

# INTEGRATION OF ATOMIC LAYER DEPOSITED $\text{Al}_2\text{O}_3$ DIELECTRICS WITH GRAPHENE

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## 1. Introduction

The accurate measurement of chemical concentrations is important for many industrial and medical technologies. Sensitivity, selectivity and rapid response are all virtues for sensors [1]. Graphene is emerging as a promising candidate for the goal of rapid, sensitive and inexpensive sensor due to its exceptionally high carrier mobility and single atomic thickness. It has been demonstrated that graphene exhibits the highest carrier mobilities exceeding  $200\,000\text{ cm}^2/\text{V s}$  [2] and critical current density is large approximately  $2 \times 10^8\text{ A/cm}^2$  [3]. For these reasons and many others graphene is regarded as a highly promising material for high-speed electronics.

Preparation of large area graphene films for electronic devices has been intensively studied since its discovery. Subsequently, standard silicon technology procedures can be applied for fabrication of electronic devices. For manufacturing field effect devices, the most advanced components in current electronics, integration of graphene with dielectric materials is necessary. Deposition of dielectric material onto graphene is of significant challenge due to the intrinsic material incompatibility between pristine graphene and dielectric oxide materials [4].

Atomic layer deposition emerges as promising technique for deposition of thin oxide dielectric films on graphene owing to its precise control of the film thickness, uniformity and ability to grow thin oxide films without damage to underlying graphene lattice [5–7].

In this work, the growth of dielectrics  $\text{Al}_2\text{O}_3$  thin films by different types of ALD on graphene was investigated. Graphene was firstly deposited on copper foil by chemical vapour deposition (CVD) and then transferred onto  $\text{SiO}_2/\text{Si}$  substrates. We summarize results on investigation of  $\text{Al}_2\text{O}_3$  thin film growth at  $100^\circ\text{C}$  in thermal, ozone and plasma enhanced ALD. More importantly, we demonstrate that these methods bring no substantial deterioration of graphene properties.

## 2. Experimental details

Graphene was grown on commercial  $25\text{-}\mu\text{m}$  thick polycrystalline copper foil (99.5%) in a home-assembled chemical vapour deposition reactor. The foil was annealed for 30 minutes at  $1000^\circ\text{C}$  in argon/ hydrogen (both 99.999%) flow and then exposed to the flow of the mixture of 10% methane (99.999%) in argon at the same temperature for 35 minutes. Then the sample was cooled at  $25^\circ\text{C}/\text{min}$  to room temperature in argon flow.

The as-grown graphene film was transferred to SiO<sub>2</sub>/Si substrate by using polymethyl methacrylate (PMMA) as a supporting material. The graphene layer deposited onto other side of the copper foil was removed in argon plasma. The copper foil was then removed by ammonium persulfate solution. The floating PMMA/graphene film was rinsed using deionized water and transferred to SiO<sub>2</sub>/Si substrate. After drying the sample the PMMA supporting layer was dissolved by dichloromethane.

Thin Al<sub>2</sub>O<sub>3</sub> films were prepared on top of the graphene films by different types of ALD at temperatures 100°C. Films were deposited by using thermal and plasma enhanced atomic layer deposition. Trimethylaluminium Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> was used as a metal precursor. In thermal ALD processes H<sub>2</sub>O or ozone was used as reactant while in plasma enhanced ALD, oxygen/argon plasma was employed.

Samples were grown in a Beneq TFS 200 ALD reactor equipped by capacitively-coupled plasma source operating at 13,56MHz. Nitrogen was used as a carrier gas and oxygen/argon mixture was used as a plasma gas. The process time parameters for all ALD process studied are shown in Table 1.

