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ABSTRACT
Atmospheric-pressure Plasma-Enhanced spatial Atomic Layer Deposition (PE-s-ALD) is a high-throughput technique for synthesizing thin films at low temperatures for large area applications. The spatial separation of the ALD half-reactions and the use of an atmospheric pressure plasma as the reactant give rise to complex surface chemistry which is not yet well understood. Here, we employed gas-phase infrared spectroscopy and optical emission spectroscopy (OES) to study the underlying chemistry of the PE-s-ALD process of Al$_2$O$_3$ films grown at 80 °C using Al(CH$_3$)$_3$ and an Ar-O$_2$ plasma. We identified the reaction products and investigated their dependence on the exposure time of the substrate to the precursor. Infrared absorbance spectra show CO, CO$_2$, H$_2$O, and CH$_4$ as the main ALD reaction byproducts originating from (i) combustion-like reactions of the methylated surface with O plasma radicals and O$_3$ and (ii) a concurrent latent thermal ALD component due to produced and/or residual H$_2$O molecules. In addition, CH$_2$O and CH$_3$OH were identified as reaction by-products either originating at the surface or formed in the plasma. The OES spectra provide a corroborative proof of the combustive nature of the PE-s-ALD reactions showing OH and CH emissions arising during the spatial ALD process while excited O species are being consumed.

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The unparalleled capability to deliver ultrathin film materials with superior quality and conformity makes Atomic Layer Deposition (ALD) a well-established technique for state-of-the-art semiconductor applications. 1 Conventional ALD synthesizes materials with atomic level control through cyclic reactions between temporally separated precursors and coreactants. Additionally, using plasmas as the coreactant in the so-called Plasma-Enhanced ALD (PEALD) processes allows for lower substrate temperatures on extended set of materials and new classes of precursors. 2, 3 However, due to commonly long cycle times and expensive vacuum equipment involved, temporal (PE)ALD remains often less economically feasible for large-area applications. Within this framework, a suitable candidate for cost-effective ALD is atmospheric pressure spatial ALD, which is based on spatially separated half-reactions offering a unique high-throughput performance. 4–11 Recently, atmospheric pressure Plasma Enhanced spatial ALD (PE-s-ALD) has been developed enabling ultrafast ALD of oxides at relatively low temperatures. 12–15 A detailed understanding of the nature of atmospheric pressure PE-s-ALD processes is key to achieve the best performances for a wide range of processes and materials.

In this letter, we present a way to study the fundamentals of the surface chemistry at the base of atmospheric pressure PE-s-ALD. Al$_2$O$_3$ has been selected as the case-study by virtue of its wide use in large-area applications and the rich knowledge on the thermal and plasma ALD processes using Al(CH$_3$)$_3$ and H$_2$O, 16 O$_3$, 17, 18 or O$_2$ plasma. 19–21 The diagnostics employed are gas-phase infrared spectroscopy involving a single-pass gas cell and optical emission spectroscopy (OES), which is often used to study PEALD processes. 21, 22 On the contrary, the number of infrared studies on the ALD exhausted gases is rather limited. Among them, Najafabadi et al. analyzed effluent ALD gases to determine the time needed to achieve saturated chemisorption of a cobalt precursor onto an Al$_2$O$_3$ surface as well as to investigate ligands combustion during the O$_3$ step. 23 Jung et al. made use of infrared spectroscopy to monitor the O$_3$ composition at both the inlet and the outlet of the ALD reaction chamber. 24 Figure 1 shows a schematic of the diagnostics assembled on the atmospheric pressure PE-s-ALD reactor, which was previously described in Refs. 5 and 6. Gas-phase infrared spectroscopy is performed on reactor effluent gases which are individually delivered to the quartz gas cell.
inserted inside the infrared interferometer. In this work, we report on the analysis of the plasma exhaust gases. OES is carried out inside the reactor oven with a thermally resistant optical fiber inserted in a dedicated transparent version of a Dielectric Barrier Discharge (DBD) plasma source, providing a direct view of the plasma above the substrate surface.

