Low temperature plasma-enhanced atomic layer deposition of metal oxide thin films

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Many reported atomic layer deposition (ALD) processes are carried out at elevated temperatures (>150°C), which can be problematic for temperature-sensitive substrates. Plasma-enhanced ALD routes may provide a solution, as the ALD temperature window can, in theory, be extended to lower deposition temperatures due to the reactive nature of the plasma. As such, the plasma-enhanced ALD of AlOx, TiO2, and Ta2O5 has been investigated at 25–400°C using [Al(CH3)]3, [Ti(OiPr)4], [Ti(CpMe)][(OPr)3], [TiCp'(OMe)3], and [Ta(NMe3)5] as precursors. An O plasma was employed as the oxygen source in each case. We have demonstrated metal oxide thin-film deposition at temperatures as low as room temperature and compared the results with corresponding thermal ALD routes to the same materials. The composition of the films was determined by Rutherford backscattering spectroscopy. Analysis of the growth per cycle data and the metal atoms deposited per cycle revealed that the growth per cycle is strongly dependent on the film density at low deposition temperatures. Comparison of these data for Al2O3 and TiO2 ALD processes in particular showed that the number of Al atoms deposited per cycle was consistently high down to room temperature for the plasma-enhanced process but dropped for the thermal process at substrate temperatures lower than 250°C.

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Atomic layer deposition (ALD), a method of ultrathin-film deposition by alternate dosing of gaseous precursors, gives dense, pure, and highly conformal films with excellent step coverage. Each ALD process is considered to have a temperature window, which is governed by the reactivity and stability of the precursors and surface functional groups.1 The ALD temperature window typically spans 200–400°C for the majority of processes, although many studies on metal oxides have been investigated over the range 100–600°C.2 It is often assumed that, within the temperature window, the growth per cycle remains constant with varying substrate temperature (Fig. 1a). However, in several cases it is possible to see a small reduction in the growth per cycle with increasing temperature due to a small loss of reactive surface groups (Fig. 1b).3 Outside the temperature window, the growth per cycle can change dramatically. At lower temperatures, excess condensation of the precursors can result in a rapid increase in growth (A), for example, when the substrate temperature is lower than the bubbling temperature required to obtain an adequate vapor pressure. Also at lower temperatures, there may be insufficient thermal energy for a chemical reaction to occur, resulting in slower growth (B). At higher temperatures, decomposition of the precursors (chemical vapor deposition) can occur, leading to an increase in growth, which is not self-limiting (C), or, if the film material is volatile it may evaporate, thereby reducing the growth (D). However, as previously mentioned, a change in growth per cycle does not always accurately indicate whether or not true ALD is occurring, exemplified by the gradual loss of surface groups with increasing substrate temperature in Fig. 1b.

Generally, the ALD window (spanning 150–400°C) for most metal oxide processes has proved sufficient for many applications requiring ultrathin films. However, for emerging applications employing temperature-sensitive substrates, even temperatures as low as 200°C can be problematic, for example, in polymers or small organic molecules, whose structure can be affected at such temperatures. Applications that require such low temperatures include or–dendrimers, a method of ultrathin-film deposition by alternate dosing of gaseous precursors, gives dense, pure, and highly conformal films with excellent step coverage. Each ALD process is considered to have a temperature window, which is governed by the reactivity and stability of the precursors and surface functional groups.1 The ALD temperature window typically spans 200–400°C for the majority of processes, although many studies on metal oxides have been investigated over the range 100–600°C.2 It is often assumed that, within the temperature window, the growth per cycle remains constant with varying substrate temperature (Fig. 1a). However, in several cases it is possible to see a small reduction in the growth per cycle with increasing temperature due to a small loss of reactive surface groups (Fig. 1b).3 Outside the temperature window, the growth per cycle can change dramatically. At lower temperatures, excess condensation of the precursors can result in a rapid increase in growth (A), for example, when the substrate temperature is lower than the bubbling temperature required to obtain an adequate vapor pressure. Also at lower temperatures, there may be insufficient thermal energy for a chemical reaction to occur, resulting in slower growth (B). At higher temperatures, decomposition of the precursors (chemical vapor deposition) can occur, leading to an increase in growth, which is not self-limiting (C), or, if the film material is volatile it may evaporate, thereby reducing the growth (D). However, as previously mentioned, a change in growth per cycle does not always accurately indicate whether or not true ALD is occurring, exemplified by the gradual loss of surface groups with increasing substrate temperature in Fig. 1b.