*Table 1. Pulsing times for ALD processes*

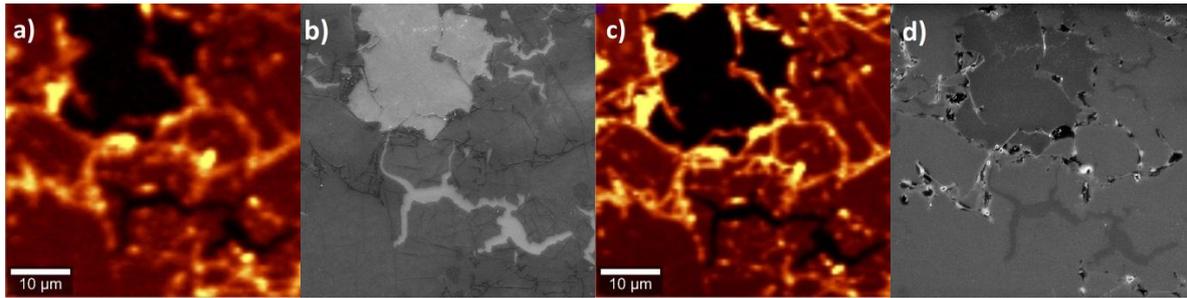
Sample number	ALD Process	Temperature [°C]	Pulsing times [s] Precursor dosing/purging/reactant exposure/purging
1	Thermal (H <sub>2</sub> O)	100	0.25/10/0.3/20
2	Thermal (ozone)	100	0.25/10/0.4/10
3	Plasma enhanced	100	0.25/10/4/20

Properties of graphene films before and after ALD growth were studied by using Raman spectrometry and scanning electron microscopy. Raman spectra of graphene excited with a wavelength of 532 nm were obtained via the Alpha 300R Confocal Raman Microscope. Thickness of the prepared Al<sub>2</sub>O<sub>3</sub> films was measured by X-ray reflectivity on a AXS-D8 Discover Bruker diffractometer. Characterization of Al<sub>2</sub>O<sub>3</sub> films was performed by energy dispersive X-ray spectroscopy (EDS) using a JEOL JSM 7600F microscope equipped with Oxford Instruments EDS analysis.

### 3. Results and discussion

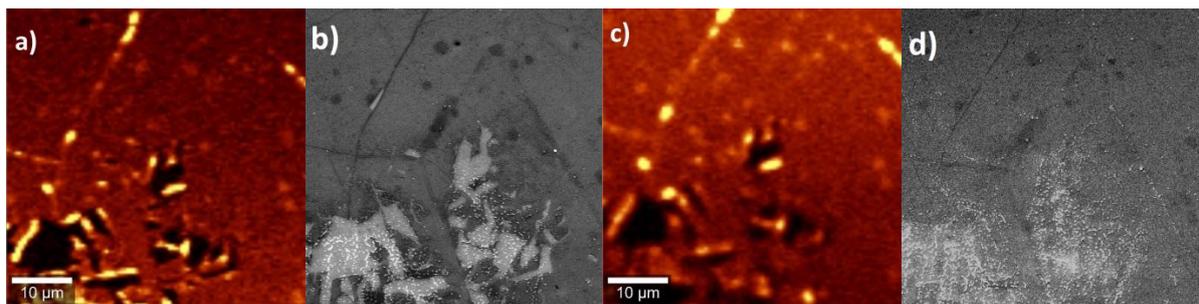
According Raman spectroscopy studies predominantly single-layer graphene was obtained in this way on all three prepared graphene samples. Graphene showed two main features: the zone-centre G peak and the second-order 2D band, which peak at ~ 1580 cm<sup>-1</sup> and 2680 cm<sup>-1</sup>, respectively. The Raman 2D band fingerprint of the graphene samples was sharp with a symmetric peak.

Moreover there was no evident difference in Raman maps of graphene before and after deposition dielectrics layer onto graphene for all samples. In the case of sample 1, fig. 1a shows the Raman measurements of graphene before Al<sub>2</sub>O<sub>3</sub> deposition and fig. 1c represent Raman measurement from the same place of graphene after deposition Al<sub>2</sub>O<sub>3</sub> by thermal ALD. We performed also scanning electron microscopy studies on the same place of sample 1 before (fig. 1b) and after deposition Al<sub>2</sub>O<sub>3</sub> onto graphene (fig. 1d). These results were consistent with Raman measurements. We observed only expected changes between SEM image of graphene before and after ALD due to deposition of Al<sub>2</sub>O<sub>3</sub> layer onto graphene.



