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Infrared and optical emission spectroscopy study of the surface chemistry in atmospheric-pressure plasma-enhanced spatial ALD of Al₂O₃ *

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Atmospheric-pressure plasma-enhanced spatial atomic layer deposition (PE-s-ALD) is an emerging high-throughput technique used to deposit thin films at low temperatures on large-area substrates. The spatial separation of the ALD half-reactions and the use of an atmospheric-pressure plasma in the co-reactant step give rise to a complex surface chemistry which to date is not well understood. In this study, we employed gas-phase infrared spectroscopy and optical emission spectroscopy (OES) to unravel the underlying chemistry of the PE-s-ALD process for Al₂O₃ films grown at 80 °C using Al(CH₃)₃ as the precursor and Ar-O₂ plasma as the co-reactant. We identified the reaction products generated at various exposure times of the substrate to the precursor. Infrared absorbance spectra show CO, CO₂, H₂O and CH₄ as the main reaction by-products formed from a) combustion-like reactions of the methylated substrate surface with oxygen radicals and O₃ species, and b) H₂O molecules either residual or formed in the process that give rise to a concurrent latent thermal ALD component. In addition, CH₂O and CH₃OH were identified as reaction by-products formed either at the substrate surface or in the plasma. The OES spectra confirmed the combustive nature of the PE-s-ALD reactions as shown by the OH and CH emission peaks that appeared during the spatial ALD process while excited O-species are being consumed.

Introduction

Atomic Layer Deposition (ALD) is rapidly emerging as the technology of choice to produce ultrathin film materials with superior quality and conformality, especially in state-of-the-art semiconductor manufacturing.¹ Conventional low-pressure ALD produces materials with atomic-scale control through cyclic reactions between temporally separated precursors and co-reactants. By adding plasmas to the co-reactant step in so-called plasma-enhanced ALD (PE-ALD) one can realize lower process temperatures, and enable the use of new classes of precursors and temperature-sensitive (including flexible) substrates.^{2,3} However, the characteristic long purge times between the half-reactions and the expensive vacuum equipment make temporal (PE-)ALD less economically feasible for large-area production. In this context, a more viable alternative for cost-effective production is atmospheric-pressure spatial ALD.

Here, the concept of spatially separated half-reactions practically eliminates the intermediate purging thus yielding uniquely high throughput numbers.^{4–11} Obviously, atmospheric-pressure plasma-enhanced spatial ALD (PE-s-ALD) is emerging as a technique for ultrafast ALD of oxide films at relatively low temperatures.^{12–15} To further improve the performance of this technique and to extend the range of materials involved a detailed understanding of the nature of atmospheric pressure PE-s-ALD is necessary.

Experimental

In this paper, we present a method to study the fundamental surface chemistry at the base of atmospheric pressure PE-s-ALD. Al_2O_3 was selected as case-study material because of its wide application in large-area substrate coating and the rich literature on thermal and plasma ALD processes using $\text{Al}(\text{CH}_3)_3$ and H_2O ¹⁶, O_3 ^{17,18} or O_2 plasma.^{19,20} The diagnostics employed are exhaust gas analysis by infrared spectroscopy using a single-pass gas cell, and *in situ* optical emission spectroscopy (OES), which is often used to study PE-ALD processes.^{21,22} To date, only a few infrared studies have been published on ALD exhaust gas analysis. Among them Najafabadi *et al.* analyzed the gases abated at the outlet to determine the time needed to achieve saturated chemisorption of a cobalt precursor onto an Al_2O_3 surface and also to study the ligand combustion during the O_3 step.²³ Jung *et al.* used infrared spectroscopy to monitor the O_3 content at the inlet and outlet of their ALD reactor.²⁴ Finally, Zoubian *et al.* analyzed the exhaust gas from their spatial reactor by FTIR spectroscopy and micro-gaschromatography.²⁵

Figure 1 shows a schematic of the diagnostics assembled on the PE-s-ALD reactor which was described in more detail elsewhere.^{5,6} Gas-phase infrared spectroscopy is used to analyze the effluent plasma gases that are individually fed from the reactor exhaust into a quartz gas cell inserted inside the interferometer. In addition, OES is carried out inside the plasma reactor with a thermally resistant optical fiber inserted in a dedicated Dielectric Barrier Discharge (DBD) plasma source. The DBD-source was supplied with a transparent electrode, allowing for a direct view of the emitted plasma wavelengths above the substrate surface.

