What is limiting low-temperature atomic layer deposition of Al₂O₃? A vibrational sum-frequency generation study

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What is limiting low-temperature atomic layer deposition of Al_2O_3 ? A vibrational sum-frequency generation study

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The surface reactions during atomic layer deposition (ALD) of Al_2O_3 from $\text{Al}(\text{CH}_3)_3$ and H_2O have been studied with broadband sum-frequency generation to reveal what is limiting the growth at low temperatures. The $-\text{CH}_3$ surface coverage was measured for temperatures between 100 and 300°C and the absolute reaction cross sections, describing the reaction kinetics, were determined for both half-cycles. It was found that $-\text{CH}_3$ groups persisted on the surface after saturation of the H_2O half-cycle. From a direct correlation with the growth per cycle, it was established that the reduced reactivity of H_2O towards $-\text{CH}_3$ is the dominant factor limiting the ALD process at low temperatures. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4939654>]

Atomic layer deposition (ALD) has become an enabling technology in the fabrication of semiconductor and photovoltaic devices due to its unique capability to conformally deposit ultra-thin films with sub-nanometer thickness precision.¹ In recent years, the adoption of ALD as the method of choice in numerous applications has sparked a drive towards the development of new ALD processes. Simultaneously, the operating range of existing processes is being explored with the main goal of obtaining greater flexibility in deposition conditions, while at the same time retaining all the merits of ALD. Of special interest is low temperature ALD,^{2,3} enabling deposition on temperature sensitive samples. When exploring a new process or extending the operating range of an established process, insight into the surface chemistry that is governing ALD is a key. Yet gaining understanding of ALD film growth by directly studying the surface groups, ruling the ALD chemistry, requires highly sensitive *in-situ* diagnostic techniques.

This work focuses on the ubiquitous thermal ALD process of Al_2O_3 , using trimethylaluminum ($\text{Al}(\text{CH}_3)_3$, TMA) as a precursor and water as a co-reactant and addresses the question what limits Al_2O_3 growth at low temperature. The steady-state growth mechanism of this ALD process has been studied extensively with techniques such as quadrupole mass spectrometry,⁴ spectroscopic ellipsometry,⁴ quartz-crystal microbalance (QCM),⁵ and Fourier-transform infrared (FTIR) absorption spectroscopy.^{6–8} The generally accepted and dominant reaction mechanism for steady-state growth is as follows:

where an “–” symbol designates surface species. In addition to hydroxyls which form the most important chemisorption site for TMA, it has been reported that TMA can chemisorb on bridged oxygen on a dehydroxilated Al_2O_3 surface,⁹

formates,¹⁰ and carbonates.¹¹ One of the unresolved issues in understanding the growth of Al_2O_3 by ALD is the exact cause of the decrease in growth per cycle (GPC) reported at low temperatures.^{2,3} Figure 1 shows the GPC of Al_2O_3 ALD in terms of Al atoms deposited as a function of deposition temperature as measured with Rutherford back-scattering spectrometry (RBS, this metric gives more insight than the GPC in terms of thickness). Comparing the GPC of this thermal process with its plasma enhanced counterpart using O_2 plasma instead of H_2O , also included in Fig. 1, shows that the decrease in GPC at low temperatures only occurs for the thermal process while the GPC of the plasma process keeps increasing when going to lower temperatures.^{3,11} Because both processes only differ in the co-reactant, the likely cause

FIG. 1. The growth-per-cycle (GPC) as a function of temperature for thermal ALD of Al_2O_3 with $\text{Al}(\text{CH}_3)_3$ and H_2O as well as for the plasma-enhanced ALD process with $\text{Al}(\text{CH}_3)_3$ and O_2 plasma. The GPC is given in terms of Al atoms per cm^2 per cycle as obtained by RBS measurements (solid markers). At low temperatures, the thermal process shows a significant decrease in the GPC, whereas the plasma process does not. The trends in the GPC can also be predicted by the change in $-\text{CH}_3$ coverage $\Delta\theta$ measured with BB-SFG (open markers). The measured and predicted GPC data show a good agreement.

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of the lower GPC for the H₂O-based process is the lack of reactivity of the co-reactant at low temperatures. However, the precise ALD surface chemistry related to this lower reactivity is unclear. So far, the aforementioned diagnostic techniques have not been able to resolve this issue and therefore a different approach is needed.