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Despite the low temperature requirement, it is a generalization that the lower the substrate temperature, the higher the concentration of impurities. Examples of possible impurities include hydroxyl and labile. It is also the oxidants that play an important role, particularly in terms of reactivity. Films of fair to good quality are possible at lower temperatures where more reactive precursors, such as ozone or an oxygen plasma, are employed. The high reactivity of the plasma is attributed to the fact that it contains reactive ionic and radical oxygen species, which makes it an appealing candidate for obtaining high purity films at temperatures as low as room temperature.20 For this reason, we have been investigating the potential of plasma-enhanced ALD as a route to Al2O3, TiO2, and Ta2O5 thin films at temperatures down to 25°C. This paper describes the work carried out, using a variety of metal precursors, and compare the results with thermal ALD processes from the literature.

Experimental

The experiments were carried out on three remote plasma ALD reactors. The home-built ALD-I reactor and the commercially built Oxford Instruments FlexAL reactor are described in detail elsewhere.22 The Oxford Instruments OpAL apparatus, an open-load system, was employed for the deposition of Al2O3 and operates in a similar manner to the FlexAL, although without a turbo pump. The base pressure was ~1 mTorr for the OpAL and ~10−3 mTorr for the ALD-I and FlexAL, and typical operating pressures were 100–200 mTorr for the plasma. 

1. M. C. M. van de Sanden, and W. M. M. Kessels *z
Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

z E-mail: s.e.potts@tue.nl; w.m.m.kessels@tue.nl

2. W. Keuning, E. Langereis, G. Dingemans, S. E. Potts, *, W. Keuning, E. Langereis, * G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels*z

S. E. Potts,* W. Keuning, E. Langereis,* G. Dingemans,
M. C. M. van de Sanden, and W. M. M. Kessels*z

* The Electrochemical Society Active Member.

4 E-mail: s.e.potts@tue.nl; w.m.m.kessels@tue.nl

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The plasma-enhanced ALD of Al₂O₃, TiO₂, and Ta₂O₅ has been investigated at substrate temperatures down to 25°C. Every process was routinely monitored using in situ SE to determine the film thickness. The slope of the resulting thickness vs ALD cycles plot gave the growth per cycle for the process (an example for the depositions at 100°C is shown in Fig. 2). All ALD processes showed linear growth at every deposition temperature reported in this paper (with the exception of the TiO₂ depositions from [Ti(O'Pr)₂] at substrate temperatures >250°C, with no significant nucleation delay.

### Aluminum oxide
Al₂O₃ has been a material of high interest with respect to ALD (see the review by Puurunen). However, it is relatively recently that low substrate temperatures have been investigated. The growths per cycle of two of the most-reported thermal processes are compared with the plasma-enhanced route in Fig. 3. We deposited Al₂O₃ using both the plasma-enhanced and thermal processes on an Oxford Instruments FlexAL reactor and OpAL reactor. The growth of the plasma-enhanced method showed a gradual decrease from 0.17 nm/cycle at 25°C to 0.11 nm/cycle at 300°C. The decrease was essentially linear, with the exception of the runs at 25 and 50°C, which were slightly higher. The corresponding thermal process showed a maximum value of 0.10 nm/cycle at 250°C. Our results for the thermal process differ from those of Groner et al., where the growth was higher at ~0.13 nm/cycle. These two thermal processes were carried out in different reactors and were clearly optimized at different temperatures (where the peak of the data is). A possible reason for such a difference in growth per cycle is the water dose. Increasing the water dose (i.e., the mass of water per unit time) leads to an increase in growth per cycle without affecting the film composition, as more surface hydroxyl groups are created with higher doses. So despite the difference in water dose time (20 ms for our work, 2 s for Groner et al.), it is likely that our water flow rate was lower, affording a lower growth per cycle, because the water on the OpAL reactor was actively cooled to 19°C to avoid overdosing. The reduction

