Comparative study of thermal and plasma enhanced atomic layer deposition of aluminum oxide on graphene

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Abstract. Atomic layer deposition of alumina on graphene was studied in thermal and plasma enhanced process. Deposition was controlled by in situ ellipsometry every half cycle, which allows measuring of Al₂O₃ thickness and graphene equivalent thickness during the process. Properties of graphene were measured by Raman spectroscopy prior and after deposition of dielectric layer. It was shown that plasma enhanced deposition leads to decrease of effective graphene thickness, while thermal deposition does not affect graphene layer. No substantial nucleation lag was observed in both types of deposition.

1.Introduction
Graphene became one of promising materials that could improve the performance of high-frequency and low-power information processing, and THz detectors. Developing of graphene based nanoelectronics devices requires deposition of ultrathin gate dielectric on graphene in a process that do not lead to structural changes in graphene. Alumina has high dielectric constant (9.0), excellent barrier properties for moisture and for diffusion of impurities, and high breakdown field which make it candidate for gate dielectric and passivation layer for advanced electronic devices [1]. Although plasma enhanced ALD produce alumina with higher purity and excellent dielectric properties oxygen plasma could damage graphene layer, because carbon is subject to oxidation reaction with oxygen plasma. Thermally activated ALD growth uses water vapor as a source of oxygen. Another effect which could present in the ALD process is so called nucleation lag. This effect consists in the fact that the growth of the film does not begin immediately, but only after several cycles. As a rule, this is due to the peculiarities of the adsorption of a precursor by an untreated surface. The effect of ALD growth of dielectric on graphene layer is studied by Raman spectroscopy and spectral ellipsometry.

2.Experimental
In present work 5 nm thick Al₂O₃ films were deposited in FlexAl ALD tool (Oxford instruments plasma technology, UK) accompanied by in situ ellipsometry measurements and ex situ Raman spectroscopy. We used CVD deposited one-layer and multilayer graphene on Si substrate with 300-500 nm of SiO₂ insulating layer. Samples 2x2 cm² in size were placed on the heated table of ALD reactor with controllable temperature (300°C).

A typical ALD cycle consists of four steps. The cycle starts by introducing the first precursor to the reactor chamber which is purged then by flow of inert gas. Then the second precursor is introduces and purged. As a result of surface reaction one complete monolayer of deposited layer is added to the surface. For plasma enhanced ALD (PEALD) process TMA (Al(CH₃)₃) as metal precursors and remote ICP plasma of O₂ as non-metal precursor were used. ICP plasma was excited at pressure of oxygen of 15 mTorr with applied power of 250W. This step lasts for 2 seconds.

Thermal ALD (TALD) process was performed using water vapor as oxidizing precursor. Growth rate was 0.1 nm per cycle for both processes.

Samples of graphene were placed in the vacuum chamber from atmosphere through the loadlock. No additional annealing was done prior the process. Thermostabilisation of sample on the heated table takes
about 3 minutes at the pressure of 200 Torr. Wafer temperature was also controlled by spectral ellipsometry measurements and did not differ from table temperature by more than 25°C [2].

Spectral ellipsometry (SE) was performed in situ by J.A. Woollam Co M2000X 65 degrees ellipsometer in wide optical range of wavelength (245-1000 nm). SE measurements were done on every half of ALD cycle (during purge by argon after metalorganic precursor dosage and after oxidizing step as well). Special corrections were done to take into account sample tilt which cannot be adjusted in reactor chamber. In order to prevent optical windows contaminations automated shutters were used to close windows during precursor dosage to the chamber.

Ellipsometry measurement takes about 3 seconds and doesn’t substantially affect whole duration of ALD cycle which lasts for about 10 seconds. The method is sensitive enough to measure one monolayer adsorption of precursor and deposition of dielectric [2]. Temperature effects could be corrected. Size of light spot was 2×5 mm². That means that effective thickness is averaged on that area.

We used four layer optical models. The first layer is a bulk of silicon of infinite depth, second is the predetermined thickness of silicon oxide, third is graphene, and final layer is alumina. We did measurements on pristine samples to determine thickness of three initial layers. Thickness of silicon oxide was used in subsequent calculations of apparent thickness of alumina and graphene. Due to possible removal of existing on the surface polar adsorbed molecules like water or –OH groups apparent thickness could become negative during in the beginning of deposition. Optical properties of graphene were taken from [3], assuming that one monolayer graphene should have 0.34 nm effective thickness. Since ellipsometry is able to measure single monolayer of deposited or adsorbed molecules it could provide information not only referred to growth rate, but to adsorption of first precursor. Apparent thickness of adsorbed first precursor (Al(CH₃)₃) is higher than apparent thickness of Al₂O₃. That is why after first half cycle increase of apparent thickness can be seen (by more than thickness of one monolayer), and after second half cycle, when first precursor is oxidized, apparent thickness is slightly reduced. Total increase in whole cycle is the one monolayer thickness.

