
Erik Jonsson School of Engineering and Computer Science

2012-11-21

Trimethyl-Aluminum and Ozone Interactions with Graphite in Atomic Layer Deposition of Al₂O₃

Stephen McDonnell, *et al.*

© 2012 American Institute of Physics

Trimethyl-aluminum and ozone interactions with graphite in atomic layer deposition of Al₂O₃

Stephen McDonnell, Adam Pirkle, Jiyoung Kim, Luigi Colombo, and Robert M. Wallace

Citation: *J. Appl. Phys.* **112**, 104110 (2012); doi: 10.1063/1.4766408

View online: <http://dx.doi.org/10.1063/1.4766408>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v112/i10>

Published by the AIP Publishing LLC.

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT



The advertisement banner features a green and yellow background with abstract wavy lines. On the left, the text 'AIP Advances' is displayed in a stylized font, with 'AIP' in blue and 'Advances' in green, accompanied by a series of orange dots forming a curved path. On the right, a circular seal contains the text 'Now Indexed in Thomson Reuters Databases'. Below this, a dark blue horizontal bar contains the text 'Explore AIP's open access journal:' in white, followed by a bulleted list of features.

AIP Advances

Now Indexed in
Thomson Reuters
Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

Trimethyl-aluminum and ozone interactions with graphite in atomic layer deposition of Al₂O₃

Stephen McDonnell,¹ Adam Pirkle,¹ Jiyoung Kim,¹ Luigi Colombo,²
and Robert M. Wallace^{1,a)}

¹Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080, USA

²Texas Instruments Incorporated, Dallas, Texas 75265, USA

(Received 24 June 2012; accepted 20 October 2012; published online 21 November 2012)

A study of the chemical interactions between the atomic layer deposition (ALD) Al₂O₃ precursors trimethylaluminum (TMA) and ozone (TMA/O₃) and sp² carbon surfaces is presented. *In-situ* x-ray photoelectron spectroscopy is used to study these interactions, while *ex-situ* atomic force microscopy (AFM) is used to monitor the surface morphology. Ozone functionalization of the sp² carbon surface is discussed and the dependence of TMA/O₃ reactions over a range of ALD process conditions is examined. The utilization of a 6-cycle room temperature TMA/O₃ ALD seed layer to nucleate the conformal growth of Al₂O₃ by TMA/H₂O at 200 °C as well as the quality of such films is discussed. Two stages of ozone reactions are observed: first the ozone appears to remove adsorbed species from the graphite surface before reacting with the surface. The deposition of Al₂O₃ is found to be strongly dependant on the N₂ purge time as well as the precursor pulse sequence. It is shown that the quality of these low temperature deposited films can easily be improved by removal of carbon containing species through an 300 °C anneal. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766408>]

I. INTRODUCTION

Deposition of high-k dielectrics on graphene via atomic layer deposition (ALD) is hindered by the chemically inert nature of the sp²-bonded basal plane. Many dielectric deposition and nucleation processes have been studied in efforts to overcome this problem. Thin seeding layers deposited by electron beam evaporation of aluminum have allowed for the successful ALD of thicker Al₂O₃ dielectrics.^{1,2} NO₂ non-covalent functionalization layers which have been utilized successfully for nucleation of ALD on single walled carbon nanotubes³ have also been reported to functionalize graphene and allow for conformal ALD.^{4,5} Thin organic layers such as spin coated NFC 1400-3CP,⁶ evaporated 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA)⁷ and solution-based 3,4,9,10-perylene tetracarboxylic acid (PTCA)⁸ have also been utilized for this purpose. ALD using TMA/O₃ at 200 °C results in conformal growth but structural imperfections on the surface are expected for longer ozone exposures^{9,10} and damage to epitaxial graphene on SiC using similar ozone conditions was also reported.¹¹

A thin ALD Al₂O₃ seeding layer, deposited at room temperature using TMA and ozone as precursors, has been shown to allow for the subsequent conformal growth of Al₂O₃ using TMA/H₂O precursors at 200 °C.¹⁰ It was originally suggested for the ALD TMA/O₃ process at 200 °C that ozone reacts with the basal plane of the graphene to form epoxides that nucleate the growth of Al₂O₃.¹² It was proposed that this epoxide group could be reduced by the aluminum in the TMA during room temperature deposition to

allow for conformal growth without inducing defects in the graphene.¹⁰ Recent studies on highly oriented pyrolytic graphite (HOPG) substrates showed that this *room temperature* TMA and ozone process did not result in conformal growth when the surface was annealed in UHV at 400 °C *in-situ* prior to deposition.¹³ The results of this *in-situ* annealing experiment indicated that physisorbed contamination acts as a nucleation layer that allows for uniform growth of Al₂O₃ by room temperature ALD using TMA and ozone precursors.

In this study, *in-situ* x-ray photoelectron spectroscopy (XPS) and *ex-situ* AFM are combined to study the interactions of the TMA and ozone precursors with exfoliated HOPG. The interaction between ozone and physisorbed species on the HOPG surface is characterized as well as the interactions between ozone and a clean HOPG surface. ALD parameters such as nitrogen purge time and precursor pulse sequence are studied with a view to characterizing this technologically relevant deposition method.¹⁰ HF-last silicon wafers are utilized as spectator samples so that “deposition parameter” dependent and “substrate” dependent effects can be differentiated.