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**Figure 1.** (Color online) A schematic representation of (a) an ideal ALD temperature window, where it is assumed that a sub-monolayer has been deposited per cycle and (b) a more commonly observed ALD window (especially for metal oxides), showing a slight reduction in growth per cycle with increasing temperature.
in growth per cycle for the thermal ALD process with decreasing temperature below the maximum value appears to be a result of insufficient thermal energy for the reaction between water and the methyl surface groups to occur as rapidly, resulting in fewer reactive hydroxyl surface groups with which \( [\text{Al}(\text{CH}_3)_3]_2 \) can react. Unlike water, the oxygen plasma is sufficiently reactive with the surface methyl groups down to room temperature, resulting in an almost linear decrease in growth per cycle from 25–300°C. At higher deposition temperatures for the thermal processes with water, the growth per cycle profile follows that of the plasma-enhanced process. The decrease in growth per cycle, as illustrated in Fig. 1b, is due to the gradual reduction of reactive surface groups, such as hydroxyls, with increasing deposition temperature.

Another important consideration is the oxidant purge time (Fig. 4). The post-plasma purge times required (0.5 s) were significantly lower than those required to purge water from the system in the thermal process (10 s for this work and 5–180 s for Groner et al.), which allows for a significantly reduced overall cycle time for the plasma-enhanced process. The thermal ALD process employing ozone as the oxidant reported by Kim et al. gave the lowest growth per cycle above 100°C (~0.09 nm/cycle). Ozone is more reactive than water toward the surface methyl groups, forming hydroxyl, methoxy, formate, and carbonate surface groups in the process. Therefore, Kim et al. suggested that the dramatic increase in growth per cycle observed at deposition temperatures below 100°C was attributed to the insufficient removal of the aforementioned oxygen-based surface groups in the steps subsequent to the oxidation because there was insufficient thermal energy with which to remove them. Also in this case, the ozone purge was kept constant at 3 s at 33–100°C, where a longer purge at lower temperatures may have helped to reduce the impurities. In comparison, our plasma-
enhanced route gave a more consistent growth per cycle profile down to 25°C and provided the highest growths per cycle over 50–300°C with the shortest cycle times.

In terms of film composition, the films deposited by both thermal and plasma-enhanced ALD in this work were over-stoichiometric at deposition temperatures below 200°C (Fig. 5a). The similar reduction in hydrogen content (Fig. 5b) with increasing substrate temperature suggests that this is due to the incorporation of hydroxyl groups in the film. In all cases, the carbon content was below the RBS detection limit (1 atom %); although thermal effusion measurements have suggested that a small quantity of carbon was present in the films deposited by this process. The mass density (Fig. 5c) was ~3.0 g cm⁻³ at deposition temperatures of 200°C and above for the plasma-enhanced process, which is close to the bulk value of Al₂O₃ (3.1 g cm⁻³). A gradual decrease was observed below 200°C to a minimum of 2.6 g cm⁻³ at 25°C. This decrease in mass density is likely to be the result of excess –OH in the film, which accounts for the higher than expected growths per cycle obtained below 100°C. The thermal water process showed no significant difference in terms of impurity content, and the mass density of the films over the temperature range was still within error, although slightly lower than that for the plasma-enhanced process. The thermal process with ozone gave over-stoichiometric films at all temperatures up to 300°C with up to 5 atom % carbon contamination.