Figure 1. Schematic of the atmospheric-pressure PE-s-ALD reactor equipped with exhaust gas-phase infrared absorption spectroscopy and *in situ* optical emission spectroscopy.

Al₂O₃ films have been deposited at 80 °C using Al(CH₃)₃ and Ar-O₂ plasma as precursor and co-reactant, which were independently and continuously supplied to the gas injection head.^{5,6} The two reaction zones are spatially separated by a high flow of inert N₂ gas serving not only as a separation gas curtain between these zones but also enabling frictionless substrate rotation as ‘lubrication’ gas between the fixed injection head and the rotating circular substrate table holding a 150-mm diameter silicon substrate wafer at a distance of 20-100 μm. During every rotation a full ALD cycle is achieved. Al₂O₃ film growth was studied as a function of the exposure time of the substrate to precursor and co-reactant. This was done by varying the substrate rotation speed during the deposition in a range from 150 to 10 rpm corresponding to substrate exposure times between 27 and 400 ms, respectively (see Table I). Under these conditions, the deposition process reaches saturation and the Al₂O₃ films show properties as typically expected (see Table II in the next section).

Table I. Values of rotation speed/frequency, exposure time of the substrate and number of cycles as calculated for the rotary spatial ALD reactor for a total deposition time of 600 s.

Rotation speed (rpm)	Rotation frequency (Hz)	Exposure time (ms)	Number of cycles (deposition time = 600 s)
10	0.16	400	99.6
30	0.5	133	300
60	1.0	66	600
100	1.6	40	960
150	2.5	27	1500

Results and discussion

Figure 2 shows a typical example of the infrared absorbance spectra obtained by analyzing the exhausted plasma gases in the so-called ‘*plasma-only mode*’ (i.e. without precursor injection) and ‘*ALD mode*’. The plasma-only mode spectrum shows mainly a strong O₃ absorbance peak at 1051 cm⁻¹. At low temperatures O₃ production is known to be quite strong in O₂ and air DBD-plasmas and to occur in a two-step mechanism where O-atoms are generated by electron-impact dissociation and a subsequent three-body process involving O₂ molecules and the O-atoms.²⁶ Under the present conditions, the amount of O₃ produced is found to increase with the amount of oxygen and the input plasma voltage applied (see Appendix).

In ALD mode, both the Al(CH₃)₃ and Ar-O₂ plasma are delivered to the rotating substrate surface. In addition to the O₃ absorbance peak, the ALD-mode spectrum shows absorbance peaks due to CO₂, CO, H₂O and molecules such as CH₄, CH₃OH and CH₂O. Literature on (temporal) ALD^{16,18,19} describes Al(CH₃)₃ chemisorbing on the surface by methyl ligand exchange with hydroxyl surface groups (OH) upon which CH₄ is released. In the next ALD half-cycle, the methylated surface reacts with the plasma O-species releasing several by-products. As discussed in detail later, CO₂, CO and H₂O are combustion products desorbing from the surface, while CH₄ can be formed in thermal ALD reactions.²⁷ In addition to combustion reaction products as observed in temporal ALD, we could also identify CH₂O and CH₃OH in our study case of PE-s-ALD of Al₂O₃ in the infrared spectrum in Fig. 2.

Figure 2. Infrared absorption spectra of exhausted gases for Ar-O₂ plasma (*plasma-only mode*) and *ALD mode* using both Al(CH₃)₃ and Ar-O₂ plasma. Exposure time and substrate temperature were 40 ms and 80 °C, respectively. Vibrational modes that could be assigned are: 1033 cm⁻¹ O₃ n₃ and CH₃OH CO-stretching, 1306 cm⁻¹ CH₄ degenerate deformation, 1594 cm⁻¹ H₂O bending, 1746 cm⁻¹ CH₂O CO-stretching, 2100 cm⁻¹ CO n₃, 2349 cm⁻¹ CO₂ asymmetric stretching, 2782 cm⁻¹ CH₂O CH₂-s-stretching, 3018 cm⁻¹ CH₄ degenerate stretching, and 3656 cm⁻¹ H₂O asymmetric stretching. For clarity, spectra have been offset vertically.

The by-products generated during the PE-s-ALD process were studied as a function of the exposure time of the substrate to precursor and reactant species. The results are shown in Figure 3(a). At a fixed total accumulated time of 600 s for the data acquisition, signals due to ALD by-products decrease at higher exposure times as less ALD cycles are executed. Figure 3(b) shows the dependence of the integrated peak areas normalized to the number of cycles on the exposure time for CO, CO₂ and CH₄. 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 reach nearly self-limiting surface reactions.