Al$_2$O$_3$ films were deposited at 80 °C using Al(CH$_3$)$_3$ and Ar$_2$O plasma as precursor and reactant, respectively. These are independently and continuously supplied to the gas injection head (see supplementary material S1). The two reaction zones are spatially separated by a high flow of N$_2$ gas. A silicon wafer is placed on a circular substrate table which rotates at a distance of 100 μm from the injection head executing a full ALD cycle at each rotation. Al$_2$O$_3$ film growth was studied as a function of the exposure time of the substrate to the precursor and the reactant which was varied by setting the number of rotations per minute (RPM) executed by the substrate during the deposition (see supplementary material S1). Here, we investigated exposure times between 27 ms and 400 ms corresponding to substrate rotation speeds ranging from 150 RPM to 10 RPM, respectively. Under these conditions, the deposition process shows ALD saturation behavior, and the films exhibit properties typically expected for Al$_2$O$_3$ (see supplementary material S2).

Figure 2 presents a prototypical example of infrared absorbance spectra obtained by analyzing the exhausted plasma gases in the so-called “plasma-only mode” (i.e., without precursor injection) and the “ALD mode.” The plasma-only mode spectrum shows mainly a strong O$_3$ absorbance peak at 1040 cm$^{-1}$. O$_3$ production is quite strong in O$_2$ and air DBD plasmas at low temperatures and occurs in a two-step mechanism where O atoms are created by electron-impact dissociation followed by a three-body process involving O$_2$ molecules and the O atoms. Under the present conditions, the amount of O$_3$ produced is found to increase with the amount of oxygen and the input plasma voltage applied (see supplementary material S4).

In the ALD mode, Al(CH$_3$)$_3$ and the Ar$_2$O plasma are both delivered to the surface of the rotating substrate. Besides the O$_3$ absorbance peak, the ALD mode spectrum reveals the absorbance due to CO$_2$, CO, and H$_2$O and molecules such as CH$_4$, CH$_3$OH, and CH$_2$O. According to reports on (temporal) ALD in the literature, Al(CH$_3$)$_3$ chemisorbs on the surface by reaction with hydroxyl surface groups (OH) upon which CH$_4$ is released. Subsequently, in the following step of the ALD cycle, the newly methylated surface reacts with the plasma O species releasing a number of by-products. As discussed in detail later, CO$_2$, CO, and H$_2$O are combustion products desorbing from the surface, while CH$_4$ can be formed in thermal ALD reactions. In addition to combustion reaction products observed in temporal ALD, CH$_3$O and CH$_2$OH are also identified in the infrared spectrum in Fig. 2 during PE-s-ALD of Al$_2$O$_3$.

The by-products generated during the PE-s-ALD process were studied as a function of the exposure time of the substrate to the precursor and reactant species. The results are given in Fig. 3(a). At a fixed total acquisition time of 600 s, signals due to ALD by-products decrease at higher exposure times, as less ALD cycles are executed. The dependence of the integrated peak areas normalized to the number of cycles on the exposure time is plotted in Fig. 3(b) for CO, CO$_2$, and CH$_4$. This graph shows that the production of these species tends to saturate at higher exposure times when the methylated surface is exposed to the incoming plasma species for a time sufficient to (nearly) reach self-limiting surface reactions.

