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Surface chemistry of plasma-assisted atomic layer deposition of Al_2O_3 studied by infrared spectroscopy

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The surface groups created during plasma-assisted atomic layer deposition (ALD) of Al_2O_3 were studied by infrared spectroscopy. For temperatures in the range of 25–150 °C, $-\text{CH}_3$ and $-\text{OH}$ were unveiled as dominant surface groups after the $\text{Al}(\text{CH}_3)_3$ precursor and O_2 plasma half-cycles, respectively. At lower temperatures more $-\text{OH}$ and C-related impurities were found to be incorporated in the Al_2O_3 film, but the impurity level could be reduced by prolonging the plasma exposure. The results demonstrate that $-\text{OH}$ surface groups rule the surface chemistry of the Al_2O_3 process and likely that of plasma-assisted ALD of metal oxides from organometallic precursors in general. © 2008 American Institute of Physics. [DOI: 10.1063/1.2940598]

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin and conformal high- k metal oxide films as required in next-generation memory and transistor devices. To extend the applications of ALD, processes using alternative oxidant sources, such as O_3 and O_2 plasma, are actively researched. Using these oxidant sources, additional reactivity is supplied to the surface chemistry and this potentially allows for deposition at lower temperatures (<150 °C) without compromising film quality.^{1–3}

In order to fully exploit the benefits of the ALD technique, a fundamental understanding of the underlying surface chemistry is of vital importance. To this end the ALD process of Al_2O_3 has been studied in great detail, since it shares generic features to equivalent metal oxide ALD processes. The conventional, thermal ALD process of Al_2O_3 using $\text{Al}(\text{CH}_3)_3$ precursor and H_2O was found to be ruled by the formation of $-\text{CH}_3$ and $-\text{OH}$ surface groups after the precursor and oxidant half-cycles, respectively, with the formation of volatile CH_4 in both half-reactions.^{4–6} In the O_3 -based ALD process, the formation of $-\text{CH}_3$ surface groups, and volatile CH_4 after $\text{Al}(\text{CH}_3)_3$ adsorption were found to be similar to the H_2O -based process. During the O_3 half-cycle, however, the formation of CH_4 and C_2H_4 have been reported^{1,2} and it is still debated whether $-\text{OH}$ or formate [$-\text{O}(-\text{O})\text{CH}$] groups are the dominant surface species produced by the O_3 reactions.^{2,7} In our previous work on plasma-assisted ALD of Al_2O_3 , we observed the formation of CH_4 after $\text{Al}(\text{CH}_3)_3$ adsorption, while mainly CO , CO_2 , and H_2O were formed in the O_2 plasma half-cycle through combustionlike surface reactions.^{3,8} The surface chemistry during this plasma-assisted ALD process could not be fully resolved yet, because no measurements on the surface groups were available.

Despite the different oxidant sources employed, it is intriguing to note that the dependence of growth per cycle on the deposition temperature is quite similar for the different oxidant sources for ALD of Al_2O_3 , as shown in Fig. 1 for H_2O ,^{2,9–13} O_3 ,^{2,13} and O_2 plasma.⁹ For temperatures

>100 °C, the growth per cycle of Al_2O_3 monotonically decreases with increasing deposition temperature for all three oxidant sources and the differences are relatively small. Only below 100 °C, the growth per cycle significantly differs which has been attributed to difficulties to achieve saturation when dosing H_2O .^{9,10} For the H_2O -based process, the decrease in growth per cycle with increasing temperature has been related to the thermal stability of the $-\text{OH}$ surface groups which are involved in the $\text{Al}(\text{CH}_3)_3$ chemisorption reactions.^{5,10} The O_2 plasma-based process shows a similar decrease but for the complete temperature range (25–400 °C). This resemblance might indicate some similarities between the surface groups involved in plasma-assisted and thermal ALD of Al_2O_3 . To better understand the dependence of the growth per cycle on the deposition temperature, however, insight into the surface chemistry of plasma-assisted ALD of Al_2O_3 is necessary.