The growth per cycle profiles are apparently all different, which, in part is caused by the varying mass densities. However, determination of the number of (metal) atoms deposited per cycle, obtained by dividing the atom density from RBS by the total number of ALD cycles, can show if this is the case. For example, if the number of atoms deposited per cycle does not vary significantly over a temperature range, any variation in growth per cycle is most likely due to the variation in mass density; however, if there is a difference in atoms deposited, other factors, such as chemical vapor deposition (CVD) or surface group loss, may be occurring. Figure 6 shows the growth per cycle data for the plasma-enhanced and thermal processes on both the FlexAL and OpAL reactors and the number of Al atoms deposited per cm² in a cycle. In terms of films deposited by plasma-enhanced ALD, there is no significant difference between the growths per cycle from either reactor; but for the thermal process, more atoms appear to have been deposited by the OpAL reactor. The OpAL reactor is not equipped with a turbo pump or load lock, so it may not be able to purge the water away as effectively as in the FlexAL reactor and the chamber vacuum has to be disrupted for sample loading. However, a greater difference in mass density would be expected for such a difference in Al atoms deposited per cycle where the growth per cycle remains the same. There is a clear gradient for Al atoms deposited per cycle with the plasma-enhanced process, showing the effect of dehydroxylation (loss of surface groups) with increasing substrate temperature. A similar gradient was observed for the growth per cycle, although this is enhanced at 25 and 50°C as a result of the decreased film density and increased OH concentration (as shown in Fig. 5). For the thermal processes, the effect of lower temperatures is clear; with the number of Al atoms deposited being half of that of the plasma-enhanced process at 100°C, suggesting that the rate of reaction is lower at these temperatures. The temperature at which the thermal process was optimized (i.e., the saturation of each ALD step was determined, which was
Carbon was not detected in the films (RBS detection limit = 1 atom %). Analysis of the Al atoms deposited per cycle showed that the temperature window could easily be extended down to room temperature with fixed cycle settings for the plasma-enhanced ALD of Al₂O₃. For the thermal process, temperatures lower than the optimization temperature could be considered outside the temperature window; however, if saturation curves were determined for each deposition temperature and the water flow rate were increased, this could be overcome.

**Titanium dioxide.**—TiO₂ is a well-studied ALD material, and a selection of the low temperature ALD studies is summarized in Fig. 7. For the plasma-enhanced ALD of TiO₂, we employed [Ti(OPr)₃], [Ti(Cp⁵Me)₃(OPr)₃], and [TiCp⁴(OMe)₃] as precursors. The heteroleptic mono Cp-based alkoxides are not sufficiently reactive with water during ALD, but they are reactive with ozone and an oxygen plasma. The growths per cycle for our plasma-enhanced processes were 0.05–0.06 nm/cycle, over the deposition temperature range 100–250°C. The growths per cycle using [Ti(Cp⁵Me)(OPr)₃] were slightly higher than those of the other two Ti precursors, as more Ti atoms were deposited per cycle for this precursor (Fig. 8a). Again, a gradual decrease in growth per cycle was observed with increasing substrate temperature for all of the Ti precursors, which can be attributed to increasing mass density. The loss of surface groups is not likely to be a significant factor for the Cp-based precursors, as the Ti atoms deposited per cycle were constant over the temperature range. At 25°C, the growth per cycle obtained using [Ti(OPr)₃] was higher than the expected trend, which is a result of the excess OH groups in the film, as for the Al₂O₃ films (Fig. 8b-d). All precursors gave significantly higher growths per cycle in the plasma-enhanced ALD process than for those obtained for the thermal routes using [Ti(OPr)₃] and water, as reported by Ritala et al. and Rahtu and Ritala, and [TiCp⁴(OMe)₃] and ozone, as reported by Katamreddy et al. This shows the benefits of the high reactivity of the plasma: although it is somewhat surprising that ozone, itself a highly reactive gas, could not allow for a higher growth per cycle. The growths per cycle of the TiCl₄ and water process were extended down to 100°C by Aarik et al. The data were more comparable to the plasma-enhanced ALD at substrate temperatures around 150°C because TiCl₄ is more reactive toward surface groups than [Ti(OPr)₃] (see Fig. 7). The lower data points for the TiCl₄/water process at 150 and 175°C were reported to be the result of etching of the film by HCl formed during the ALD process at these temperatures. The increase in growth per cycle at higher temperatures for the TiCl₄/H₂O process was attributed to the crystallization of the films, and below 150°C the increase was due to the condensation of water on the substrate, leading to a dramatic increase in surface hydroxyl groups. The presence of such additional surface groups at low temperatures was less prominent for the plasma-enhanced ALD using [Ti(OPr)₃], [Ti(Cp⁵Me)(OPr)₃], and [TiCp⁴(OMe)₃].
more Ti atoms per cycle and afforded a higher growth per cycle, when compared with [TiCp(OMe)3]. In addition to the experimental inaccuracy of RBS, the [Ti(OPr)3]3 was not so straightforward, as there is no real, clear-cut linear trend. The rise in Ti atoms deposited at 300°C can be attributed to the decomposition (CVD) of the precursor, as a significant amount of carbon (~17 atom %) was present in films deposited at that temperature. For depositions using [Ti(OPr)3]3 at temperatures ≥250°C, crystallization was observed in the anatase form, resulting in higher growths per cycle.28 At 250 and 300°C, the growth began in the amorphous phase at a lower growth per cycle, after which anatase TiO2 was deposited at a much higher rate. The transitions were observed between 400–700 cycles at 250°C and above 200 cycles at 300°C. Where [TiCp3(OMe)3] was the precursor, anatase TiO2 was also observed at substrate temperatures ≥250°C, but this did not seem to have such a dramatic effect on the growth per cycle, suggesting that the CpMe group inhibits the anatase formation to some extent.