OES was performed to measure the excited species present in the plasma, and the results are given in Fig. 4. In the plasma-only mode, the Ar$_2$O plasma spectrum is characterized by emission lines of atomic argon (5p $\rightarrow$ 4s at 415–426 nm)$^{27}$ and the first negative system of oxygen, O$_2^+$ (b$^3\Sigma_g^+ - a^3\Pi_g$) at 557.8 nm). In the ALD mode, the O$_2^+$ signal reduces, which is in line with O species being consumed through combustion reactions with –CH$_3$ ligands during the ALD.
cycle. Simultaneously, OH emission centered at 309 nm \((\Delta^2 \Sigma^+ \rightarrow X^2 \Pi)\) appears in the ALD spectrum, likely originating from electron impact induced dissociative excitation of \(H_2O\) molecules.\(^{20}\) Furthermore, CH emission is also detected at 389 nm \((B^2 \Sigma \rightarrow X^2 \Pi)\) and 431 nm \((A^2 \Delta \rightarrow X^2 \Pi)\) which could originate from dissociative excitation of \(CH_4\). The energy thresholds for these CH emission lines by electron impact excitation are 7.8 eV and 7.5 eV which fall within the range of energies typical for electrons in DBD plasmas.\(^{28}\)

Infrared absorbance from \(CO_2\) and \(H_2O\) in the ALD spectrum indicates that the spatial PEALD process at atmospheric pressure is driven by combustion-like reactions, while the presence of \(CH_4\) is associated with a concurrent thermal reaction path. Starting from a methylated surface, the results obtained in this study are in line with the study on PEALD of \(Al_2O_3\) under low pressure conditions by Heil et al. who proposed the following surface reaction for the second half-cycle:\(^{20,26}\)

\[
\text{||-AlCH}_3 \text{+ 4O} \rightarrow \text{||-AlOH + CO}_2 + \text{H}_2O.
\]

Desorbed \(H_2O\) can react with the surrounding methyl groups producing \(CH_4\) in a thermal reaction

\[
\text{||-AlCH}_3 + \text{H}_2O \rightarrow \text{||-AlOH + CH}_4.
\]

CO could either originate from incomplete combustion reactions or it could result from electron impact dissociation of \(CO_2\) in the plasma.

At low temperatures, however, \(O_3\) is abundantly present in DBD-generated \(O_2\) plasmas. Therefore, in our case, the coreactant is a mixture of \(O_2\) plasma species and \(O_3\), where \(O_3\) supposedly reacts with the surface by decomposition into \(O_2\) and monoatomic reactive \(O\).\(^{18}\)

Based on literature reports, \(O_3\) can also contribute to desorption of \(CO\), \(CO_2\), and \(H_2O\) via combustion-like reactions and, in turn, \(H_2O\) can act as a co-reactant in a thermal reaction desorbing \(CH_4\). The ALD process of \(Al(CH)_3\) and \(O_3\) has been extensively studied. Elliot et al. predicted that oxidation of the methylated surface can take place via insertion of \(O\) atoms in \(Al-C\) bonds with consequent formation of surface methoxy groups.\(^{18}\)

Methoxy groups can then combine at the surface into formates, which can be further oxidized to surface carbonates. The presence of these surface species was experimentally confirmed by an infrared study by Goldstein et al.\(^{17}\) Rai et al. studied the surface reaction mechanism for both \(O_3\) and \(O_2\) plasma coreactants finding that in both cases the chemistry is driven by combustion reactions where \(OH\) and \(CO_3\) (carbonates) act as reactive sites. In particular, surface carbonates are found to be more stable, long-term surface intermediates in the case of \(O_3\), while these decompose under long \(O_2\) plasma exposures.\(^{29}\)

Besides combustion-like by-products, \(CH_2O\) and \(CH_3OH\) appear in the ALD spectrum as well. \(CH_2O\) and \(CH_3OH\) have not been

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FIG. 3. (a) Infrared spectra of exhausted plasma gases for PE-s-ALD of \(Al_2O_3\) at 80 °C for different exposure times of the substrate to the precursor and the reactant (corresponding to 10–150 RPM). For each exposure time, the total acquisition time in the spatial ALD mode was kept constant at 600 s. The number of cycles per deposition is also indicated. (b) Integrated peak area of absorbance for \(CO_2\), \(CO\), and \(CH_4\) normalized to the number of cycles as a function of the exposure time.

