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Citation for published version (APA):

DOI:
10.1149/1.2737629

Document status and date:
Published: 01/01/2007

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Download date: 04. Oct. 2019
PLASMA AND THERMAL ALD OF A12O3 IN A COMMERCIAL 200 MM ALD REACTOR

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The deposition of A12O3 by remote plasma atomic layer deposition (ALD) in the Oxford Instruments FlexAL reactor was studied and compared with results from thermal ALD in the same reactor. Trimethylaluminum [A1(CH3)3] was used as the metal precursor and O2 plasma and H2O were used as oxidizing agents for the plasma and thermal processes, respectively. For remote plasma ALD with a total cycle time of 4 s, the growth per cycle decreased monotonically with substrate temperature, from 1.7 A/cycle at 25°C to 1.0 A/cycle at 300°C. This growth per cycle was consistently higher than that obtained for thermal ALD. For the latter a maximum growth per cycle of ~1.0 A/cycle was found at 200°C. The film properties investigated were nearly independent of oxidant source for temperatures between 100 and 300°C, with a slightly higher mass density for the remote plasma ALD A12O3 compared with 2.0–2.5 g/cm3 as-deposited and forming gas annealed A12O3, respectively.

To widen the ALD process window, O2 plasmas have recently been considered as alternative oxidants. Particularly O2 plasmas are very effective oxidants that can easily remove organic ligands by O-radical-driven combustion-like surface reactions. Therefore, the plasma-based process generally yields more process flexibility, including the potential of depositing higher quality materials at lower substrate temperatures while also avoiding the use of the difficult-to-purge H2O. The plasma-assisted processes can be divided in three categories: (i) direct plasma ALD where the substrates are positioned on an electrode used for plasma creation, (ii) remote plasma ALD, where plasma creation takes place remotely from the substrate but with all plasma species still present at the position of the substrate, and (iii) radical-enhanced ALD where the plasma is created far from the substrate such that ions and electrons from the plasma do not reach the substrate at all. Direct plasma ALD plasma damage can occur due to high ion energies, while for radical-enhanced ALD ion damage is completely absent at the cost of a lower reactivity due to reduced fluxes of reactive species. Remote plasma ALD combines high reactivity with a low ion energy, typically below the threshold energy for plasma damage.

Experimental

ALD reactor and film synthesis.— Both the remote plasma and thermal ALD of A12O3 was carried out in the FlexAL ALD tool recently developed by Oxford Instruments Plasma Technology. The
system, described extensively in Ref. 23, is an advanced research and development reactor equipped with a loadlock and capable of handling wafers up to 200 mm in diameter. For remote plasma ALD the system is equipped with an inductively coupled plasma source located above the wafer. It can be isolated from the reactor by a gate valve. The plasma source can be operated with various gases or gas mixtures. Multiple precursor pods can be connected to the reactor such that several precursors are available simultaneously. The temperature of the precursor pods, the precursor lines, reactor walls, and substrate holder can be individually controlled. Furthermore, the system is equipped with optical viewports that can be used for in situ monitoring of film growth. Especially the techniques of in situ spectroscopic ellipsometry (SE) have proven to be particularly powerful to study ALD processes and the material properties obtained.24,25

For Al₂O₃ ALD, trimethylaluminum [TMA,Al(CH₃)₃] [Akzo-Nobel, SSG grade] was vaporized at 25°C and a saturated dose was obtained by 20 ms vapor injection using fast switching ALD valves. For the plasma process, the oxidation step took place via a 400 W O₂ plasma at a pressure of 15 mTorr and ignited for a duration of typically 2 s. O₂ also served as a purge gas because O₂ does not react with Al(CH₃)₃.24 The O₂ flow was kept constant at 60 sccm during the entire cycle. A cycle time of 4 s was obtained by employing an Al(CH₃)₃ purge of 1.5 s and a post-plasma-purge of 0.5 s. For thermal ALD, H₂O was vaporized at 25°C and dosed in steps of at maximum 120 ms. If higher doses were required the 120 ms step was repeated with 0.5 s intermediate delays. A 110 sccm Ar flow at a pressure of 15 mTorr was used as purge gas and a pump-purge step (7 s evacuation and 5 s purging) was found most effective in removing residual H₂O from the reactor. Typical cycle times for the thermal ALD process were 16 s but it should be noted that no efforts were undertaken to optimize this cycle time. This can for example be done by increasing the residence time during water exposure and operating at higher pressure. The substrate temperature was varied between 25 and 300°C for remote plasma ALD. The lowest substrate temperature used for the thermal ALD process was 100°C to avoid extensive purge times necessary to remove H₂O at low temperatures.26 The reactor wall temperature was kept constant at 120°C, except for the remote plasma depositions at 25°C for which the wall was also kept at 25°C.