In terms of film composition, films deposited by plasma-enhanced ALD from all of our Ti precursors gave stoichiometric TiO2 at 50°C and above (Fig. 8b). The film from [Ti(OPr)3]3 at 25°C was over-stoichiometric, which, as with the [Al(CH3)3]/water process, is the result of the incorporation of hydroxyl groups in the film, evident by the 8 atom % hydrogen present (Fig. 8c) and the lower mass density of the film (Fig. 8d). At other temperatures, the carbon and hydrogen concentrations were below their detection limits for RBS and ERD (1 and 5 atom %, respectively) where [Ti(OPr)3]3 was the precursor. The stoichiometry of the films deposited by [TiCp3(OMe)3] and [TiCp3(OMe)3] were the same as those obtained using [Ti(OPr)3]3 (and so the data overlap in Fig. 8b), and no carbon was detected at any temperature for the Cp-based precursors. Hydrogen was detected in the films from [TiCp3(OMe)3] (2–3 atom %), and similar quantities are possibly present in the films from the other two precursors, as the detection limit in those experiments was higher. As such, it is difficult to directly compare the hydrogen content of our films with those of Ritala et al.,35 as they reported a hydrogen content of ~0.3 atom % (measured using nuclear reaction analysis with a 15N2+ beam), which is below the lowest detection limit (1 atom %) for ERD in our experiments. The films grown from TiCl4 and water at 100°C were also stoichiometric but contained 1.2 atom % chlorine, which can lead to films with a high surface roughness, due to the aforementioned etching.41 In terms of mass density (Fig. 8d), the films deposited by all precursors had densities over the range 3.6–4.2 g cm−3, which is comparable to the bulk density of anatase TiO2 (3.9 g cm−3). The films from [Ti(OPr)3]3 had the most variation in density owing to the larger experimental inaccuracy in the RBS experiments. The low density at 25°C was a result of –OH incorporation as mentioned previously, whereas the higher density of 4.18 g cm−3 at 300°C is likely to be a result of the crystallization. For the noncrystalline films below 200°C, the high density is a feature of the plasma-enhanced ALD method.

The plasma-enhanced ALD processes TiO2 using [Ti(OPr)3]3, [TiCpMe3(OMe)3], and [TiCp3(OMe)3] afford higher growths per cycle compared with the [Ti(OPr)3]3 and water process. They were preferable to the TiCl4/H2O process, in that the possibility of the films containing chlorine is negligible. The films grown in this study were consistently stoichiometric down to 50°C.

**Tantalum oxide.**—Ta2O5 is another thoroughly studied ALD material, particularly via thermal routes using halide-10,24,25 alkoxide-19 and amide-based25,26 precursors. However, films grown at <150°C are not so commonly known. We recently reported the low temperature plasma-enhanced ALD of Ta2O5 using [Ta(NMe2)5] on the ALD-1 reactor,27 which gave a growth of ~0.08 nm/cycle over the temperature range 100–225°C (Fig. 9), which is comparable to the TaCl5/water process above 100°C.25 All films were stoichiometric Ta2O5 with a [O]/[Ta] ratio of 2.5 and
contained hydrogen (Fig. 10c). No nitrogen or carbon was detected. The mass density varied from 7.8 g cm\(^{-3}\) at 100°C to 8.1 g cm\(^{-3}\) at 225°C, which is comparable to the bulk density value of Ta\(_2\)O\(_5\) (8.24 g cm\(^{-3}\)).