Figure 3. (a) Infrared absorption spectra taken from exhausted plasma gases for PE-s-ALD Al₂O₃ layers grown at 80 °C for different substrate exposure times to precursor and reactant (i.e. rotation speed range 10-150 rpm). For each exposure time, the total accumulated acquisition time in spatial ALD mode was kept constant at 600 s. The number of cycles for each deposition is also indicated. (b) Integrated absorbance peak area for CO₂, CO and CH₄ normalized to the number of cycles as a function of exposure time.

OES was performed to analyze the excited species present in the plasma. The emission spectra are shown in Figure 4. In the *plasma-only mode*, the Ar-O₂ plasma spectrum contains the emission lines of atomic argon (5p→4s at 415-426 nm)²⁸ and the so-called first negative system of oxygen, O₂⁺ (b⁴Σ_g⁻ → a⁴Π_u at 557.8 nm). In *ALD mode*, the O₂⁺ signal decreases indicating that O-species are being consumed for combustive reactions taking place with -CH₃ ligands. Simultaneously, OH-emission centered at 309 nm (A²Σ⁺ → X²Π) appears in the ALD spectrum probably originating from electron impact induced dissociative excitation of H₂O molecules.²⁰ Also, CH-emission is detected at 389 nm (B²Σ → X²Π) and 431 nm (A²Δ → X²Π) which most likely originates from dissociative excitation of CH₄. The energy thresholds for these CH-emission lines by electron impact excitation are 7.8 eV and 7.5 eV, respectively, and typically fall within the range of energies for electrons in DBD plasmas.²⁹

Figure 4. Optical emission spectra (offset vertically for clarity) of the ‘*plasma-only mode*’ and the ‘*ALD mode*’ during PE-s-ALD of Al₂O₃ thin films. The plasma-only spectrum shows emission peaks from Ar and O₂⁺; the *ALD mode* spectrum shows the emission peaks from OH and CH.

Infrared absorbance from CO₂ and H₂O in the *ALD mode* spectrum indicates that the spatial PEALD process at atmospheric pressure is driven by combustion-like reactions, while the appearance of CH₄ is associated with a concurrent thermal reaction path. Starting from a methylated surface, the results obtained in this work are in line with an earlier study on PEALD of Al₂O₃ at low pressure conditions by Heil *et al.* who proposed the following surface reaction for the second half-cycle:²⁰

The H₂O formed can react with surrounding methyl groups generating CH₄ in a thermal reaction

CO could either originate from incomplete combustion-reactions or from electron-impact dissociation of CO₂ in the plasma.

At low temperatures, however, O₃ is abundantly present in DBD-generated O₂ plasmas. Therefore, in our case the co-reactant is a mixture of O₂ plasma species and O₃, where O₃ supposedly reacts with the surface by decomposition into O₂ and monoatomic reactive O.¹⁸

Based on literature reports, O₃ can also contribute to CO, CO₂ and H₂O desorbing via combustion-like reactions after which the H₂O formed can act as co-reactant in a thermal reaction desorbing CH₄. The ALD process using Al(CH₃)₃ and O₃ has been extensively studied. Elliott *et al.* predicted that oxidation of the methylated surface can take place via insertion of O-atoms in Al-C bounds 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 O₃ and O₂ plasma co-reactants and found that in both cases the chemistry is driven by combustion reactions where OH and CO₃ (carbonates) act as reactive sites. In particular, surface carbonates were found to be more stable, long-term surface intermediates in the case of O₃ while these decompose under long O₂ plasma exposures.³¹

Besides combustion-like by-products, CH₂O and CH₃OH appear in the ALD spectrum as well. To the best of our knowledge, CH₂O and CH₃OH have not been experimentally observed as reaction by-products in ALD using Al(CH₃)₃ and O₂ plasma or O₃. We speculate that these species can desorb as the result of further reactions of methoxy surface groups created by the O₃ component and water. This assumption is supported by a Density Functional Theory study by Fomengia *et al.* predicting that, for both O₂ plasma and O₃ cases, O-atoms can insert into C-H bonds producing CH₂O as the main by-product.³⁰

This reaction appears the most kinetically favored at various oxygen concentrations and when considering different oxygen-ligand reaction dynamics. The same study also concludes that in oxygen-rich environment CH₃OH can be formed by:

At atmospheric pressure conditions, the concentrations of reactive species are higher than in low- pressure plasmas. This ensures more efficient O₂ dissociation and, consequently, more O-atoms being 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 more kinetic pathways favoring the formation of CH₂O and CH₃OH compared to low pressure PE-ALD.