**Film analysis and characterization.**—Si p-type wafers with diameters up to 200 mm were used as substrates for characterization of the ALD process and film composition. The center thickness and refractive index of the Al₂O₃ films were monitored in situ by spectroscopic ellipsometry (SE) measurements (J.A. Woollam M-2000D, 193–1000 nm wavelength range) carried out between the ALD cycles. Ex situ measurements with the same ellipsometer were performed to measure the film thickness on any position of the wafer to obtain the nonuniformity of the films as defined by

\[
\text{nonuniformity} = \frac{d_{\text{max}} - d_{\text{min}}}{2d_{\text{average}}} \quad [1]
\]

where \(d_{\text{max}}\), \(d_{\text{min}}\), and \(d_{\text{average}}\) are the maximum, minimum, and average thickness, respectively. The Al, O, and C-content of the film were determined by Rutherford backscattering spectrometry (RBS). Elastic recoil detection (ERD) was used to determine the H-content. A 2 MeV \(^{4}\)He beam was applied in these measurements. The conformality of the remote plasma ALD process was examined for an 80 nm thick Al₂O₃ film deposited in 2–2.5 µm wide and \(\sim 19 \mu m\) deep silicon macropore structures. After sputtering a 2 nm platinum conductive layer for imaging purposes, high-resolution scanning electron microscopy (SEM) images using a FEI Nova NanoSEM 600 electron microscope revealed the conformality. For electrical characterization of the Al₂O₃ films, the Si substrates were HF-dipped (1% HF solution) prior to deposition to remove the native oxide. Aluminum electrodes (areas ranging from 0.02 to 1.2 mm²) were sputtered on the Al₂O₃ films using a shadow mask.

![Figure 1. (Color online) Al₂O₃ film thickness as a function of the number of cycles for both remote plasma ALD and thermal ALD. The thickness was determined by in situ spectroscopic ellipsometry and the growth per cycle was obtained from the linear fits shown in the figure. The substrate temperature was 200°C.

Both as-deposited and forming gas annealed films (30 min 425°C, 10% H₂–90% N₂) were characterized electrically. The dielectric constant and breakdown voltage of these test structures were determined by 10 kHz capacitance-voltage (C-V) and current-voltage (I-V) measurements with an HP4275A multifrequency LCR meter and an Agilent 4155B parameter analyzer.

**Results and Discussion**

**Growth per cycle and saturation behavior.**—Figure 1 shows an in situ SE measurement of the Al₂O₃ film thickness as a function of the completed number of ALD cycles for both the remote plasma and the thermal ALD process. The substrate temperature was 200°C. As expected, the thickness increases linearly with the number of completed ALD cycles for both the remote plasma and the thermal ALD process. From these in situ thickness measurements the growth per cycle (GPC) can be determined from a linear fit of the data. Clearly, the growth per cycle is higher for remote plasma ALD than for thermal ALD, i.e., 1.2 Å/cycle for remote plasma ALD and 1.0 Å/cycle for thermal ALD.

The saturation behavior of the oxidation step was investigated for the remote plasma and thermal ALD by considering the GPC as a function of the O₂ plasma exposure time and H₂O dosing time. For remote plasma ALD, the results are shown in Fig. 2 for a substrate temperature of 200°C. The corresponding nonuniformity of the film thickness over a 150 mm wafer is also given. Figure 2 reveals that surface reactions saturate during the oxidation step when the O₂ plasma exposure time is greater than 1.0 s, with a saturated value of the GPC of 1.2 Å/cycle. For shorter plasma exposure times, the GPC is not saturated and the plasma step becomes a source of film nonuniformity. This can be explained by a shortage of oxidizing plasma species at these short plasma exposure times. In this subsaturated regime the growth rate is slightly higher in the center where the flux of plasma species is greatest. Note that if the surface reaction kinetics were slow, the flux of plasma species would be more isotropic within the reactor and a good uniformity would also be achieved at plasma exposure times shorter than required for saturation. For a plasma exposure of 2 s the growth per cycle was found to saturate over the whole substrate area for all substrate temperatures investigated between 25 and 300°C. The nonuniformity determined over 200 mm wafers decreased from 1.2% at 25°C to 0.5% at 300°C for this setting.