Maeng et al. previously carried out a comparison of the thermal and plasma-enhanced ALD of Ta\(_2\)O\(_5\) from Ta\(_5\)NMe\(_2\) using water and an oxygen plasma, respectively. The thermal process afforded comparable growths, ~0.085 nm/cycle, to those obtained in our plasma-enhanced process at 200–300°C (Fig. 9). The growths per cycle for the thermal process increased at both the higher and lower substrate temperatures due to precursor decomposition and condensation of water, respectively. The plasma-enhanced ALD of Ta\(_2\)O\(_5\) using Ta\(_5\)NMe\(_2\)/water process gave much higher growths per cycle of 0.12 nm. These films had a O/Ta ratio of 2.6, and no nitrogen or carbon incorporation was reported. The mass density reported, 7.75 g cm\(^{-3}\) (94% of the bulk value of Ta\(_2\)O\(_5\) although the precise substrate temperatures were not reported), was slightly lower than our previously reported values, but this difference cannot be the reason for such a significant difference in growth. It may be a result of the use of different ALD equipment, where the design of the reactor may affect the way in which precursors are introduced to the substrate.

To investigate the use of different reactors, the Ta\(_5\)NMe\(_2\)/water process was transferred to from the ALD-I to the FlexAL reactor, extending the investigation down to 25°C. The increase in growth per cycle at temperatures below 100°C was significant, which was again a result of the low mass density of the film as the number of Ta atoms deposited did not change dramatically over the temperature range (Fig. 10a and d). At 250°C, there was also an increase in growth per cycle, due to the decomposition of the TaCl\(_5\)/water process, although the [Ta(NMe\(_2\))\(_5\)]/water process gave similar growths per cycle.

Despite the similarity in the numbers of atoms being deposited per cycle between the ALD-I and FlexAL reactors, the film compo-
sitions were different (Fig. 10b-d). The films deposited on the ALD-I reactor had a density close to that of the bulk, were stoichiometric Ta2O5, and contained very low concentrations of hydrogen. At 50 and 100°C on the FlexAL reactor, the films were overstoichiometric with an excess of oxygen (Fig. 10b). The films also contained significant concentrations of hydrogen (up to 35 atom %), which are very high when compared with the Al2O3, TiO2, and other Ta2O5 processes. However, in common with these processes, the hydrogen concentration decreased with increasing substrate temperature. It is likely that there is a significant presence of OH groups in the film; therefore, it might just be coincidence that the film at 25°C was stoichiometric, as there was a significant presence of hydrogen and oxygen in that film. Carbon and nitrogen were not detected at any temperature (RBS detection limit = 5 atom % in each case). There was a positive correlation between substrate temperature and film density (Fig. 10d), but the densities were much lower than expected for a good ALD film, less than half the bulk value below 50°C. This is in contrast to the 94% of the bulk value reported by Maeng et al., despite similar growths per cycle, probably due to the excess of hydroxyl groups. Why the film densities were low and hydroxyl groups were present in such high quantities is not clear. Why the film densities were low and hydroxyl groups were present in such high quantities and why the mass densities were so low, is still unclear. The differences observed between the two reactors could be a result of the composition of the plasmas used, which interact with the NMe2 ligands in different ways. However, such a difference in growth per cycle and film density has not been observed for other processes. A possible reason is that the ion flux and ion energies in the ALD-I system are generally higher than in the FlexAL reactor. The plasma composition in all reactors and the effects on film growth are currently under investigation.

Conclusions

We have deposited Al2O3, TiO2, and Ta2O5 thin films using plasma-enhanced ALD and addressed the ability of plasma-enhanced ALD to deposit metal oxide thin films at temperatures as low as room temperature. Analysis of the metal atoms deposited per cycle aids in the clarification of where the boundaries of the temperature window lie as it is not affected by variations in film density.

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