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Toward plasma enhanced atomic layer deposition of oxides on graphene: Understanding plasma effects

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Integration of dielectrics with graphene is essential for the fulfillment of graphene based electronic applications. While many dielectric deposition techniques exist, plasma enhanced atomic layer deposition (PEALD) is emerging as a technique to deposit ultrathin dielectric films with superior densities and interfaces. However, the degree to which PEALD on graphene can be achieved without plasma-induced graphene deterioration is not well understood. In this work, the authors investigate a range of plasma conditions across a single sample, characterizing both oxide growth and graphene deterioration using spectroscopic analysis and atomic force microscopy. Investigation of graphene and film quality produced under these conditions provides insight into plasma effects. Using their method, the authors achieve ultrathin (<1 nm) aluminum oxide films atop graphene. © 2017 American Vacuum Society. [http://dx.doi.org/10.1116/1.4997421]

I. INTRODUCTION

Realizing the promise of graphene as a material for next generation electronics requires the successful integration of graphene with high quality dielectrics. Therefore, the deposition of metal oxides on graphene is a growing field of interest. While there are several thin film deposition techniques for oxides, atomic layer deposition (ALD) is amongst the most powerful techniques in terms of producing films with superior homogeneity and nanoscale thickness control.¹ ALD works by alternately exposing surfaces to precursor and reactant gases, with only one vapor species in the chamber at a given time. The vapor will undergo self-terminating reactions with the surface, and a cycle consisting of precursor, purge gas, and reactant species will result in the growth of a monolayer or a submonolayer of the desired film.

While this technique works on a wide variety of surfaces, the inert nature of graphene makes it a particularly challenging surface for ALD. Indeed, the nucleation of ALD films on pristine graphene occurs selectively on grain boundaries, edges, and defects.² To overcome this challenge, functionalization layers such as perylene-based acids have been added to the graphene surface prior to ALD,^{3,4} which results in films with higher coverage than the coverage on unmodified graphene.

Another strategy to achieve nucleation is ozone pretreatment, which increases hydrophilicity via ozone molecules which adsorb on and undergo reversible reactions with graphene to form hydrophilic epoxide groups.⁵ This technique has been used to increase the reactivity of graphene and graphite in a variety of contexts, including nucleation of aluminum oxide (AlOx) via thermal ALD on graphite^{5,6} and graphene.^{7,8} Enhancing nucleation can also be achieved by graphene substrate selection. In particular, copper was demonstrated as an effective substrate for increasing ALD nucleation of AlOx.⁹ The impact of substrates on graphene chemistry is substantial,¹⁰ and therefore, their importance in ALD nucleation is to be expected.

While each of these oxide growth on graphene studies has achieved some success with thermal ALD, plasma enhanced atomic layer deposition (PEALD) is emerging as a technique to deposit ultrathin dielectric films with superior densities and interfaces^{11–13} yet remains largely unexplored for deposition on graphene. The oxygen source in a PEALD system differs from the ozone treatment described above. The majority of oxygen species in a PEALD plasma are O₂, atomic oxygen, and metastable excited oxygen such as O(¹D) and O₂($a^1\Delta_g$), in addition to a small but significant amount of ionized oxygen species.¹¹ Plasma-based depositions have their own set of challenges: the oxygen plasma can damage or entirely etch graphene.¹⁴ In addition, vacuum ultraviolet (VUV) light emitted from the plasma provides energy (9.5 eV)¹⁵ to drive damaging reactions.¹¹

In this work, we show that by mounting a sample with one surface facing away from the plasma source and one surface facing the plasma, a single sample can experience a range of plasma conditions, which in turn results in a range of plasma-induced graphene damage and film properties.

To take advantage of the superior reactivity of graphene on copper, we use graphene that was grown via chemical vapor deposition on copper foil and mounted as shown in Fig. 1. Since both sides of the copper foil have graphene, we can compare the film properties at several positions on the front and back of the sample to effectively measure various plasma conditions. We find that even for relatively low power plasmas, the graphene on the front of the sample is damaged; however, in the center of the back side, we find

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FIG. 1. (Color online) In this work, graphene as-grown on copper foil is used as the substrate for PEALD of aluminum oxide films. Shown are a schematic illustration and photograph of the graphene sample suspension geometry. Graphene-coated copper foil samples, which have graphene grown on both sides, are cut from a large sample, suspended with wire supports and spacers, and subjected to PEALD. This configuration is to expose both sides of the graphene-coated copper to the PEALD process. Comparison of the growth on the front and back of the sample is the subject of this work.

minimal damage to the underlying graphene. By our method, we achieve ultrathin (<1 nm) AlOx films.