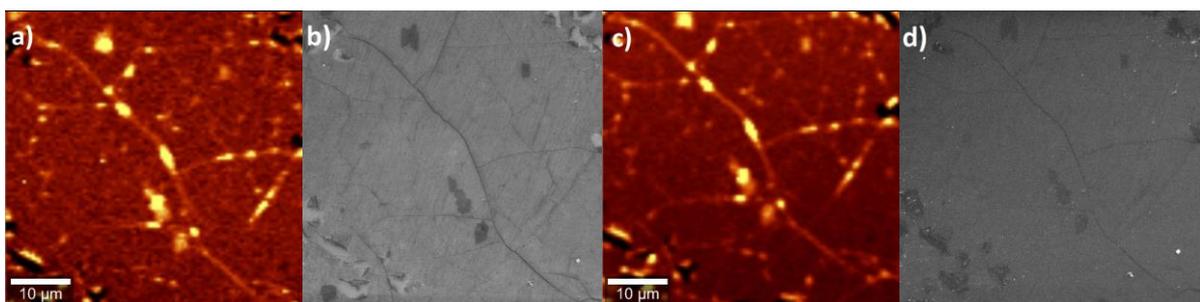
**Fig.1:** Sample 1 (a) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene before deposition  $\text{Al}_2\text{O}_3$  layer. (b) SEM image 50x50 $\mu\text{m}$  of graphene before deposition  $\text{Al}_2\text{O}_3$  layer in SE mode at the 10 kV. (c) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene after deposition  $\text{Al}_2\text{O}_3$  layer onto graphene by thermal ALD. (d) SEM image 50x50 $\mu\text{m}$  of  $\text{Al}_2\text{O}_3$  onto graphene in SE mode at the 10 kV.

In the case of sample 2, we performed Raman measurements also from the same place before (fig. 2a) and after deposition of  $\text{Al}_2\text{O}_3$  by ozone-based ALD (fig. 2c). There were no any visible differences in the images obtained. Significant similarities were observed in the case of SEM images recorded before (fig. 2b) and after deposition dielectrics layer (fig. 2d).



**Fig2:** Sample 2 (a) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene before deposition  $\text{Al}_2\text{O}_3$  layer. (b) SEM image 50x50 $\mu\text{m}$  of graphene before deposition  $\text{Al}_2\text{O}_3$  layer in SE mode at the 10 kV. (c) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene after deposition  $\text{Al}_2\text{O}_3$  layer onto graphene by ozone ALD. (d) SEM image 50x50 $\mu\text{m}$  of  $\text{Al}_2\text{O}_3$  onto graphene in SE mode at the 10 kV.

Finally, we also performed the same measurement with sample 3. Fig. 3a and 3c present Raman maps of graphene before and after deposition  $\text{Al}_2\text{O}_3$  by plasma enhanced ALD. Next, figs. 3b and 3d show SEM images before and after deposition of a dielectric layer. The results were similar to those obtained in the case of sample 1 and 2.



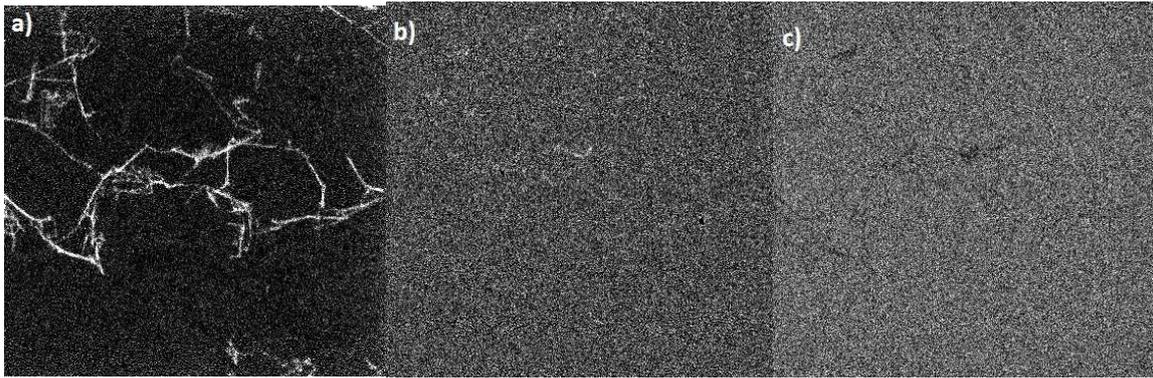
**Fig.3:** Sample 3 (a) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene before deposition  $\text{Al}_2\text{O}_3$  layer. (b) SEM image 50x50 $\mu\text{m}$  of graphene before deposition  $\text{Al}_2\text{O}_3$  layer in SE mode at the 10 kV. (c) Graphene map 50x50 $\mu\text{m}$  generated by monitoring the area of the Raman 2D peak of graphene after deposition  $\text{Al}_2\text{O}_3$  layer onto graphene by plasma enhanced ALD. (d) SEM image 50x50 $\mu\text{m}$  of  $\text{Al}_2\text{O}_3$  onto graphene in SE mode at the 10 kV.