II. EXPERIMENTAL

ALD and XPS characterization were carried out in a multi-chamber clustered UHV system, with *in-situ* deposition, thermal processing and deposition capabilities as described previously.¹⁴ This work focuses on HOPG substrates that are used as a model system to simulate reactions with graphene. Large-area samples are required due to the ~1 mm diameter XPS analytical spot size. While single-layer graphene grown by CVD can be transferred to SiO₂,¹⁵

^{a)}Author to whom correspondence should be addressed. Electronic mail: rmwallace@utdallas.edu.

the process requires exposure to various wet chemical processes, leaving residues that could react with ALD precursors which would confuse these studies.^{16,17} Studies utilizing CVD graphene as grown on a metal surface¹⁸ could also be confused by reactions with the metal substrate if the graphene coverage was <100%. In order to consider HOPG as a model system, one must acknowledge observations of anomalously large chemical reactivity of single-layer graphene,¹⁹ as these results indicate that reaction rates on graphene will be very different than those on HOPG. However, some authors argue that these reaction rates are related to extrinsic factors such as defects or charge transfer between graphene and the SiO₂ substrate,²⁰ implying that intrinsic or near-intrinsic single-layer graphene samples may exhibit a reactivity that is much lower than the “dirty” samples that are presently available. Therefore, studies of reactions with the HOPG surface are likely to become more relevant as “cleaner” near-intrinsic graphene samples with lower defect densities are achieved.

All HOPG substrates were exfoliated in air using adhesive tape and immediately (<5 min) loaded into the UHV system load lock. Samples prepared in this fashion are referred to hereafter as “exfoliated.” In order to obtain clean graphene surfaces, previous studies utilized an *ex-situ* 600 °C anneal followed by fast loading into the ALD chamber.⁸ Similarly, it was shown that *in-situ* UHV anneals at 400 °C were sufficient to remove surface contamination and thereby impact ALD nucleation on HOPG surfaces.¹³ For this study, the cleanest possible HOPG surfaces were obtained by utilizing an *in-situ* 400 °C UHV anneal. Samples prepared in this fashion are referred to hereafter as “exfoliated + annealed.”

After surface treatments and initial XPS analysis, ozone exposures and ALD were carried out in a Picosun SUNALETM ALD reactor attached to the UHV system. A TMEIC model OP-250 H was employed for this study with an O₃ concentration $\geq 350 \text{ g/m}^3$ at the generator which is located 25 m from the ALD reactor. The vendor reports that such concentrations are maintained for lines up to 60 m in length due to the relatively long O₃ lifetime and normal flow rates (10 l/min) employed. Previous reports showed that conformal growth of Al₂O₃ on graphene was possible utilizing TMA and ozone as precursor and a substrate temperature of 200 °C.⁹ Subsequent studies showed that such depositions at 200 °C induced defects in the graphene but that a 6 cycle seed layer grown at room temperature using the same precursors facilitated subsequent conformal growth of Al₂O₃ by TMA and water at 200 °C.¹⁰ As such the ozone exposures in this study were carried out at substrate temperatures of 30 °C or 200 °C. Full ALD cycles are defined in this study as consisting of the sequence “Precursor A” (pulse) $\rightarrow$ N₂ (purge) $\rightarrow$ “Precursor B” (pulse) $\rightarrow$ N₂ (purge). The precursor pulse time was held constant at 0.2 s for all samples, while the N₂ purge time between pulses was varied in some experiments. In a separate study of high dose ozone exposures, an *in-situ* chamber with capability for exposure to gas pressures ranging from $<10^{-9}$ mbar to 1000 mbar was also utilized. After precursor exposures, samples were transferred under UHV to a clustered XPS analysis chamber where they were analyzed using a monochromatic Al K α X-ray source and Omicron EA125

hemispherical analyzer. An analyzer acceptance angle of 8°, a takeoff angle of 45°, and pass energy of 15 eV were employed in this study. The estimated error in binding energy assignments is 0.05 eV and 0.1 eV where values of binding energy separation are quoted. In order to distinguish between substrate induced reactions and those intrinsic to room temperature ALD using TMA and ozone precursors, results were compared to HF-Last Si(100) spectator samples. HF-Last Si(100) was obtained by etching previously RCA cleaned Si(100) pieces in HF 2% by volume for 1 min followed by a deionized water rinse. For the silicon spectator samples, the Si 2*p* features were aligned to 99.3 eV to account from dopant variations across the range of samples used. *Ex-situ* AFM images were collected using a Veeco MultiMode V SPM. AFM images were processed using the GWYDDION software package.²¹

Three experiments will be outlined in this study. The first in Sec. III A examines ozone reactions with HOPG. “Exfoliated” HOPG and “annealed + exfoliated” HOPG surfaces were exposed to a range of ozone doses at room temperature as well as at 200 °C. Reactions between ozone and the sp² carbon surfaces were monitored with *in-situ* XPS. In the second, outlined in Sec. III B, XPS is used to characterize room temperature TMA + O₃ 6 cycle nucleation layers on HOPG. This room temperature process has been previously utilized as a nucleation layer that enables subsequent growth of Al₂O₃ on graphene at 200 °C with a TMA/H₂O process.¹⁰ The impact of varying the ALD purge time and of altering the pulse sequence (TMA first vs ozone first) is examined. These results are compared with those from the parallel experiments on Hf-last silicon discussed in more detail in the supplementary information.²⁴ Finally, in Sec. III C, the affect of a post deposition anneal on this nucleation layer is examined as a possible route to improving the quality of this seed layer.