In this work, the surface chemistry of ALD Al₂O₃ is investigated with the technique of broadband sum-frequency generation (BB-SFG). BB-SFG is a state-of-the-art nonlinear optical technique used predominantly in surface science which is used here to study ALD chemistry. BB-SFG is inherently interface selective with a sub-monolayer sensitivity for –CH₃ groups and with fairly short acquisition times (120 s for a sensitivity better than 10% of a –CH₃ monolayer). One of the key features of BB-SFG is that the measured signals are directly correlated to the absolute surface density, revealing more information than the so-called differential techniques (such as FTIR) from which only *changes* in surface coverage can be extracted. By its very nature, the surface selectivity of BB-SFG leads to the simultaneous detection of species which are *changing* after an ALD half-cycle and species which are *persistent* over the ALD half-cycles. In this letter, it will be shown that these persistent surface species play a key role in ALD of Al₂O₃ at low temperatures. Water is not reactive enough at low temperatures to remove all the –CH₃ groups from the surface; even when saturation conditions are reached, a significant amount of –CH₃ groups persist on the surface. These persistent –CH₃ groups limit the uptake of TMA in the next half-cycle causing the reduction in GPC. The reduction in the areal density of the Al atoms deposited per cycle is found to be directly proportional to the persistent –CH₃ coverage.

ALD of Al₂O₃ was studied with BB-SFG in a setup designed and built for this purpose. The setup consisted of a vacuum chamber equipped with two turbo-molecular pumps (base pressure below 10^{–7} mbar) and fast ALD valves to dose the vapor drawn reactants. A pump down step of ~140 s reaching a pressure below 10^{–6} mbar was performed after dosing the reactants. The sample was heated radiatively from the back side and the temperature of the sample was controlled with a thermocouple glued to the substrate within 5 mm of the spot measured with BB-SFG. The sample itself was a free-standing 2 in. Si(100) wafer with a 90 nm SiO₂ film on top for optical enhancement purposes of the BB-SFG signal.¹² The sample was mounted such that BB-SFG could be performed in reflection mode. The laser system used for the experiments produced a ~90 fs pulsed IR (3.3 μm) beam and visible (800 nm) beam with a repetition rate of 1 kHz. A band-pass filter was used to reduce the bandwidth of the visible pulse to ~1 nm. Both the IR and visible beams (pulse energy ~5 μJ each) were focused on the sample in a non-collinear geometry. The spectra shown in this work were acquired with an integration time of 120 s to reach a noise level of <1% for typical signals. Except for dark-field subtraction and the removal of features due to cosmic rays, the data are presented as-obtained.

The surface chemistry occurring during both ALD half-cycles was monitored with BB-SFG by probing the spectral region of the C-H stretching modes. The C-H stretching mode of –CH₃ was detected at ~2950 cm^{–1} after precursor

exposure, similar to what is typically observed with FTIR for chemisorbed TMA.⁶ The mode is in the same range as, for example, –CH₃ groups of self-assembled monolayers (SAM) when probing them with BB-SFG.¹³ BB-SFG was used to detect the –CH₃ groups during steady-state ALD at 200 °C. Recording a spectrum after a saturated H₂O dose shows no –CH₃ groups as can be deduced from the featureless spectrum in Fig. 2(a). This corresponds to a fully –OH terminated surface.^{6–8} Subsequently, the –OH covered surface was exposed to a pulse of TMA by activating the ALD valve for 20 ms. As expected from Eq. (1a), the spectrum recorded after the TMA exposure shows the spectral feature indicative of the C-H stretching mode of –CH₃ groups on the surface. A subsequent 20 ms pulse yields only a slight increase in peak height indicating a small additional uptake of TMA. Ensuing TMA pulses do not show any change in –CH₃ coverage, implying that saturation has already been reached. When continuing with the H₂O half-cycle after the TMA half-cycle, the first 20 ms H₂O exposure results in a significant decrease in the amount of –CH₃ on the surface as can be seen in Fig. 2(b). Subsequent pulses of water remove –CH₃ groups from the surface until all –CH₃ groups have disappeared. To recapitulate, the surface chemistry at 200 °C is described by Eq. (1) which is reflected by the uptake and removal of –CH₃ for the TMA and water half-cycle, respectively. This happens in a self-limiting fashion as is characteristic for ALD.

In order to reveal how the sample temperature influences the surface chemistry during steady-state film growth, the experiments have been carried out at temperatures ranging between 100 °C and 300 °C. A set of saturation plots was obtained for each temperature yielding the dependence of the –CH₃ coverage on the precursor and co-reactant dose as shown in Fig. 3. In this figure, the BB-SFG spectra were normalized for each temperature to the –CH₃ coverage obtained after a saturated TMA exposure. The reason is that the acquisition of the spectra for these experiments was relatively time consuming and necessary day-to-day adjustments of the

FIG. 2. BB-SFG spectra showing the C-H stretching mode of –CH₃ surface groups on the surface, recorded as a function of subsequent TMA (top) and H₂O (bottom) exposures during ALD at a sample temperature of 200 °C.