Figure 3 shows the GPC for the thermal process as a function of H₂O dosing time for substrate temperatures of 100 and 200°C. Different pump and purge steps have been used for the different data points shown in Fig. 3, which can explain the scatter between data points. Note that the H₂O dosing time required to obtain saturation...
is significantly longer than the Al(CH₃)₃ dosing time of 20 ms, even though the delivery details and vapor pressure are similar for both H₂O and Al(CH₃)₃ [saturated vapor pressure of H₂O and Al(CH₃)₃ are ~24 and ~16 Torr at 25°C, respectively]. The relatively long time required to achieve saturation of the surface reactions is probably due to slow kinetics of the H₂O half reaction, which also explains the excellent uniformity of the thermal ALD process under all conditions studied. The nonuniformities were <1% as determined over 200 mm wafers. In addition, for shorter cycle times with reduced purging (and pumping) using high H₂O dosing times (>240 ms), a slightly decreased GPC was observed using the same Al(CH₃)₃ dose. Generally, one expects an increase in growth per cycle due to parasitic chemical vapor deposition (CVD) reactions when there is residual H₂O during Al(CH₃)₃ dosing. Yet, it is also possible that some Al(CH₃)₃ is consumed by parasitic CVD, at spots within the reactor that are more difficult to purge. In the remainder of this work a typical H₂O dosing time of 240 ms was used in the thermal ALD process of Al₂O₃. Under this condition, the GPC appears to be saturated while it also prevents the need for the very long purge times required when using longer H₂O dosing times.

Figure 2 shows the GPC of the remote plasma ALD process measured as a function of substrate temperature between 25 and 300°C. For remote plasma ALD, the GPC decreases monotonically with increasing substrate temperature from 1.7 Å/cycle at 25°C to 1.0 Å/cycle at 300°C. This agrees well with values obtained in our home-built remote plasma reactor as reported previously. Studies using direct plasma ALD report GPCs that are slightly higher than reported here, i.e., 1.75 Å/cycle at 100°C down to 1.0 Å/cycle at 350°C. Remarkably, the GPC values reported for radical assisted ALD of Al₂O₃ were as high as 3.2 Å/cycle. For thermal ALD the GPC is 1.0 and 0.9 Å/cycle for 200 and 300°C, respectively, which corresponds well to the literature values within the error margins. For temperatures lower than 200°C, there is some scatter in the literature values and our GPC of 0.8 Å/cycle at 100°C is for example relatively low compared to the maximum value of 1.3 Å/cycle reported by Groner et al. Although not apparent from Fig. 3, we found that it was difficult to reach saturation for the H₂O dose at 100°C. This difficulty might explain relatively low GPC at 100°C found in this study and might also explain the relatively wide spread in the literature values.

The decrease of the GPC of Al₂O₃ at increasing substrate temperatures for remote plasma and thermal ALD (for substrate temperatures > 200°C) is in line with observations reported in the literature for thermal ALD and plasma assisted ALD. This decrease is generally attributed to thermally activated recombination reactions of surface hydroxyl groups (-OH), the so-called dehydroxylation. Assuming that the reactive Al₂O₃ surface sites created during O₂ plasma exposure are also hydroxyl groups, these dehydroxylation reactions can also explain the decrease of the GPC for the remote plasma ALD case. Furthermore, note that the GPC for the remote plasma ALD process exceeded in all cases the GPC for thermal ALD. Especially at lower temperatures, this effect becomes very apparent. A similar result was reported by Lim et al., who compared direct plasma ALD with thermal ALD of Al₂O₃. It appears that the O₂ plasma is more effective as oxidant than H₂O, especially at low substrate temperatures. At higher temperatures the discrepancy becomes relatively small. This suggests that the GPC becomes dictated by the stability of the hydroxyl groups at the surface at these temperatures.