III. RESULTS

A. Ozone reactions

It has been suggested that O₃ may form epoxide groups on the surface of HOPG at room temperature and that this epoxide functionalization would allow for the conformal deposition of Al₂O₃ on HOPG and graphene.¹⁰ However, a later study comparing the conformality of such films on both “exfoliated” HOPG and “exfoliated + annealed” HOPG showed that deposition occurred only at the step edges when surface contamination was removed, indicating that nucleation can be attributed entirely to reactions with surface contamination in some cases.¹³

In order to better understand the interactions between ozone and the graphene/graphite surface, “exfoliated” HOPG samples were exposed to varying doses of O₃. Each sample was transferred to a UHV chamber with a base pressure of $<5 \times 10^{-9}$ mbar and ozone was admitted to the chamber using a precision leak valve. Dose was determined by integrating the readout of a full-range pressure gauge over the exposure time. Pressures ranged from 10^{-6} mbar for the 10² L dose to 1000 mbar for the 10¹² L dose. The O 1s feature was monitored using XPS before and after ozone

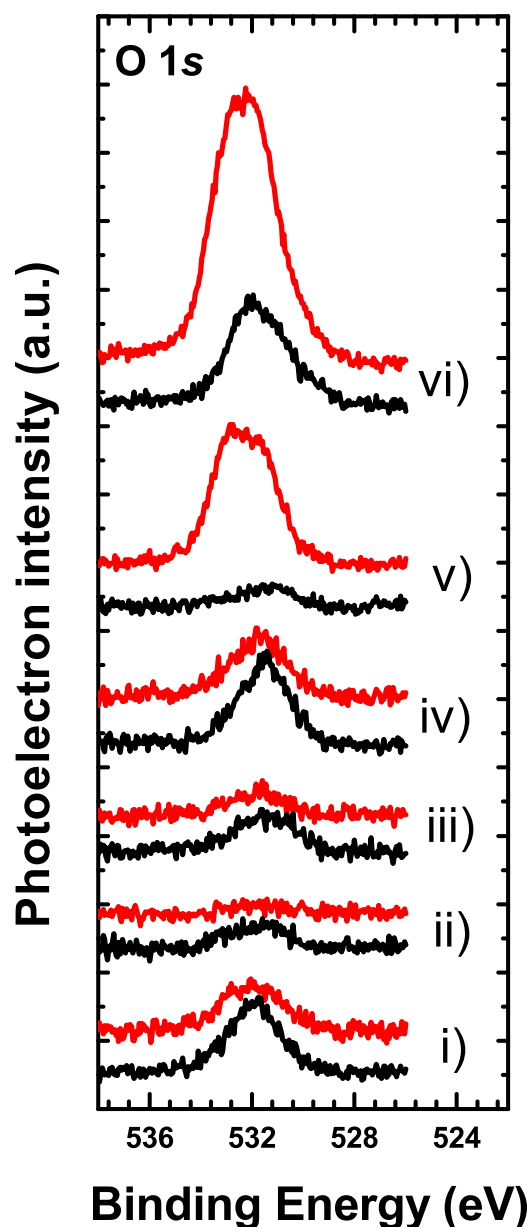


FIG. 1. Photoelectron spectra of the O 1s core-level for “exfoliated” HOPG samples before (Black—bottom spectra) and after (Red—top spectra) exposure to (i) 10^2 L, (ii) 10^4 L, (iii) 10^6 L, (iv) 10^8 L, (v) 10^{10} L, (vi) 10^{12} L of ozone.

exposure as shown in Figure 1 (i)–(vi). It is clear that an O 1s signal of varying intensity is present on exfoliated surfaces and is most likely due to physisorbed species. On some samples (not shown) this signal can be below the limit of detection of XPS. Exposure to relatively small doses of O_3 ($<1 \times 10^8$ L) reduces the intensity of this feature, which suggests that the ozone is reacting with, and removing surface contamination through formation of volatile, possibly CO and/or CO_2 , species. At higher pressures however ($>1 \times 10^{10}$ L) the O 1s feature increases and is a clear indication of reactions between O_3 and the HOPG surface.

The effect of exposing the graphite surface to ozone was also examined under realistic processing conditions in the *in-situ* ALD reactor by exposing the surface to multiple ozone pulses. The samples were exposed to 100 pulses of ozone

each with a 1 s duration. This was estimated to be equivalent to no more than 2×10^8 L based on the pressure rise in the ALD chamber during a pulse. Analysis of the XPS (a) O 1s and (b) C 1s core-levels shown in Figure 2 demonstrates that there is no detectable oxygen present after the sample is annealed at 400°C . Exposure to ozone at room temperature shows an increase in the amount of oxygen on the surface. It is difficult to detect changes in the corresponding C 1s spectra due to the intense bulk peak and associated shake-up features. The C 1s difference spectra are obtained by subtracting the substrate reference spectrum; acquired after annealing, i.e., before ozone exposure, from the spectra obtained after ozone exposure. This technique has been shown previously to be very useful for detecting smaller changes in the carbon spectra.¹³ However, even using this method there is no detectable change in the carbon feature indicating that there is no evidence of epoxide formation within the limits of detection of XPS. The presence of an O 1s feature combined with the lack of any detectable change in the C 1s spectrum suggests that the surface is most likely functionalized by physisorbed oxygen species, perhaps hydroxyls.

