work using 3 seed layer approaches and 2 different oxygen precursors for ALD.

2. Experimental

Monolayer graphene was grown on commercial 25-μm thick polycrystalline copper foils (99.999%, Alfa Aesar) using recipe by van der Zande et al. [9]. Before graphene deposition copper foils were annealed at 960 °C in a CVD reactor for 30 minutes in a flow of Ar/H₂ (99.999%, AGA) gas. For graphene formation copper was exposed to a flow of 10% CH₄/Ar (99.999%, AGA) gas for about 20 minutes. To avoid possible damages and unintentional functionalization of graphene in the transfer process, Al₂O₃ films were deposited on graphene in its as-grown state on copper foils.

ALD of Al₂O₃ was carried out in a hot-wall flow-type reactor from the sequential pulses of TMA (98%, Aldrich) and H₂O or O₃. BMT Messtechnik equipment was used to produce ozone from O₂ (99.999%, AGA). During the growth experiments O₃ concentration was around 200–220 g/m³ whereas corresponding partial pressure in the reaction chamber was 34 Pa during O₃/O₂ pulse. Seed layers were deposited by EBE or by applying 1–3 ALD cycles at room temperature, if not stated otherwise. In few experiments, the ALD seed layers were deposited also at temperatures up to 50 °C. The rest of the dielectric layer was grown by applying up to 100 ALD cycles at 200 °C. To compare the film growth on different substrates, Al₂O₃ was simultaneously grown on copper foils and HF etched Si(100) too.

The thicknesses of alumina films were determined from X-ray fluorescence (XRF) data using a reference sample with known thickness and density measured by X-ray reflection (XRR). The Raman spectroscopy method was applied to estimate the quality of graphene before and after ALD processes. The Raman spectra were recorded with a Renishaw inVia micro-Raman spectrometer with an incident laser beam wavelength of 514 nm. A silicon reference sample was used for the calibration of the Raman shift. In addition, X-ray photoelectron spectroscopy (XPS) measurements were carried out using SCIENTA SES 100 electron energy analyser and a non-monochromatic twin anode Thermo XR3E2 X-ray tube with characteristic Al Ka (1486.6 eV) energy to analyze the films.

3. Results and Discussion

3.1. Nucleation and growth rate of Al₂O₃

Figure 1 show that the seed layers deposited on graphene had a significant influence on the dependence of the Al₂O₃ film thickness on the number of ALD cycles applied at 200 °C.

![Figure 1. Dependencies of film thickness on number of ALD cycles for Al₂O₃ films deposited on graphene (G), copper foil (Cu) and silicon (Si).](image)

![Figure 2. GPC of Al₂O₃ on graphene as a function of the number of ALD cycles.](image)
Expectedly, nucleation at the initial growth stage (inset of Figure 2) markedly determined the overall film thickness. The results indicate that employment of 1 ALD cycle for deposition of a seed layer was insufficient to initiate uniform growth on graphene in the TMA-H2O as well as TMA-O3 process (Figures 1 and 2). Al2O3 nucleation on hydrophobic graphene surface was inhibited and the initial growth dead-time (IGDT) was about 3 cycles for the TMA-H2O process (inset of Figure 2). In contrast, on bare copper foil this effect was not dominant meaning that enough surface sites were present for precursor adsorption already in the beginning of deposition. When 3 ALD cycles were applied for seed layer deposition, IGDT was reduced to almost zero also on graphene and high values of growth per cycle (GPC) were obtained for very thin films in both ALD processes studied. Smallest variation and highest mean value of GPC were observed on EBE seed layer (Figure 2). The GPC values of the films deposited on those sufficiently thick (0.15–0.4 nm) seed layers are very similar to respective values, which have been obtained for the TMA-H2O and TMA-O3 ALD processes on Si substrates at 200 °C and are highlighted by gray area between 0.10 and 0.13 nm/cycle in Figure 2.

3.2. Structure of graphene

Raman spectra recorded before and after Al2O3 deposition (Figure 3) showed characteristic G and 2D bands of graphene on strong background that was caused by the copper substrate. No D band formation at 1340 cm\(^{-1}\) could be seen. Thus, the seed layer deposited by applying only 1 ALD cycle protected graphene against marked damages that might have caused by O3 at 200 °C [8]. Nevertheless, Raman spectra of graphene showed blueshift of main bands after deposition of Al2O3 by applying 1 TMA-O3 cycles at 22 °C and 10 cycles at 200 °C (Figure 3(a)). A possible reason for the shift was partial oxidation of graphene [10]. XPS C1s spectra showing additional C=O, COOH component at higher binding energies (Figure 4) seemed to confirm this conclusion.