Film composition.—Figure 5 shows the RBS and ERD results for the remote plasma and thermal ALD films. The mass density, depicted in Fig. 5a was calculated from the atomic areal densities and the film thickness determined by SE. The mass density for remote plasma ALD increases from 2.6 ± 0.1 g cm⁻³ at 25°C to 3.0 ± 0.1 g cm⁻³ for temperatures higher than 200°C. The densities obtained with thermal ALD were comparable but always slightly lower than the remote plasma ALD values. Figure 5b shows that the ratio of oxygen to aluminum [O]/[Al] in the Al₂O₃ films were very similar for the remote plasma ALD and thermal ALD process. Films deposited at temperatures of 200°C and higher were stoichiometric ([O]/[Al] = 1.5) whereas the films were oxy-
Figure 5. (Color online) Material composition as a function of substrate temperature. (a) Mass density as determined from RBS and ellipsometry. (b) \([\text{O}]/[\text{Al}]\) ratio as determined from RBS. (c) H content as determined by elastic recoil detection. For the deposition at 25°C, data is given for both the standard recipe (4 s cycle time, 2 s plasma exposure) and for extended plasma exposure (6 s cycle time, 4 s plasma exposure).

gen rich at lower temperatures. At 25°C the \([\text{O}]/[\text{Al}]\) ratio was even \(-2.15\). Figure 5c shows that the H-content in the film also increased at lower substrate temperatures. At 300°C the H-content was \(<1\) atom % while a value over 15 atom % was reached at 25°C. Although within the absolute accuracy of the data, from a relative comparison it can be concluded that the H-content was slightly higher in the thermal ALD \(\text{Al}_2\text{O}_3\) films. This observation is consistent with the slightly lower mass density of these films. The fact that the films increase in O and H-content at low temperatures suggests that a significant amount of hydroxyl groups are incorporated into the film at these temperatures. This is observed by the \(-\text{OH}\) stretch vibrations observed by infrared transmission spectroscopy in films deposited at 25°C.\(^{10}\) The C-content was below the RBS detection limit of \(-1\) atom % in all cases, with the exception of the film deposited by remote plasma ALD at 25°C which contained 5 atom % carbon. Upon doubling the plasma exposure time from 2 to 4 s for this temperature, the C-content decreased below the detection limit and the film became more stoichiometric (i.e., \([\text{O}]/[\text{Al}] = 1.88\) and slightly denser (i.e., 2.7 ± 0.1 g cm\(^{-3}\)), as also shown in Fig. 5.

The results reported here show good agreement with the properties of the \(\text{Al}_2\text{O}_3\) films obtained in our home-built remote plasma ALD reactor under saturated conditions.\(^{27}\) Compositional data on radical-enhanced ALD yielded also similar trends but the films were more oxygen rich (\([\text{O}]/[\text{Al}] = 1.81\) at 100°C) and contained also more carbon, (2.3 atom % at 100°C).\(^{17}\) Other studies on plasma assisted ALD of \(\text{Al}_2\text{O}_3\) did not focus on film composition. For thermal ALD, the densities of the \(\text{Al}_2\text{O}_3\) films agree with values obtained by Groner et al.,\(^{28}\) however the H content found in the present study is somewhat lower (7.9 atom % instead of 14 atom % at 100°C). Furthermore, the refractive index of 1.64 ± 0.02 that we found for films deposited at temperatures higher than 100°C by spectroscopic ellipsometry agrees well with other thermal ALD studies.\(^{27,28}\) From the aforementioned results, it can be concluded that the remote plasma process yields higher growth per cycle values at reduced cycle times than thermal ALD. The material properties of remote plasma are very similar and at least as good as that of thermal ALD for substrate temperatures beyond 100°C. For low substrate temperatures, the discrepancy between remote plasma ALD and thermal ALD becomes more apparent. At low temperatures, remote plasma ALD provides the option to deposit \(\text{Al}_2\text{O}_3\) with fair to good material properties at high growth rates, i.e., with a high growth per cycle and short cycle times.