Exposure to ozone at 200°C shows a clear increase in the O 1s signal. However, from the C 1s difference spectra, it is difficult to say whether the small increase in the signal over the binding energy range 285–287 eV is a real change in the C 1s feature or simply a fluctuation in noise. A reaction with the HOPG surface was expected since a previous study of ozone reactions with graphene showed using Raman spectroscopy that a D band at 1340 cm^{-1} , which is a signature of defects in the graphene structure, could easily be observed after similar ozone exposures at 200°C .¹⁰ It would not be surprising for such a reaction to result in the formation of an sp^3 carbon or C-O features in the binding energy range 285–287 eV, however, since the change in the C 1s spectrum in this region is at the limit of detection it should be considered that many of the reaction products may be volatile and desorb leaving an etched surface that is difficult to differentiate from the pristine HOPG surface with XPS.

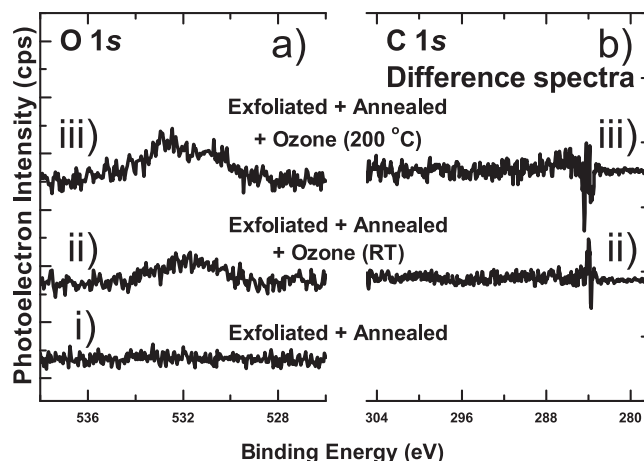


FIG. 2. (a) O 1s core-level feature for “exfoliated” HOPG after (i) no exposure (ii) 100×1 s cycles of ozone at room temperature (iii) and 100×1 s cycles of ozone at 200°C , in the ALD reactor. (b) C 1s difference spectra obtained by the subtraction of the “exfoliated” HOPG spectra from spectra obtained after (ii) 100×1 s cycles of ozone at room temperature and (iii) 100×1 s cycles of ozone at 200°C , in the ALD reactor.

B. Seed Layer of room temperature grown Al_2O_3 on HOPG

The quality of the previously reported 6 cycle Al_2O_3 nucleation layer will clearly have an important impact on device performance.¹⁰ As shown previously, the removal of surface contamination has a detrimental impact on the conformality of the metal oxide layer.¹³ Here, Al_2O_3 has been deposited on “exfoliated” HOPG and analyzed *in-situ* with XPS. These samples did not receive a pre-deposition *in-situ* anneal in order to correlate the film chemistry with the previously reported devices which underwent an *ex-situ* deposition process.

1. Pulse sequence

Figure 3 shows the (a) O 1s and (b) Al 2p features for a film grown in (i) a process similar to the nucleation layer used by Lee *et al.*¹⁰ (i.e., TMA first process) as well as (ii) a film grown with a reversed pulse sequence (i.e., ozone first process) on HOPG. It is immediately evident that the TMA-first process results in greater Al 2p and O 1s signals representative of an increase in the amount of Al_2O_3 on the surface. The HF-last silicon spectator sample (see supplementary information)²⁴ shows the opposite trend, which suggests that this is not a purely processing parameter effect and is due to differences between how the initial precursors react

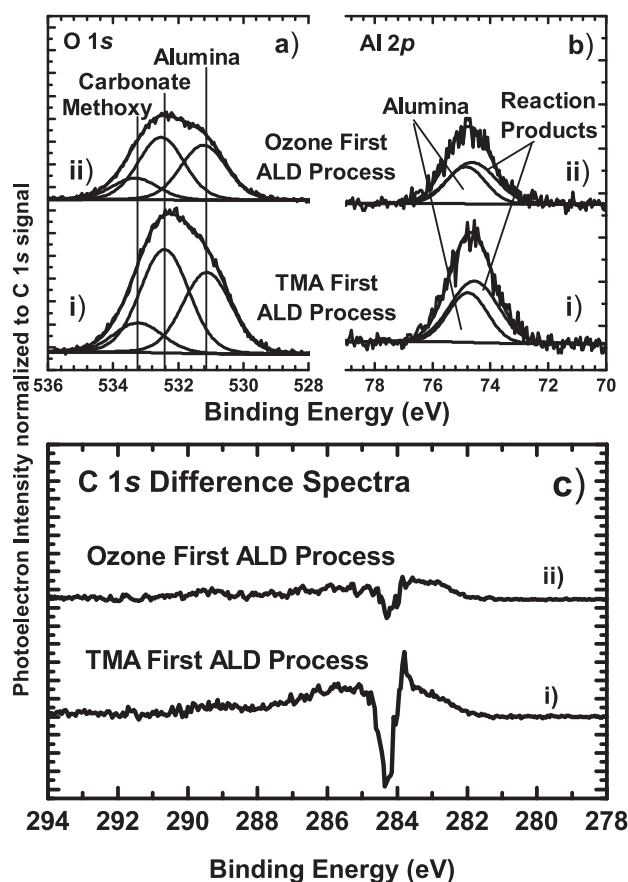


FIG. 3. Photoelectron spectra for (a) the O 1s, (b) Al 2p, and (c) C 1s core-levels for Al_2O_3 grown on “exfoliated” HOPG at room temperature with 6 cycles of TMA and ozone precursors. For (a) the first pulse was TMA, for (b) the first pulse was ozone.

with adsorbed species on the “exfoliated” graphite surface. The C 1s spectrum shows that both films have significant additional carbon species after the deposition of Al_2O_3 . These states have previously been assigned to partial reaction products and not direct interactions with the HOPG surface.^{13,22} This is reconfirmed here by the presence of similar carbon species on the HF spectator samples discussed in the supplementary information.²⁴ The binding energy positions of the Al 2p and O 1s indicate that the chemical state of aluminum oxide is unaffected by altering the pulse sequence.