II. EXPERIMENT

Graphene-coated copper foil is obtained from Graphene Supermarket (Single Layer Graphene on Copper Foil). From a 4×4 in. sample, we cut with scissors a 3×3 cm piece, mount with spacers, and expose to ten PEALD cycles with dimethylaluminum isopropoxide as the precursor, using a power of 50 W and a substrate heater set to $155 \,^{\circ}$ C. The RF pulse time for the plasma is 8 s. Nitrogen is used to purge the chamber with a purge time of 40 s, and the aluminum precursor pulse time is $1.2 \,$ s.

Following deposition, atomic force microscopy (AFM), Raman spectroscopy, and elemental analysis are used to characterize both AlOx films and graphene damage. For elemental analysis, we use x-ray photoelectron spectroscopy (XPS) and monitor aluminum, copper, and copper oxide peaks.

III. XPS RESULTS

Figure 2 shows representative XPS measurements on the front and various positions on the back of the sample. The XPS system is calibrated with H-plasma cleaned gold foil at the 84.0 eV 4f 7/2 peak.

Between graphene and copper, there exists a native copper oxide that is dependent upon the age and quality of graphene.¹⁶ Since defects in the graphene enable copper oxide growth beneath the graphene layer, the intensity of the copper oxide peaks (940–945 eV) can be used as a proxy for the quality and continuity of the graphene post plasma exposure.

As Fig. 2 shows, on the back of the sample, the strength of the copper oxide peaks increases as the position of the XPS measurement shifts from the center (position 1) to the edge (position 3). Notably, the front of the sample (position 4) shows substantially more copper oxide. Furthermore, the intensity of the $2p_{3/2}$ copper line at position 4 is reduced, indicative of a thicker film on copper (a combination of copper and AlOx). Thus, we conclude that the graphene on the front of the sample has been significantly disrupted relative to the back of the sample. We also measure the C1s peak in the range of 275–295 eV and find a carbon oxidation peak at 288 eV. The ratio of the sa² C1s peak at 284 eV to the carbon



 112
 114
 116
 118
 120
 122
 124

 Binding Energy (eV)

 FIG. 2. (Color online) X-ray photoemission spectroscopy (XPS) is used to determine the presence of copper oxide and aluminum oxide after PEALD deposition and on a control sample. Lines 1–4 correspond to XPS data from various positions on the sample after PEALD, as indicated in the schematic in the upper right corner. For instance, line 1 is from the center of the backside of the sample, where the sample is most protected from the direct schema to the control source.

side of the sample, where the sample is most protected from the direct plasma. Line 5 corresponds to the control sample. The same sheet of graphene-coated copper foil was used for both the control sample and the PEALD sample; the only difference between them is that the control sample is not exposed to the PEALD process. These results show that there is very little copper oxide or aluminum oxide on the as-obtained graphene-coated copper. However, after deposition, aluminum and copper oxide lines increase in intensity, particularly for the front of the sample, while copper lines decrease. The Al 2s line occurs at ~119 eV, copper $2p_{3/2}$ at 933 eV, copper 3s at ~123 eV, and copper oxides in the range of 940–945 eV. We find that the aluminum oxide film is present at each position on the post-PEALD sample but is not present on the control sample, as expected.

oxide peak is 8.2:1 for the back of the sample and 4.3:1 for the front of the sample.

Next, we turn our attention to the elemental analysis of aluminum. We use the aluminum 2s line (\sim 119 eV) in favor of the more intense aluminum 2p line (73 eV) to avoid the overlap with copper 3p peaks. We find aluminum to be present on all areas of the PEALD sample, with the front of the sample showing a slightly more intense AlOx peak. Correspondingly, in the front of the sample, the energetically nearby copper 3s peak also decreases in intensity, consistent with the results for the copper 2p_{3/2} (933 eV) line discussed above.