The thicknesses of the films, which are summarised in Table 2, were determined by the X-ray reflection (XRR).

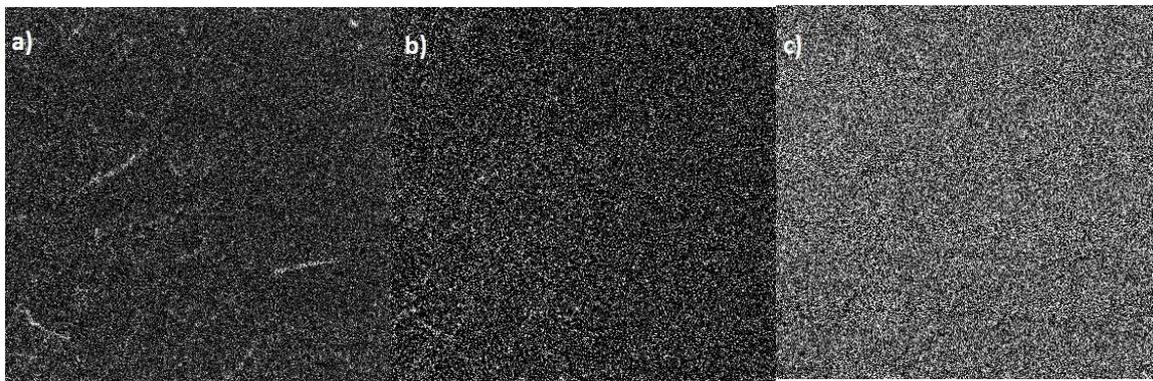
*Table 2. Thickness of  $\text{Al}_2\text{O}_3$  layers deposited onto graphene by different types of ALD measured by XRR, average k Al and standard deviation k Al.*

Sample number	ALD Process	Thickness [nm]	Average k Al	Standard deviation k Al
1	Thermal	25.6	0.04395	0.002645
2	Ozone	11.9	0.04640	0.006393
3	Plasma enhanced	5.9	0.01746	0.0004429