Furthermore, it should be mentioned that these species are also likely to be formed in the plasma by dissociation of CH₄ into highly reactive CH₃-radicals which can further react with oxygen forming CH₂O and CH₃OH.^{32,33}

The integrated peak areas of CO, CO₂ and CH₄ gives 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 results in unsaturated ALD growth and these Al₂O₃ films are characterized by a high carbon incorporation and low mass density (Table II). Accordingly, this translates into suppressed ALD surface reactions and, consequently, less reaction by-products being produced. At longer exposure times, instead, the by-products

produced show a saturation behavior indicating that $-\text{CH}_3$ ligands have been fully removed and the surface reactions take place in a self-limiting manner.

Table II. Al_2O_3 film properties obtained for different substrate exposure times. The refractive index was measured by *ex situ* spectroscopic ellipsometry and the error was determined as statistical error by repeating the measurement a number of times. The GPC in terms of deposited Al atoms. $\text{nm}^{-2}.\text{cycle}^{-1}$ and the chemical composition were determined by RBS and ERD, respectively. For each element, the errors were calculated as the sum of statistical errors (H: 5 at.%, C: 2.5 at.%, O: 2%, Al: 2.5 at.%) and systematic errors (H: 7 at.%, C: 2 at. %, O: 2%, Al: 2 at.%). The mass density was obtained by combining the RBS and SE results.

t_{exp} (ms)	Refractive index (at 2 eV and $\lambda = 632 \text{ nm}$)	GPC (Al at. $\text{nm}^{-2} \text{ cycle}^{-1}$)	Mass Density (g/cm^3)	[H] (at.%)	[C] (at.%)	O/Al ratio
27 (150 rpm)	1.57 ± 0.01	-	-	-	-	-
40 (100 rpm)	1.57 ± 0.01	3.3 ± 0.1	2.3 ± 0.1	15.2 ± 1.9	3.9 ± 0.4	2.2 ± 0.2
66 (60 rpm)	1.59 ± 0.01	3.9 ± 0.2	2.3 ± 0.1	15.0 ± 1.9	4.0 ± 0.4	2.1 ± 0.2
133 (30 rpm)	1.61 ± 0.01	-	-	-	-	-
400 (10 rpm)	1.62 ± 0.01	5.4 ± 0.2	2.6 ± 0.1	7.4 ± 0.9	< 1	1.7 ± 0.1

Concluding remarks

Summarizing, a combination of gas-phase infrared spectroscopy and *in situ* optical emission spectroscopy was used to study the gas-phase chemistry of the atmospheric pressure plasma-enhanced spatial ALD process of Al_2O_3 films using $\text{Al}(\text{CH}_3)_3$ and Ar- O_2 plasma. The underlying surface reaction mechanism appears to be driven by three concurring reactants: O_2 plasma species, O_3 and H_2O . The appearance of H_2O , CO and CO_2 in the infrared absorbance spectra indicates that part of the deposition process proceeds via combustion-like reactions of the methylated surface by O_2 plasma species as well as O_3 . OES confirmed the combustion-like reaction mechanism revealing OH and CH-emission arising during the ALD process while O-species are consumed. Moreover, H_2O formed from ligand combustion could explain the appearance of CH_4 resulting from concurrent thermal reactions. Next to combustion-like

reaction products, CH₂O and CH₃OH were also identified which have not been observed at low-pressure conditions but can be formed in the atmospheric plasma and at the surface: the higher concentration of the O-atoms in atmospheric plasma is likely to open up more diverse kinetic pathways in the PE-s-ALD reactor thus favoring the formation of these species.

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Appendix: Ozone formation

Ozone generation is a well-known phenomenon taking place in atmospheric pressure DBD plasmas generated in air and oxygen gas.⁴ Ozone formation consists of a two-step reaction process where O₂ molecules are first dissociated by

After the dissociation, a three-body reaction takes place

where X is most likely O₂ or Ar in the present case.

One common way to control the O₃ formation is by varying the plasma operating conditions. This could be verified by measuring gas phase infrared spectra of the *plasma only* mode. Figure 5 shows the integrated peak area of ozone as a function of the plasma input voltage (a) and the O₂ gas flow (b).

Figure 5. Integrated area of the ozone peak in the infrared spectra as a function of input voltage (a) and O₂ flow (b) at an Al(CH₃)₃ flow of 0.075 slm). Spectra were measured via gas phase infrared spectroscopy in *plasma-only* mode at 133 ms exposure time.