The primary objective of this letter is to elucidate the surface chemistry of plasma-assisted ALD of Al_2O_3 through detection of the surface groups generated in the half-cycles by means of transmission infrared spectroscopy measurements. The main result of this study is the observation that $-\text{CH}_3$ and $-\text{OH}$ surface groups are predominantly formed after the $\text{Al}(\text{CH}_3)_3$ and O_2 plasma half-cycles, respectively.

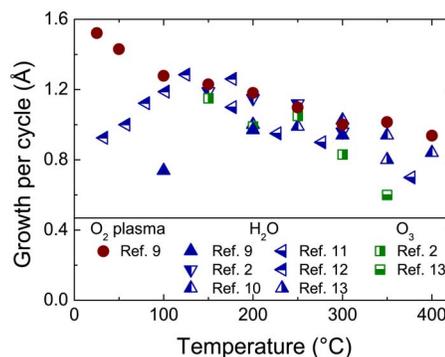


FIG. 1. (Color online) Literature data on the growth per cycle of Al_2O_3 as a function of deposition temperature for ALD processes using $\text{Al}(\text{CH}_3)_3$ as precursor and H_2O , O_3 , or O_2 plasma as oxidant source. The data presented were corrected for differences in mass density and represent the growth per cycle of a film with a mass density of 3.0 g cm^{-3} as typically reported for ALD Al_2O_3 films.

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This observation implies that $-OH$ surface groups rule the surface chemistry during plasma-assisted ALD of Al_2O_3 similar to the H_2O -based process. Also the influence of the deposition temperature (25–150 °C), the incorporation of impurities, and a direct comparison with the thermal ALD process at 150 °C are addressed. The results will facilitate the design of improved low temperature (<150 °C) ALD processes and it is expected that they have generic implications for plasma-assisted ALD processes of other metal oxide films.

Plasma-assisted and thermal ALD processes of Al_2O_3 were studied in a wall-heated reactor equipped with an O_2 -operated inductively coupled plasma source and bubblers with $Al(CH_3)_3$ (99.9999%, Akzo Nobel) and H_2O (Ultrapur®, >99.9999%, Merck). The cycles consisted typically of 25 ms of $Al(CH_3)_3$ dosing followed by 2 s O_2 plasma exposure or 2×240 ms H_2O dosing in the plasma-assisted and thermal ALD process, respectively. The Al_2O_3 films were deposited onto KBr flats that also served as infrared viewports in the reactor. It was verified that the growth per cycle and Al_2O_3 film quality were similar to results obtained on substrates positioned on the substrate holder.^{9,14} In between the ALD half-reactions, transmission infrared spectra (2 \times 256 scans) were collected by an infrared interferometer (Bruker, Tensor 27) with an external liquid- N_2 cooled HgCdTe detector (Bruker, D313). The absorbance spectra were averaged over 40 ALD cycles to reduce the noise level to $\sim 5 \times 10^{-6}$.

The surface species created during the plasma-assisted ALD half-cycles of Al_2O_3 were studied at a deposition temperature of 150 °C and were directly compared to the results of the thermal ALD process carried out at the same temperature. From qualitative comparison of the differential vibrational spectra shown in Fig. 2(a), it is clear that the same types of surface species are created in both ALD processes. After the $Al(CH_3)_3$ precursor adsorption, $-CH_3$ surface groups appear as observed in stretching (asymmetric ~ 2937 cm^{-1} , symmetric ~ 2896 cm^{-1} , and bending overtone ~ 2831 cm^{-1}), deformation (~ 1208 cm^{-1}), and rocking (~ 750 cm^{-1}) modes, while $-OH$ surface groups disappear as observed in the broad stretching (3750–2770 cm^{-1}) mode.^{4,5,15} This broad $-OH$ stretching feature originates from various types of $-OH$ groups on the Al_2O_3 surface, ranging from unassociated $-OH$ (3800–3700 cm^{-1}) to associated $-OH$ (3700–2700 cm^{-1}) modes.^{5,16–18} For both ALD processes, the differential spectra clearly show that $-OH$ surface groups are created after the reaction of the O_2 plasma and the H_2O oxidant with the $-CH_3$ surface groups.