Figure 4 shows the corresponding AFM images for these samples measured *ex-situ* after XPS analysis. It is clear that the ozone first process results in not just a thinner Al_2O_3 oxide film, but in fact yields a non-conformal layer with the majority of the Al_2O_3 decorating the step edges rather than the basal plane. Considering that ozone has been shown in Sec. III A to “clean” the HOPG surface and that previous reports showed that growth is non-conformal on “clean” HOPG surface, it is thus not surprising that the ozone first process results in significantly different growth to that of the TMA first process.

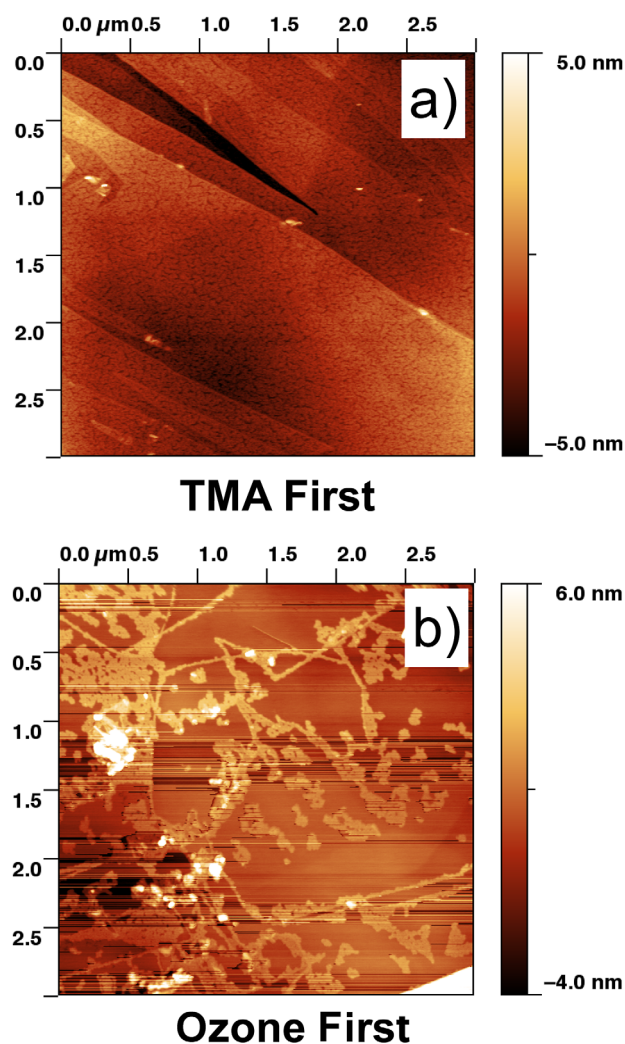


FIG. 4. (a) $3\ \mu\text{m} \times 3\ \mu\text{m}$ AFM image after TMA first process. (b) $3\ \mu\text{m} \times 3\ \mu\text{m}$ AFM image of ozone first process. It is clear that the TMA first process results in an almost conformal layer that can be used for seeding further ALD. The ozone first process results in deposition primarily on step edges.

2. Purge time

It has been shown previously that, due to the inert nature of the sp^2 carbon surface, certain ALD precursors have short residence times on sample surface. For example, it was shown electrically for the case of NO_2 on carbon nanotubes³ that, while NO_2 induced changes in the conductance of the carbon nanotubes, the conductance would repeatedly return to the original value within 2 min. However when the NO_2 exposure is followed by a 7 s nitrogen purge and then TMA exposure, a permanent change in the CNT conductance can be induced. Recently, a similar experiment showed that ozone can temporarily dope graphene with the effect reducing over time in vacuum, indicating a physisorption mechanism.²³ Described here is a comparison of a half-cycle experiment with an uninterrupted deposition. For the uninterrupted deposition 3 cycles of alternating 0.1 s TMA and O_3 pulses are separated by 30 s nitrogen purge steps which are a standard part of an ALD process. For the half cycle experiment, the samples are exposed to identical precursor pulses, however, after each pulse the samples are removed from the reactor during the nitrogen purge step and moved *in-situ* to an attached XPS analysis chamber for characterization. Figure 5 shows (a) the O 1s and (b) the Al 2p for a comparison between 3 full uninterrupted ALD cycles followed by XPS and the 6 half cycles (3 full cycle equivalent) where each half cycle was followed by 6 h of XPS analysis (all in UHV). It is clear that the long interruption between the precursor pulses inhibit the growth of Al_2O_3 on the HOPG surface. These results highlight the importance of understanding the effect of the ALD purge time on the deposition of Al_2O_3 on sp^2 carbon surfaces.