Micro Raman spectra of graphene films before and after Al₂O₃ film deposition were obtained with a SENTERRA BRUKER Raman microscope using 532 nm excitation wavelengths. A diameter of the laser spot was about 1 µm.

3. Results and discussion

Decrease in effective thickness of graphene exposed to oxygen plasma was measured. In conditions same to deposition, but without dosing precursor, mean rate of decreasing in effective graphene thickness was 0.014 nm/sec.

In case of plasma enhanced ALD (Figure 1) we observe linear growth of graphene since second cycle. Decrease of graphene thickness lasts for about 10 cycles of deposition. It could be concluded that 2 nm layer of alumina could prevent further degradation of graphene.

In thermal process decrease of effective graphene thickness does not exceed 0.02 nm over 20 cycles (Figure 2). Growth of Al₂O₃ is completely linear with small nucleation delay of no more than 1 cycle. There is not substantially degradation of effective graphene thickness in thermal ALD on multilayer graphene (Figure 3).

![Figure 1](image-url)  
**Figure 1.** Apparent thickness of deposited alumina (left) and effective thickness of graphene (right) during 50 cycles of plasma enhanced ALD by in situ ellipsometry.
Figure 2. Apparent thickness of deposited alumina (left) and effective thickness of graphene (right) during 50 cycles of thermal ALD by in situ ellipsometry.

Figure 3. Thickness of deposited alumina (left) and effective thickness of multilayer graphene (right) during 50 cycles of thermal ALD by in situ ellipsometry.

Figure 4 shows Raman spectra collected from pristine graphene and from graphene with deposited PEALD and TALD Al₂O₃. The defect-activated peaks (D, D' and D+D') are seen in spectrum obtained from graphene coated by PEALD Al₂O₃. G- and 2D- peaks have low intensities and are broaden. D'- peak almost merges with the G- peak. From the ratio of the D and G peak intensities, we can estimate the concentration of defects formed as a result of exposure to oxygen plasma. In [4] it was shown that defect density in graphene after plasma etching can be determined using the formula:

\[ n_d (\text{cm}^{-2}) = (7.3 \pm 2.2) \times 10^9 E_L^4 \left( \frac{I_D}{I_G} \right), \]

\( E_L \) – laser excitation energy.

Figure 4. Raman spectra collected from pristine graphene and from graphene coated by alumina deposited by plasma enhanced ALD (PEALD) and and thermal ALD (TALD).
In graphene used in this work the defect density $n_D$ is not more than $10^9$ cm$^{-1}$, $I_D/I_G$ is less then 0.01. After exposure to oxygen plasma $I_D/I_G$ is around 2.2, the defect density is around $5 \times 10^{11}$ cm$^{-1}$. Raman spectrum obtained from graphene coated by TALD Al$_2$O$_3$, practically does not differ from that of the pristine graphene. Thus we can conclude that the number of defects in graphene after deposition of TALD alumina is almost not increased.

In multilayer graphene there are areas with different number of layers, so Raman spectra (Figure 5) for one-layer areas of graphene sample exhibits plasma damage. Areas with multilayer graphene is less damaged. Ellipsometric observations during PEALD on multilayer graphene is similar to data of PEALD on graphene. This is due to the fact that damage appears only in the upper layers of graphene, and the lower layers remain intact.

![Figure 5. Micro Raman spectrum of multilayer graphene after exposure to oxygen plasma.](image)

4. Conclusion

Atomic layer deposition of alumina on graphene was studied in thermal and plasma enhanced ALD process. Deposition was controlled by in situ ellipsometry every half cycle, which allows measuring of Al$_2$O$_3$ thickness and graphene equivalent thickness during the process. Properties of graphene were measured by Raman spectroscopy prior and after deposition of dielectric layer. It was shown that plasma enhanced deposition leads to decrease of effective graphene thickness, while thermal deposition does not affect graphene layer. In multilayer graphene there are areas with different number of layers, so Raman spectra for one-layer areas of graphene sample exhibits plasma damage. Areas with multilayer graphene is less damaged.

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