For the O_2 plasma-based process, the influence of deposition temperature on the surface groups was studied for films deposited at 25, 100, and 150 °C, as shown in Fig. 2(b). From the similarities in the differential vibrational spectra, it is concluded that the surface chemistry at lower temperatures also proceeds predominantly via the formation of $-CH_3$ and $-OH$ surface species. At lower temperatures, the amount of $-OH$ surface groups created by the O_2 plasma strongly increased and a broadening of the $-OH$ stretching modes was observed. The broadening at lower deposition temperatures can be attributed to the dipole interaction (in particular, hydrogen bonding) between the densely packed $-OH$ surface groups. Moreover, the presence of physisorbed H_2O on the Al_2O_3 surface can also be of influence.^{19,20} In

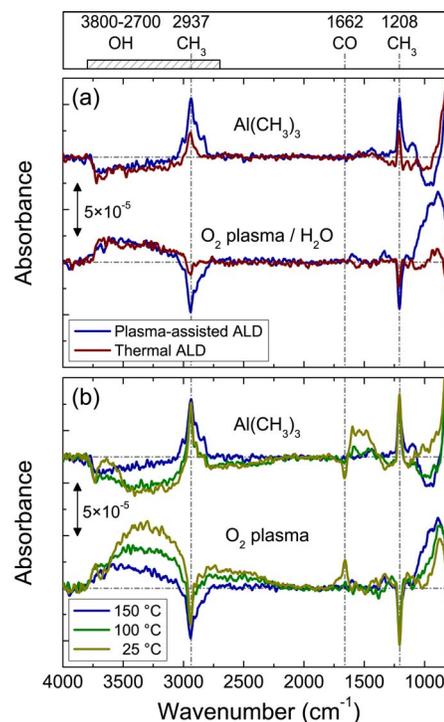


FIG. 2. (Color online) Differential infrared spectra after the $Al(CH_3)_3$ precursor and oxidation half-cycles showing appearance and disappearance (with respect to the baseline) of surface groups in the two ALD half-reactions. (a) Comparison between the surface groups involved in plasma-assisted and thermal ALD of Al_2O_3 at a deposition temperature of 150 °C. (b) Surface groups involved in plasma-assisted ALD at deposition temperatures of 25, 100, and 150 °C. The relevant peak positions of the $-CH_3$ groups, $-OH$ groups, and CO-containing impurities (with C=O or COO bonds) are indicated.

addition, an unassigned broad feature around ~ 900 cm^{-1} is observed for the films deposited by plasma-assisted ALD. The feature is most-likely not related to the broad Al–O phonon mode (~ 954 cm^{-1} in Ref. 15), since its magnitude increased with increasing temperature opposite to the trend observed for the growth per cycle of the Al_2O_3 films (Fig. 1).

Insight into the type and relative amount of impurities incorporated into the Al_2O_3 films can be deduced from a differential spectrum obtained after a full ALD cycle (i.e., basically adding the differential spectra for the two half-cycles). From such differential spectra, it is concluded that $-OH$ groups were incorporated in the Al_2O_3 bulk with the amount of $-OH$ incorporated increasing when going to lower deposition temperatures. This observation is in line with previous reports,^{5,9,14} as well as with the compositional data of Al_2O_3 films deposited in the temperature range studied, i.e., $x=[O]/[Al]=1.6$ with ~ 4 at. % H at 150 °C, $x=1.7$ with ~ 7 at. % H at 100 °C, and $x=2.1$ with ~ 15 at. % H at 25 °C (all using 2 s O_2 plasma exposure).⁹ From the spectra, no evidence is found for the incorporation of $-CH_x$ groups into the bulk Al_2O_3 film at the studied temperatures. Interestingly for the film deposited at 25 °C, carbon-related impurities appeared (~ 1662 cm^{-1}) after the O_2 plasma step, which changed into a broad feature (1600–1450 cm^{-1}) after the $Al(CH_3)_3$ dosing. The peaks observed can be attributed to impurities containing C=O or COO bonds indicating incomplete removal of the carbon from the surface during the 2 s O_2 plasma step at 25 °C. The incorporation of these surface features into the Al_2O_3 bulk after $Al(CH_3)_3$ precursor adsorption is expected to account for the shift and broaden-