Figure 6 shows the (a) O 1s and (b) Al 2p spectra for 18 cycles of TMA + O_3 grown on “exfoliated + annealed” HOPG with purge times of 30 s and 300 s. “Exfoliated + annealed” HOPG is utilized to avoid reactions with surface contamination that could be misinterpreted as metal oxide graphitic interactions. The purge times were chosen to be 30 s, which is the standard purge time used in this picosun re-

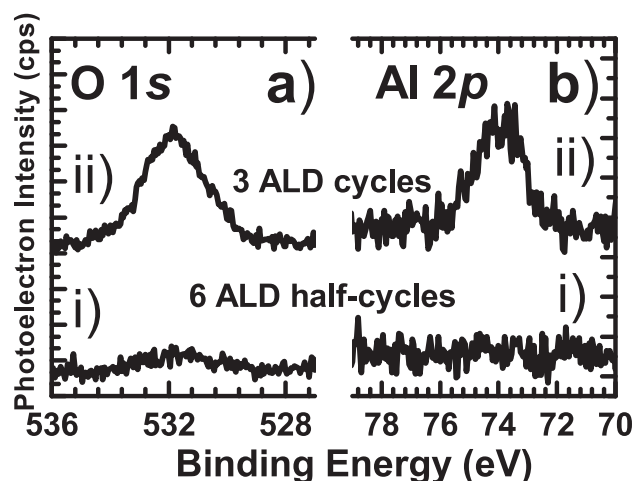


FIG. 5. Photoelectron spectra of (a) O 1s, (b) Al 2p for (i) 6 ALD half-cycles interrupted for 6 hours of UHV XPS analysis between each half cycle and (ii) 3 uninterrupted ALD cycles (6 half-cycle equivalent) on “exfoliated + annealed” HOPG.

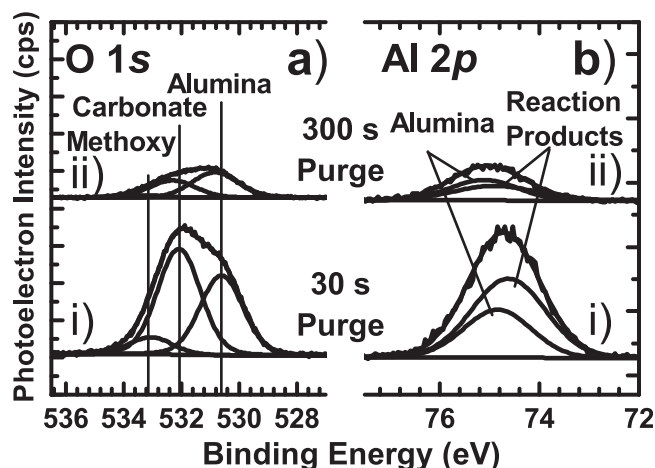


FIG. 6. Photoelectron spectra of (a) O 1s and (b) Al 2p core-levels for Al_2O_3 grown on “exfoliated + Annealed” HOPG at room temperature with 18 cycles of TMA and ozone precursors. Precursor pulses were both 0.2 s, while the nitrogen purge time was (i) 30 s and (ii) 300 s.

actor for a range of dielectric depositions, and 300 s to be 1 order of magnitude greater. It can be seen that the ratio of incomplete reaction products (methoxy and carbonate species in the O 1s and the low binding energy feature in the Al 2p) to the fully reacted Al_2O_3 features is dependent on the purge time, with the longer purge resulting in a decreased concentration of partial reaction products. This result is believed to be a process driven phenomenon rather than substrate driven because the HF-last silicon spectator samples show the same trend (see supplementary information).²⁴ The total amount of alumina deposited on the surface is clearly decreased for both the 300 s purge process with respect to the 30 s purge process. It should be noted that no dependence on purge time was observed for these same depositions on the HF-last Si(100) surface (see supplementary information).²⁴ This suggests that the residence time of ozone and TMA precursors as well as any reaction products with the HOPG surface have very short lifetimes on the order of the nitrogen purge time. This results in a notable decrease in the deposition of Al_2O_3 on HOPG with increased purge time due to the desorption of these species before they can be reacted with the next precursor. Such species can only be inferred in this study and cannot be positively identified since their residence times are too short to be observed with XPS. This is consistent with the previously reported 30% increase in Al-O bonds formation on graphite for room temperature depositions using TMA and ozone precursors when compared to depositions on a substrate at 200 °C.

C. Optimization of the nucleation layer process

The use of thin Al_2O_3 deposited at room temperature as a seed layer may have a drawback in that high leakage currents can be expected through this portion of the dielectric layer. It was shown previously that while the TMA/ O_3 process results in a film with a higher breakdown field than the TMA/ H_2O process at the same temperature, the breakdown field still decreases with decreasing temperature.¹⁰ Ideally either the whole film should be grown at an adequately high

temperature to ensure ligand liberation or the seed layer could be subsequently improved with a post deposition anneal. To date, high temperature deposition of conformal Al_2O_3 by ALD on graphene has not been possible without the use of either a seed layer^{4-7,10} or a high temperature ozone process⁹ which was found to damage the film.

Figure 7 shows the oxygen and carbon spectra for 6 cycles of TMA/ O_3 Al_2O_3 on HOPG and a spectator HF-last silicon sample before and after *in-situ* UHV annealing at 300 °C for 1 h. For the HOPG substrate the C 1s difference spectra (referenced to the C 1s spectra before deposition) is shown Figure 7(a). It is clear that the additional carbon features added by the room temperature ALD process are removed by the post deposition anneal (PDA). This is confirmed to be the removal of carbon from the Al_2O_3 layer on the silicon substrate shown in Figure 7(b). The O 1s features on HOPG and silicon shown in Figures 7(c) and 7(d) are consistent with the removal of the higher binding energy oxygen components attributed to the same incomplete reaction products within the film.