FIG. 3. Relative $-\text{CH}_3$ surface coverage θ , extracted from the BB-SFG spectra as a function of TMA and H_2O exposure for various temperatures. The solid lines represent fits to the data in order to extract information about the reaction kinetics.

laser system influenced the optical alignment, preventing a direct comparison of absolute intensities between measurements at different temperatures. As can be seen from the figure, the saturation of the TMA half-cycle is fast and the dose for which saturation is achieved is independent of temperature. For low temperatures, the initial $-\text{CH}_3$ coverage is not equal to zero and both $-\text{OH}$ and $-\text{CH}_3$ groups coexist on the surface at the beginning of the TMA half-cycle. This $-\text{CH}_3$ can be traced back to the reactivity of the H_2O co-reactant as can be seen in Fig. 3(b). This figure shows that water is reactive towards the $-\text{CH}_3$ groups at high temperatures and quickly removes all the $-\text{CH}_3$. However, for lower temperatures, the reaction slows down. Furthermore, below 200°C , there are $-\text{CH}_3$ groups which are no longer reactive towards H_2O and these $-\text{CH}_3$ groups therefore persist on the surface. In other words, the half-cycle saturates while there are still $-\text{CH}_3$ groups present on the surface. An additional check with two extra-long H_2O exposures of 400 and 800 ms at 150°C (not shown) did not yield an additional decrease of the $-\text{CH}_3$ signal. This implies that during thermal ALD of Al_2O_3 at low temperatures, there is a significant amount of $-\text{CH}_3$ present on the surface at the beginning of the TMA half-cycle.

To obtain more quantitative information on the influence of the temperature on the ALD process, a less time consuming experiment was carried out such that the $-\text{CH}_3$ coverages for different temperatures could be compared with each other. Instead of recording saturation curves, spectra were only recorded after a saturated half-cycle. Figure 4 shows the BB-SFG spectra of the C-H stretch mode after the TMA and H_2O half-cycles. Again, at high temperatures, the $-\text{CH}_3$ surface groups added to the surface during the TMA half cycle are completely removed in the water half cycle, while at lower temperatures $-\text{CH}_3$ groups persist. Moreover, the influence of temperature induced dehydroxylation is observed in the $-\text{CH}_3$ coverage after a saturated TMA.⁸ Due to dehydroxylation, fewer reactive sites are available for TMA chemisorption at high temperature than at low

FIG. 4. BB-SFG spectra recorded after the TMA and H_2O half-cycle at various temperatures. For each temperature, data for four half-cycles are shown (i.e., subsequent TMA, H_2O , TMA, H_2O exposures) revealing the excellent reproducibility of the data.

temperature, hence the $-\text{CH}_3$ coverage shows a decrease with temperature.

The trend in growth per cycle shown in Fig. 1 can be reproduced using the data in Fig. 4. The density of Al atoms deposited per cycle is proportional to the TMA uptake in the TMA half-cycle. The TMA uptake is directly related to the change in $-\text{CH}_3$ coverage if the number of $-\text{CH}_3$ ligands, n , which remain attached to the Al atom after chemisorption, is temperature independent. QCM studies showed that this is indeed the case over the temperature range investigated here.^{9,14} For the thermal ALD process, the TMA uptake will be limited by the persistent $-\text{CH}_3$ groups in the H_2O half-cycle. Therefore, the TMA uptake should be proportional to the difference in $-\text{CH}_3$ coverage between the TMA and H_2O half-cycles. The increase in $-\text{CH}_3$ coverage caused by the TMA exposure was determined from Fig. 4, and the predicted GPC from this change in $-\text{CH}_3$ coverage was plotted in Fig. 1. The validity of this procedure can be evaluated by also predicting the GPC of the plasma process. For the plasma process, there should be no persistent groups due to the high reactivity of the O_2 plasma. In this case, the change in $-\text{CH}_3$ coverage is equal to the $-\text{CH}_3$ coverage after TMA exposure. This result is also plotted in Fig. 1 on the same scale as the data set for thermal ALD. Both data sets indeed show a good agreement with GPC determined by RBS. The agreement between the measured and predicted GPC for ALD of Al_2O_3 using TMA and H_2O corroborates therefore that the persistent $-\text{CH}_3$ groups are the limiting factor in the Al_2O_3 ALD process at low temperatures.