IV. RAMAN RESULTS

Raman spectra are used to further assess graphene quality. We collect the Raman spectra on the samples as-grown on the copper foil. The copper oxide photoluminescence produces a large background; however, measuring G and D peaks of graphene on copper has been shown to be nearly equivalent to measuring G and D peaks of graphene on an insulating substrate.¹⁷ We chose this technique of measuring the G and D peaks on untransferred graphene to mitigate any damage from transfer of the films. In order to mitigate effects from local inhomogeneity, spectra are obtained from 100 data points over $100 \times 100 \,\mu$ m regions and are averaged together. This is repeated for three different locations: on the back of the sample, the front of the sample, and a control sample.

The Raman results verify a strong dependence of the graphene quality on the sample position, as shown in Fig. 3. A control sample was cut from the same graphene-coated copper foil used for the PEALD deposition, and its spectra suggest minimal defects with an indistinguishable D peak (1350 cm⁻¹); similarly, the data collected from the center of the back of the sample (position 1) suggest high quality graphene, with approximately 80% of the area showing a G:D peak intensity ratio greater than 1. Moving from the center toward the edges of the sample, the spectra show reduced G peak intensity.

The XPS and Raman results indicate that graphene is substantially damaged on the front side of the sample and remained better on the back side of the sample. Thus, in the following discussion of AFM results, we focus on the film grown on the back of the sample.

V. AFM RESULTS

For AFM analysis, we transfer a section $(5 \times 5 \text{ mm})$ from positions 1–3 of the graphene/AlOx stack. We use the PMMA transfer technique¹⁸ and mica as the target substrate.



FIG. 3. (Color online) Raman spectra for the PEALD sample postdeposition and a control sample. The control sample was cut from the same sheet of graphene-coated copper foil that was used for the PEALD sample. Each line represents the average of 100 measurements, obtained by mapping Raman spectra over areas of 100 μ m² with a step size of 10 μ m. The plots are shifted in intensity for clarity. These show that the graphene in the center of the back of the sample is better preserved than that at the edge or front of the sample.

For conducting atomic force microscopy measurements (C-AFM), gold-coated mica is used as the target substrate. Following transfer, the PMMA is removed with acetone and methanol. The AFM results are shown in Fig. 4. Since only chemical methods were used to remove the PMMA, the \sim 5 nm particles are most likely PMMA residues. Post-transfer, the presence of graphene is confirmed by Raman spectroscopy and the presence of the AlOx film is confirmed by insulating regions as measured by C-AFM.

We measure the thicknesses of the aluminum oxide films by taking average height profiles at ten different positions along the edges of the transfers. At the center of the protected side of the sample (position 1), we find a thickness of 1.8 ± 0.3 nm for the graphene/oxide stack. In contrast, transfers of unmodified graphene yield an average thickness of about 1 ± 0.1 nm, which includes the thickness of the graphene as well as a layer of water introduced by the transfer process.¹⁹ Thus, the thickness of aluminum oxide is approximately 0.8 nm or 1–2 monolayers. Away from the center, the film thickness increases. At position 2, we find a thickness of 2.4 ± 0.4 nm, and at position 3, we find a thickness of 2.5 ± 0.3 nm for the graphene/oxide stack, resulting in film thicknesses of 1.4 and 1.5 nm, respectively.

AFM scans of the graphene with oxide transferred onto mica are shown in Fig. 4. For the center of the sample, shown in Fig. 4(a), the roughness is \sim 475 pm. Scans from positions 2 and 3 show films with roughnesses of \sim 389 pm for position 2 and \sim 364 pm for position 3. Our results show that films of many square microns were successfully deposited. We note, however, that some parts of the sample showed a roughness of up to 1.3 nm as a result of incomplete film coverage. To understand the origin of this inhomogeneity, we measured the surface roughness of copper-graphene without AlOx growth. We find that native copper oxide is inhomogeneously rough. Such a rough surface coupled with inhomogeneous orientations between the copper and graphene grains, which



FIG. 4. (Color online) AFM topography of (a) aluminum oxide films grown on graphene, transferred to mica from sample position 1 (center of the back of the sample), (b) transferred films from position 2 (between the center and the edge of the back of the sample), and (c) transferred films from position 3 (edge of the back of the sample). (d) C-AFM image of the current through the film at a bias of -600 mV; the regions that are dark are areas which are conducting and light areas are insulating. In each, the inhomogeneity of the film is a result of incomplete or variable thickness films. The larger particles are PMMA residues.

are known to cause differences in the chemical and electrical properties of graphene,^{16,20} may be responsible for some of the inhomogeneous growth patterns and is a question for future work.