IV. DISCUSSION

From previous reports in the literature, it has been suggested that ozone may react with sp^2 carbon forming epoxides.⁹ In this study, no direct spectroscopic evidence of

epoxide formation was detected and two separate ozone reactions were observed. First, at low exposures, ozone is seen to remove surface contamination as evidenced by the reduction in the intensity of the XPS O 1s feature assigned to these species. However, at higher concentrations a clear increase in the O 1s intensity is observed. While no definite evidence of C-O bonding is observed, the presence of physisorbed oxygen species with short resident life times on the surface may indeed facilitate the growth of Al_2O_3 reported by Lee *et al.*¹⁰ When comparing multiple ozone ALD pulses at room temperature and 200 °C, it was noted that both processes resulted in an increased O 1s feature. However in neither case were significant C-O concentrations detected. Since a 200 °C exposure to ozone has previously been shown to induce damage to graphene layers evidenced by an increase in the Raman D band intensity,¹⁰ it is suggested that many of the reactions with carbon surfaces form volatile species resulting in an increase in defect sites but changes in carbon chemistry below our limit of detection.

XPS and AFM analysis of Al_2O_3 deposited using 6 cycles of TMA/ O_3 at room temperature has shown the importance of pulse sequence for the uniformity of the Al_2O_3 layer. For the TMA-first process on an “as-exfoliated” sp^2 carbon surface, TMA can adsorb, possibly with the aid of surface contaminants, and form Al_2O_3 after the first ozone pulse allowing for subsequent uniform film deposition. In contrast, when the first pulse is a single cycle of ozone, the result is a non-uniform layer. This implies that the ozone reacts with and removes some of the surface contamination, which inhibits the reaction mechanism of the subsequent TMA pulse. This is consistent with the ozone exposure experiments, which showed that for low exposures of ozone the O 1s feature is actually reduced. In our system, the exposure of O_3 for a single ALD pulse is on the order of 10^5 – 10^6 L; a precise calculation of ALD dose using the reactor pressure is difficult as the precursors are diluted in flowing N_2 .

On annealed HOPG, where TMA adsorption is not aided by surface contaminants, due to their desorption during the UHV anneal, the nitrogen purge time between the precursor pulses has a notable effect on the amount of Al_2O_3 that is deposited. With increased purge time, the amount of TMA (or ozone) that can desorb from the surface between pulses increases and therefore greatly reduces the subsequent concentration of Al_2O_3 deposited on the surface. It should be noted that previous studies have shown that almost all of the deposition on “exfoliated + annealed” HOPG is on the step edges and not the basal plane.¹³

The problem of increased leakage current that is expected for the room temperature grown 6 cycle seed layer¹⁰ is considered here. By annealing the nucleation layer, incomplete reaction products can be removed before the remainder of the Al_2O_3 film is grown. Electrical characterization would be required to determine what effect this has on the quality of the film. The previously reported two-step deposition process effectively implements this approach, as the sample is annealed in the ALD reactor when temperature is ramped from room temperature to 200 °C between the TMA/ O_3 seed layer and subsequent TMA/ H_2O deposition.

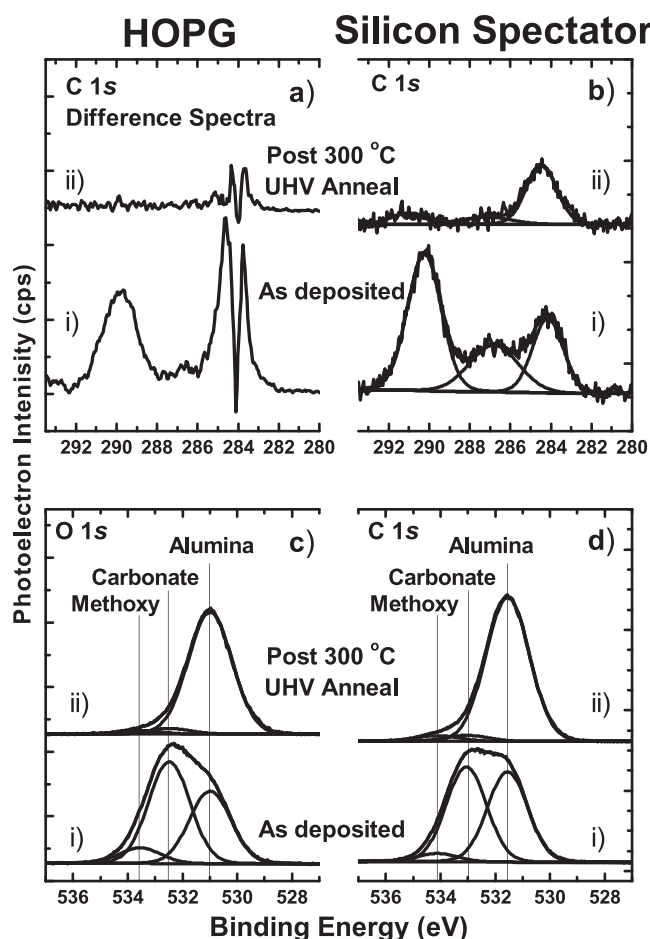


FIG. 7. Photoelectron spectra of the C 1s (a) and (b), and O 1s (c) and (d) core-level features for (i) before and (ii) after a 300 °C UHV 1 h anneal for Al_2O_3 on HOPG (left) and HF-last silicon (right).