FIG. 4. OES spectra of the plasma-only mode and the ALD mode during PE-s-ALD of \(Al_2O_3\) thin films. The spectrum of the plasma-only mode shows emission from \(Ar\) and \(O\); the spectrum of the ALD mode reveals emission from \(OH\) and \(CH\). The spectra have been offset vertically for clarity.
experimentally observed as reaction-by-products in ALD using Al(CH₃)₃ and O₂ plasma or O₂. We speculate that these species can desorb as the result of further reactions of methoxy surface groups created by the O₂ component. This assumption is supported by a Density Functional Theory (DFT) study by Fomenga et al. predicting that, for both O₂ plasma and O₃ cases, O atoms can be inserted into C-H bonds producing CH₂O as the main by-product.

\[ \text{\text{-\text{Al(CHO)}}}_3 + 2\text{O} \rightarrow \text{\text{-AlOCH}} + \text{\text{-Al(CHOO)}}_2 + \text{CH}_2\text{O}. \quad (3) \]

This reaction appears the most kinetically favored at various oxygen concentrations and when considering different oxygen-ligand reaction dynamics. According to the same study, in the oxygen-rich environment, CH₃OH can also be produced by

\[ \text{\text{-O-\text{-Al(CHO)}}}_3 + 6\text{O} \rightarrow \text{\text{-AlOCH}} + \text{\text{-AlO}_2\text{CH}_2} + \text{\text{-OH} + \text{\text{CH}_2\text{O}}}. \quad (4) \]

Under atmospheric pressure conditions, species concentrations are higher than in low pressure plasmas. This ensures more efficient O₂ dissociation and, consequently, more O atoms available for reactions. Hence, we speculate that at atmospheric pressure, the higher flux of oxygen reacting with the –CH₃ ligands along with the dynamic nature of the spatial ALD might create a richer kinetic scenario which favors the formation of CH₂O and CH₃OH with respect to low pressure PEALD. Furthermore, it should be mentioned that these species can also likely be produced in the plasma, for example, by dissociation of CH₃ into highly reactive CH₃ radicals which can further react with oxygen forming CH₂O and CH₃OH.

The integrated peak areas of CO, CO₂, and CH₄ give insights into the self-limiting growth of the PE-s-ALD process. At short exposure times, the flux of O species is insufficient to combust the –CH₃ ligands present at the methylated surface. This translates into suppressed ALD surface reactions, and consequently less reaction by-products being produced. It also results in Al₂O₃ films with high carbon incorporation and low mass density (supplementary material S2). At longer exposure times, the by-products produced instead show a saturation behavior indicating that –CH₃ ligands have been fully removed and the surface reactions take place in a self-limiting manner.

In summary, a combination of gas-phase infrared spectroscopy and optical emission spectroscopy was used to study the gas-phase chemistry of the atmospheric pressure plasma-enhanced spatial ALD process of Al₂O₃ films using Al(CH₃)₃ and Ar-O₂ plasma. The underlying surface reaction mechanism appears driven by three concurrenct reactions: O₂ plasma species, O₂ and H₂O. The presence of H₂O, CO, and CO₂ in the infrared absorbance spectra reveals that part of the deposition process proceeds via combustion-reactions of the methylated surface by O₂ plasma species as well as O₂. OES confirmed the combustion-reaction mechanism revealing OH and CH emissions arising during the ALD process while O-species are consumed. Moreover, H₂O formed from ligand combustion could explain the presence of CH₃OH resulting from concurrent thermal reactions. Next to combustion-like reaction products, CH₂O and CH₃OH were also identified, which might originate both at the surface and in the plasma. The higher concentration of O atoms at atmospheric pressure and the diverse kinetics of the PE-s-ALD reactor would favor the formation of these species which have not been observed under low pressure conditions.

See supplementary material for a detailed description of the experimental conditions and additional data on ALD behavior and material properties.

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