The underlying cause of the persistent $-\text{CH}_3$ groups can be studied in more detail by considering the reaction kinetics. The kinetics of the reactions in Eq. (1) were determined from Fig. 3 by fitting the dependence of $-\text{CH}_3$ coverages on the reactant exposure time with an exponential function.¹² Briefly, the exponential time constant is equal to the reaction cross section multiplied with the (known) impinging flux of reactant species on the surface. Figure 5 shows the temperature dependence of the reaction cross

FIG. 5. Temperature dependence of the reaction cross sections σ and the initial reaction probability for the (a) TMA and (b) H₂O half-cycle. Panel (c) shows the fraction of -CH₃ groups persisting after H₂O exposure as a function of temperature.

section in both half-cycles and the related initial reaction probability (i.e., the reaction probability when the reactant TMA or H₂O interacts with a surface that is fully covered with -OH or -CH₃ groups, respectively). The figure also shows the fraction of persistent surface groups as a function of temperature obtained from the fits to the saturation plots (Fig. 5(c)). Considering the order of magnitude of the initial reaction probabilities, it can be concluded that the values of 10^{-3} for TMA and 10^{-4} for H₂O fall inside the range of values in the reported literature.^{15,16} However, those literature values vary over several orders of magnitude for different studies. The study of the reaction kinetics in this work, i.e., by directly measuring the surface coverage, is expected to yield very accurate results. The main uncertainty, the systematic error in the calculation of the reactant flux, introduces only a scaling factor and does not affect the trend in the data with temperature. Examining the temperature dependence in Fig. 5(a) more closely reveals that the reaction cross-section—and hence the initial reaction probability—during the TMA half-cycle, is independent of temperature. This confirms that chemisorption of TMA on the predominantly -OH terminated surface is a barrierless process which is not thermally activated. For the H₂O half-cycle, the reaction cross-section in Fig. 5(b) does depend on the temperature and the behavior is more complex. The increase in reactivity at high temperatures during the H₂O half-cycle suggests a thermally activated reaction for this half-cycle.

Although the reactions described by Eq. (1) suggest simple reaction kinetics, the data in Figs. 3 and 5 show a more intricate chemistry during the H₂O half-cycle especially at low temperatures: A pseudo first order reactions can describe the chemistry at high temperatures but it cannot describe the kinetics at low temperatures due to the presence of persistent surface groups. A possible explanation for the persistent surface groups can be found in the recent *ab-initio* studies using density functional theory (DFT) performed by Shirazi and Elliott¹⁷ They proposed that the so-called cooperative effects

play an important role in the surface chemistry of ALD. For -CH₃ surface groups reacting with H₂O, they found a significantly higher activation barrier for isolated -CH₃ groups than for clusters of -CH₃. An independent DFT study from Weckman and Laasonen also reports a high activation barrier for isolated -CH₃ and cooperative effects for this ALD process.¹⁸ Such a cooperative effect could explain the persistence of -CH₃ groups at low temperatures and hence this work can be seen as experimental evidence of the cooperative effect.

In conclusion, we have addressed the question of what is causing the reduced GPC of thermal ALD of Al₂O₃ at low temperatures using the nonlinear optical technique of BB-SFG. It was found that water is not reactive enough to remove all -CH₃ groups at low temperatures, which leads to a significant amount of persistent -CH₃ groups. These persistent -CH₃ groups limit the TMA uptake and hence they limit the GPC. This was also corroborated by the fact that the predicted GPC, using the measured -CH₃ coverage as input, showed an excellent agreement with the GPC measured with RBS if the persistent groups were accounted for. These persistent -CH₃ groups are not incorporated in the film as is evidenced by the high-quality, virtually carbon-free material which is generally grown with the thermal ALD process at low temperatures.^{2,3} Furthermore, from the reaction kinetics, it was determined that for the TMA half-cycle the reaction cross-section is temperature independent indicating barrierless reaction. On the other hand, the temperature dependent reaction cross-section in the H₂O half-cycle indicates a thermally activated reaction. Finally, since the combination of H₂O as co-reactant and metal atoms with organic ligands as precursor are quite commonplace in other ALD chemistries, the presence of persistent surface groups reported in this work could play a role in other ALD processes.

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¹²See supplementary material at <http://dx.doi.org/10.1063/1.4939654> for sample details, modeling of the BB-SFG spectra, and the analysis of the reaction kinetics.

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