V. CONCLUSION

In summary, it has been shown that nitrogen purge time plays an important role in ALD of Al_2O_3 on sp^2 carbon surfaces. This purge time dependence is attributed to the short residence time of the TMA and ozone ALD precursors on the HOPG surface and step edges. Also, at room temperature, the nitrogen purge time is inversely related to the concentration of incomplete reaction products (carbon) incorporated in the Al_2O_3 film. However, these incomplete reaction products can be removed from a thin Al_2O_3 film via a 300 °C UHV anneal. Conformal deposition of Al_2O_3 is only seen when the HOPG samples are un-annealed, indicating that reaction with surface contaminants plays an important role for uniform deposition. Finally, the role of ozone in the functionalization of the sp^2 carbon surface is now better understood. At low doses, ozone can “clean-up” the surface and therefore hinder the subsequent ALD, while high doses results in detectable oxygen species that could aid in conformal growth and provide a route to graphene functionalization.

ACKNOWLEDGMENTS

This work is sponsored by the Semiconductor research Corporation Nanoelectronic Research Initiative and the National Institute of Standards and Technology through the MIND and SWAN Centers. The authors also acknowledge the support of TMEIC for the ozone generator employed in the work.

¹S. Kim, J. Nah, I. Jo, D. Shahrjerdi, L. Colombo, Z. Yao, E. Tutuc, and S. K. Banerjee, *Appl. Phys. Lett.* **94**, 062107 (2009).

²D. B. Farmer, Y. M. Lin, and P. Avouris, *Appl. Phys. Lett.* **97**, 013103 (2010).

³D. B. Farmer and R. G. Gordon, *Nano Lett.* **6**, 699 (2006).

⁴J. Williams, L. DiCarlo, and C. Marcus, *Science* **317**, 638 (2007).

⁵Y.-M. Lin, K. A. Jenkins, A. Valdes-Garcia, J. P. Small, D. B. Farmer, and P. Avouris, *Nano Lett.* **9**, 422 (2009).

⁶D. B. Farmer, H.-Y. Chiu, Y.-M. Lin, K. A. Jenkins, F. Xia, and P. Avouris, *Nano Lett.* **9**, 4474 (2009).

⁷J. M. P. Alaboson, Q. H. Wang, J. D. Emery, A. L. Lipson, M. J. Bedzyk, J. W. Elam, M. J. Pellin, and M. C. Hersam, *ACS Nano* **5**, 5223 (2011).

⁸X. Wang, S. M. Tabakman, and H. Dai, *J. Am. Chem. Soc.* **130**, 8152 (2008).

⁹B. Lee, S.-Y. Park, H.-C. Kim, K. Cho, E. M. Vogel, M. J. Kim, R. M. Wallace, and J. Kim, *Appl. Phys. Lett.* **92**, 203102 (2008).

¹⁰B. Lee, G. Mordì, M. Kim, Y. Chabal, E. Vogel, R. M. Wallace, K. Cho, L. Colombo, and J. Kim, *Appl. Phys. Lett.* **97**, 043107 (2010).

¹¹F. Speck, M. Ostler, J. Röhl, K. V. Emtsev, M. Hundhausen, L. Ley, and T. Seyller, *Phys. Status Solidi C* **7**, 398 (2010).

¹²G. Lee, B. Lee, J. Kim, and K. Cho, *J. Phys. Chem. C* **113**, 14225 (2009).

¹³A. Pirkle, S. McDonnell, B. Lee, J. Kim, L. Colombo, and R. M. Wallace, *Appl. Phys. Lett.* **97**, 082901 (2010).

¹⁴R. M. Wallace, *Electrochem. Soc. Trans.* **16**, 255 (2008).

¹⁵X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**, 1312 (2009).

¹⁶A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace, *Appl. Phys. Lett.* **99**, 122108 (2011).

¹⁷J. Chan, A. Venugopal, A. Pirkle, S. McDonnell, D. Hinojos, C. W. Magnuson, R. S. Ruoff, L. Colombo, R. M. Wallace, and E. M. Vogel, *ACS Nano* **6**, 3224 (2012).

¹⁸B. Dlubak, P. Kidambi, R. Weatherup, S. Hofmann, and J. Robertson, *Appl. Phys. Lett.* **100**, 173113 (2012).

¹⁹L. Liu, S. Ryu, M. R. Tomasik, E. Stolyarova, N. Jung, M. S. Hybertsen, M. L. Steigerwald, L. E. Brus, and G. W. Flynn, *Nano Lett.* **8**, 1965 (2008).

²⁰R. Sharma, J. H. Baik, C. J. Perera, and M. S. Strano, *Nano Lett.* **10**, 398 (2010).

²¹See <http://www.gwyddion.net> for SPM (scanning probe microscopy) data visualization and analysis.

²²D. N. Goldstein, J. A. McCormick, and S. M. George, *J. Phys. Chem. C* **112**, 19530 (2008).

²³S. Jandhyala, G. Mordì, B. Lee, G. Lee, C. Floresca, P. R. Cha, J. Ahn, R. M. Wallace, Y. J. Chabal, M. J. Kim, L. Colombo, K. Cho, and J. Kim, *ACS nano* **6**, 2722 (2012).

²⁴See supplementary material at <http://dx.doi.org/10.1063/1.4766408> for comparison studies on a HF-last Si spectator sample.