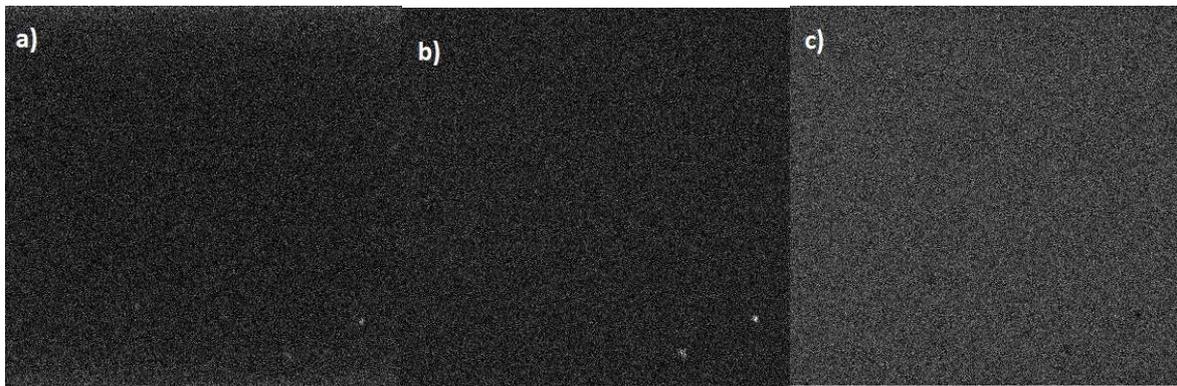
To prove presence and thickness homogeneity of  $\text{Al}_2\text{O}_3$  thin layers we used EDS analysis. Figures 4-6 show EDS chemical element maps from surface zone chosen by Raman spectroscopy (fig. 1 and fig. 3) or similar zones corresponding to those analyzed by Raman spectroscopy (fig 2).  $\text{CK}\alpha$  signal from graphene or several graphene layers is too weak to be able to illustrate changes in carbon layer thickness. Only thicker parts where carbon layer is corrugated can be distinguished (fig. 4a, 5a and 6a).  $\text{SiK}\alpha$  maps from the substrates have complementary character. The darker parts correspond to thicker parts of carbon layer, which absorb more outgoing  $\text{K}\alpha$  X-rays.  $\text{Al K}\alpha$  maps are laterally homogeneous. Stronger response came only from surface inhomogeneities where graphene layer was more significantly corrugated or impurities were present. It is in agreement with specific character of ALD processes to produce coherent growth of thin films even on rough parts of surface. Thus  $\text{Al}_2\text{O}_3$  layer deposited on sides of corrugated graphene or impurity can be regarded as thicker  $\text{Al}_2\text{O}_3$  layer in the direction normal to the substrate surface. To be sure that homogeneous  $\text{Al K}\alpha$  is not caused only by the noise signal (mainly in the case of 5.9 nm thick  $\text{Al}_2\text{O}_3$  layer) we analyzed several selected areas with graphene and without graphene throughout analyzed zones. The resulting average k-ratio and their standard deviations are summarized in Table 2. The k ratio is the ratio of measured intensities from sample and from standard after subtracting continuum background. The measured k ratios do not correspond to the  $\text{Al}_2\text{O}_3$  thickness because we needed to change beam current during analysis due to danger of graphene layer degradation in the case of thinner  $\text{Al}_2\text{O}_3$  layers. However, presence of  $\text{Al K}\alpha$  maximum in all EDS spectra as well as the relatively small standard deviation of measured k ratios proved that  $\text{Al}_2\text{O}_3$  layers were grown on all observed samples with good lateral thickness homogeneity.



**Fig.4:** Sample 1 after deposition of  $Al_2O_3$  onto graphene by thermal ALD (a) Al K $\alpha$  EDS map. (b) C K $\alpha$  EDS map. (c) Si K $\alpha$  EDS map.



**Fig.5** Sample 2 after deposition of  $Al_2O_3$  onto graphene by ozone ALD (a) Al K $\alpha$  EDS map. (b) C K $\alpha$  EDS map. (c) Si K $\alpha$  EDS map.



**Fig.6:** Sample 3 after deposition of  $Al_2O_3$  onto graphene by plasma enhanced ALD (a) Al K $\alpha$  EDS map. (b) C K $\alpha$  EDS map. (c) Si K $\alpha$  EDS map.

#### 4. Conclusion and future work

In summary, we have deposited thin  $Al_2O_3$  films by thermal, ozone and plasma enhanced ALD at temperatures  $100^\circ C$  onto graphene. The obtained results show, that  $Al_2O_3$  dielectric layer with good thickness homogeneity can be grown on graphene in these ALD processes without substantial deterioration of graphene properties. We have demonstrated that ALD is suitable deposition technique for preparation of dielectric films onto graphene.

In future we will work on preparation of sensor based on graphene and dielectrics layers. Our next step will be to prepare source and drain electrodes at the graphene layer. Subsequently gate electrode will be prepared and it will be separated from the graphene layer through an Al<sub>2</sub>O<sub>3</sub> insulating thin film. Last steps will be polymer encapsulation, Ni layer removal and finally bonding of contacts will complete preparation of the FET structure.

### Acknowledgement

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