Conformality and electrical properties.— For the application of the \(\text{Al}_2\text{O}_3\) films as dielectric material in demanding three-dimensional topologies, both the electrical properties and the conformality of the films deposited in high-aspect ratio structures are important. Figure 6 shows a high-resolution SEM image of a remote plasma \(\text{Al}_2\text{O}_3\)-film deposited in 700 cycles at a substrate temperature of 200°C in a macropore structure with an aspect ratio of \(\sim 8:1\). Arrays of such macropores are used for the synthesis of metal oxide semiconductor (MOS) “trench” capacitors that serve as rf decoupling capacitors integrated in silicon.\(^{19}\) The thickness of the film measured with spectroscopic ellipsometry on the top surface of the wafer was 83 nm. The thicknesses measured with high-resolution SEM at the bottom and sidewall of the macropores was 80 ± 3 nm. The remote plasma is therefore able to deposit highly conformal films in these high aspect ratio structures. Recombination losses of reactive oxygen species such as O-radicals are apparently not significant under the present conditions. This can be understood from the low surface recombination coefficient of O-radicals on oxide surfaces.\(^{17}\)

Preliminary results of the electrical characterization of \(\text{Al}_2\text{O}_3\) films deposited by remote plasma ALD on planar substrates at a substrate temperature of 200°C are shown in Fig. 7. In this figure, the equivalent oxide thickness (EOT) values calculated from the
Figure 7. (Color online) EOT vs physical thickness of Al$_2$O$_3$ films deposited at 200°C by remote plasma ALD. Results for both the as-deposited and the annealed (425°C, forming gas) material are shown.

C-V measurements are shown as a function of the physical Al$_2$O$_3$ film thickness $d$. The EOT increases linearly with the Al$_2$O$_3$-film thickness for both the as-deposited films and for the films which were forming gas annealed at 425°C. Using the expression

$$EOT = \frac{e_d(SiO_2)}{C/A} = \frac{k(SiO_2)}{k(Al_2O_3)} d(Al_2O_3) + d(SiO_2)$$

[2]

where $C/A$ is the measured capacity density and $e_d$ is the vacuum permittivity, the dielectric constant can be determined as $k = 7.8$ and $k = 8.9$ for the as-deposited and annealed Al$_2$O$_3$, respectively. The offset of the linear fit can be most probably attributed to the presence of an interfacial SiO$_2$ layer. Other ALD studies also reported on such an interfacial layer$^{13}$ and we found a 1.2 nm thick SiO$_2$ interfacial layer for Al$_2$O$_3$ deposited in our home-built remote plasma ALD reactor.$^{10}$ Investigation of the formation of this interfacial oxide layer is outside the scope of the present study and no effort was undertaken to minimize its thickness. Furthermore, the breakdown voltage was investigated by current density measurements using the same samples. The catastrophic breakdown field, defined as the field where the current reaches the compliance setting (i.e., 100 mA) of the parameter analyzer, was determined to be 9.7 ± 0.5 MV/cm for as-deposited films and 8.4 ± 0.5 MV/cm for the postdeposition annealed films. The dielectric constants obtained for thermal ALD of Al$_2$O$_3$ have been summarized by Groner et al.$^{32}$ For deposition temperatures below 300°C, the dielectric constants reported were 7.6 or lower. The breakdown field reported here is relatively high but cannot easily be compared to values reported in the literature due to the use of different definitions for breakdown. Although these results are promising, more investigations are required to get full insight into the electrical properties of the Al$_2$O$_3$, also under other operating conditions.

Conclusions

The remote plasma ALD process of Al$_2$O$_3$ from Al(CH$_3$)$_3$ and O$_2$ plasma was characterized and compared to the well-established thermal ALD process of Al$_2$O$_3$ employing H$_2$O as the oxidant. This comparison was carried out for films deposited in the same commercial 200 mm reactor. The growth per cycle, saturation of the surface reactions, and material properties were investigated for substrate temperatures between 25 and 300°C. It was demonstrated that uniform high-quality films can be obtained for substrate temperatures above 100°C. For these temperatures, the mass densities of the remote plasma ALD films are slightly higher than those of the thermally deposited films. Remote plasma ALD also yields fair material properties below 100°C at a relatively high growth per cycle and short cycle times. Conformal films in high-aspect ratio structures were achieved using remote plasma ALD and preliminary results on electrical characterization reveal that the Al$_2$O$_3$ show good dielectric performance.

Acknowledgments

The authors thank G. Nieuwland and T. Dao of Philips Research for the high-resolution SEM and RBS measurements, respectively. The skillful technical assistance of J.J.A. Zeebregts and M.J.F. van der Sande is acknowledged. This work has been supported by the Dutch Technology Foundation STW and by SenterNovem, an agency of the Netherlands Ministry of Economic Affairs ("Innovia" project IS 040401). The research of W.M.M.K. was made possible by a fellowship from the Royal Netherlands Academy of Arts and Sciences.

Eindhoven University of Technology in meeting the publication costs of this article.

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