In addition to surface roughness, we also characterize the film's insulating properties using conductive atomic force microscopy. Figure 4(d) shows the current map of a sample taken from position 1 and transferred onto gold-coated mica. Shown in white are regions which are insulating (current less than 10 pA) at an applied voltage of -600 mV. These regions extend to approximately $\sim 50 \,\mu m^2$ in area. In the noninsulating regions, the current ranges from 17 to >20 nA (20 nA is the current saturation limit of the system). While the nonuniformity of the deposition and conductivity is not ideal, we note that this growth pattern is distinct from previous reports of oxide ALD on graphene. Nonuniform deposition of oxides on graphene is the norm for new oxide growth techniques, with deposition constrained to edges and defect sites.³ Such defect-assisted nucleation yields coverage areas on the order of tens of square nanometers; in contrast, we achieve insulating areas on the order of tens of square microns. We note that typical CVD graphene domains also cover areas on the order of microns; hence, domain orientation with respect to the underlying substrate (which may also be correlated with native copper oxide growth¹⁶) may impact ALD nucleation.

VI. MODELING OXYGEN COLLISIONS

The preservation of the graphene on the back of the sample can be understood by considering the manner by which our experimental setup constrains plasma conditions and VUV exposure. First, the side of the sample pointing away from the source is shielded from the majority of VUV light emitted by the plasma. However, our results also demonstrate that graphene is better preserved at the center of the back side than at the edge, suggesting that the lack of exposure to VUV light is not solely responsible for the difference in graphene conditions. Therefore, we also expect to see a difference in the oxygen species striking various positions on the back of the sample.

This range of plasma conditions is explained by the difference in the relative number of collisions undergone by plasma molecules. The molecules striking the front of the sample may or may not have undergone any collisions; however, given the geometry of the sample holder, molecules reaching the center of the back of the sample have a much higher probability of having undergone several collisions.

These collisions significantly influence the effects of the plasma on the graphene layer due to the fact that they neutralize oxygen ions and adsorb energy from excited metastables before they reach the sample.¹¹ These ions, usually O⁺ and O₂⁺, are believed to be the primary cause of graphene damage because of their ability to sputter the material, creating structural defects which are vulnerable to further deterioration, especially upon exposure to metastable excited oxygen such as O(¹D) and O₂($a^1\Delta_g$).^{21–23} Meanwhile, without such structural defects, the presence of atomic oxygen has been shown to create thermodynamically reversible chemisorbed oxygen



FIG. 5. (Color online) Molecular dynamics simulation result showing the average number of collisions each particle undergoes after entering the sides of an open box as a function of the distance from the edge of the box (in centimeters). The opening of the box is taken to be 0.1 cm. The result is an average of ten simulations with 200 000 particles per simulation.

on graphene without damaging the graphene lattice.²⁴ Therefore, atomic oxygen is likely responsible for much of the aluminum oxide growth in areas where the graphene is well preserved. It is also worth noting that the inhomogeneous copper oxide under the graphene may translate to distinct functionalization modes, especially when coupled with distinct oxygen species introduced by the collisions. The types of graphene oxide functional groups present have a significant effect on the ALD growth mechanisms.²⁵

The oxide growth on the front of the sample is likely a combination of the above described mechanism of aluminum oxide growth on the graphene and growth of aluminum oxide on the exposed oxidized copper in regions that the graphene has been damaged or partially etched.

We demonstrate the impact of the geometry of the experiment on the number of collisions using a molecular dynamics simulation. We model the particles as entering through the sides of an open box with dimensions of 0.1×1.5 cm and count collisions with the bottom or ceiling of the box. The average result of ten simulations with 200 000 particles in each simulation is shown in Fig. 5. For each simulation, a new randomized set of initial vertical positions and velocity vectors are used. Particles near each side of the box (position 3) undergo relatively fewer collisions than particles near the middle (position 1). Since collisions will reduce the relative number of excited and ionized oxygen species, the back of the sample should be exposed to a less reactive plasma than the front of the sample, with the center of the back of the sample most protected. Indeed, this is consistent with our findings.

VII. CONCLUSIONS

In conclusion, we have found that PEALD can be used to deposit ultrathin films of aluminum oxide on graphene. The quality of the graphene post deposition is highly dependent upon the local plasma conditions, which can translate into various oxygen species in the plasma. By growing films on the side of the sample that is pointed away from the plasma source, the graphene quality is better maintained.

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