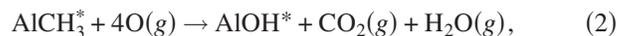
ing of the peak. The appearance of these C=O/COO bonds is most-likely characteristic for the strong oxidation power of the O₂ plasma and these bonds can be interpreted as intermediate reaction states in the combustionlike reaction from the -CH₃ covered surface to the -OH covered surface after the O₂ plasma exposure. This hypothesis is corroborated by the fact that the magnitude of the C-related absorbance could be reduced by using a longer O₂ plasma step in the ALD cycle. Furthermore, in our previous work, compositional data on the Al₂O₃ films deposited at 25 °C revealed that the amount of O, C, and H impurities was substantially reduced when using 4 s (instead of 2 s) of O₂ plasma exposure.⁹

From the quantitative amount of surface groups observed, in principle, conclusions can be drawn regarding the ALD surface chemistry at the different temperatures. For example, the increase in -OH surface groups involved in plasma-assisted ALD when going to lower temperatures can be related to the increase in growth per cycle. However, care must be taken in such interpretation, since residual H₂O (either being remnants of the excessive H₂O dosing during thermal ALD or of the H₂O reaction byproducts created during plasma-assisted ALD³) is difficult to completely purge out of the reactor, especially at the low temperatures employed. Residual H₂O can lead to -CH₃ consumption and -OH formation during the purge time and (relatively long) infrared measurement time following the Al(CH₃)₃ precursor half-cycle. Evidence for this effect was found by comparing infrared measurements consecutively acquired during the purge time. Therefore, differences in the experiment with respect to conditions and timing can partly account for the different amount of -CH₃ groups observed in thermal and plasma-assisted ALD at 150 °C [Fig. 2(a)].

Notwithstanding this influence of residual H₂O and other effects related to the experiment, the increase in -OH surface groups when going to lower temperatures is remarkable compared to the virtually temperature independent amount of -CH₃ surface groups [Fig. 2(b)]. When linked to the increase in growth per cycle (Fig. 1), these observations support a more pronounced bifunctional adsorption of the precursor when going to lower temperatures, as was also reported for thermal ALD.²¹ Upon bifunctional adsorption, the Al(CH₃)₃ molecule splits off two -CH₃ ligands consuming two -OH surface groups and, thereby, releasing two CH₄ molecules. Consequently, after bifunctional adsorption only one -CH₃ surface group remains per adsorbed Al(CH₃)₃ compared to two -CH₃ surface groups remaining after monofunctional adsorption; a process that becomes more important at higher temperatures when the amount of -OH surface groups becomes relatively low.²¹ In this respect, the virtually constant amount of -CH₃ surface groups observed in the infrared spectra in Fig. 2(b) combined with the increase in growth per cycle confirms that a larger fraction of the Al(CH₃)₃ molecules bifunctionally adsorbs when going to lower temperatures.

In summary, the surface species created during the half-cycles of plasma-assisted ALD of Al₂O₃ were measured by transmission infrared spectroscopy. Combining the results with gas phase products previously reported,³ it was established that the surface chemistry of plasma-assisted ALD of Al₂O₃ is ruled by the formation of -OH surface groups in the combustionlike reactions between -CH₃ surface groups and

the O₂ plasma species. Therefore the following surface reactions are proposed for plasma-assisted ALD of Al₂O₃:



where the asterisks designate the surface species and only the case of monofunctional adsorption is considered for simplicity. Moreover, the amount of -OH groups involved in the surface reactions increased for lower deposition temperatures which can be related to the higher growth per cycle at these temperatures. It was also demonstrated that the high reactivity delivered by the O₂ plasma allows for film deposition at temperatures down to room temperature, but under these conditions a longer plasma exposure time was required to complete the surface reactions and reduce the impurity content of the Al₂O₃ films. Tuning the plasma reactivity in the ALD process is thus key in obtaining high quality films at low deposition temperatures. Because combustionlike reactions of organic surface ligands by O₂ plasma species have been reported for more plasma-assisted ALD processes,²² it is expected that the surface chemistry discussed is generic for plasma-assisted ALD processes of high-*k* metal oxides using (similar) metal-organic precursors and O₂ plasma.

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