**Figure 3.** Raman spectra of graphene coated by Al2O3 via (a) O3-based and (b), (c) H2O-based ALD processes. Pure graphene is indicated as a reference.

**Figure 4.** XPS C1s core level spectra of graphene coated by Al2O3 (top) and SEM image of graphene (bottom).
Absence of D-band in the Raman spectra (Figure 3) suggests that graphene oxidation and growth defects that were observed by SEM (Figure 4) had relatively weak effect on overall properties of graphene. The increase of seed-layer deposition temperature degraded, however, film uniformity and, according to Raman spectroscopy studies (spectra not shown), caused appearance of honeycomb defects. In Raman spectra of some graphene samples coated by Al₂O₃ in the TMA-H₂O process, a weak band appeared at 1200 cm⁻¹ (peaks indicated by arrows in Figures 3 (b) and (c)). The band likely belongs to C-O or C-H vibrations. In the case of samples with EBE seed layers, XPS revealed formation of Cu₂O during Al₂O₃ deposition. Consequently, this seed layer was not dense enough to avoid diffusion of oxygen precursor to the substrate during the following ALD process. As graphene is considered to be a good diffusion barrier, the oxygen precursor most likely diffused into underlying copper through boundary regions in graphene (Figure 4) or areas that were not covered by graphene.

4. Conclusions

This study demonstrated that 0.2–0.4 nm thick Al₂O₃-based seed layers, prepared by ALD or EBE at room temperature, improved markedly Al₂O₃ nucleation on graphene surface during the following ALD of Al₂O₃ at 200 °C. Somewhat better nucleation was observed on EBE seed layers, partially due to greater thickness of those. Compared to the TMA-H₂O ALD process, the TMA-O₃-based one resulted in more uniform growth of the dielectric but caused also some oxidation of graphene. An advantage of the ALD seed layers compared to EBE seed layers is that the former allow deposition of a dielectric on graphene in one process.

Acknowledgements

The authors would like to thank Prof. Väino Sammelselg and Dr. Ilmo Sildos for the access of SEM and Raman measurements. The work was supported by European Science Foundation and Estonian Science Foundation under the EUROCORES Programme EuroGRAPHENE project "Entangled spin pairs in graphene" and by the European Union (FP7) through the program RODIN.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov 2004 Science 306 666-69.
[2] T. Wu, G. Ding, H. Shen, H. Wang, L. Sun, D. Jiang, X. Xie and M. Jiang 2013 Adv. Funct. Mater. 23 198-203.
[3] B. Lee, S.-Y. Park, H.-C. Kim, K. J. Cho, E. M. Vogel, M. J. Kim, R. M. Wallace and J. Kim 2008 App. Phys. Lett. 92 201302-1-3.
[4] H. Alles, J. Aarik, J. Kozlova, A. Niilisk, R. Rammula, V. Sammelselg 2011 Graphene-Synthesis, Characterization, Properties and Applications INTECH 99-114.
[5] M. D. Groner, F. H. Fabreguette, J. W. Elam and S. M. George 2004 Chem. Mater. 16 639-45.
[6] Y. Shen, Y. Li, J. Zhang, X. Zhu, Z. Hu, J. Chu 2012 Optoelect. and adv. Mater. 6 618-22.
[7] J. Yuan, L.-P. Ma, S. Pei, J. Du, Y. Su, W. Ren and H.-M. Cheng, ACS Nano, Accepted Manuscript DOI: 10.1021/nn400682u.
[8] B. Lee, G. Mordi, M. J. Kim, Y. J. Chabal, E. M. Vogel, R. M. Wallace, K. J. Cho, L. Colombo and J. Kim 2010 Appl. Phys. Lett. 97 043107-1-3.
[9] A.M. van der Zande, R.A. Barton, J.S. Alden, C.S. Ruiz-Vargas, W.S. Whitney, P.H.Q. Pham, J. Park, J.M. Parpia, H.G. Craighead, and P.L. McEuen 2010 Nano Lett. 10 4869-73.
[10] D. L. Duong, G. H. Han, S. M. Lee, F. Gunes, E. S. Kim, S. T. Kim, H. Kim, Q. H. Ta, K. P. So, S. J. Yoon, S. J. Chael, Y. W. Jo, M. H. Park, S. H. Chae, C. S. Lim, J. Y. Choi and Y. H. Lee, 2012, Nature 490 235-40.