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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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Plasma and Thermal ALD of Al₂O₃ in a Commercial 200 mm ALD Reactor

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The deposition of Al₂O₃ 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. Trimethylaluminium [Al(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 Å/cycle at 25°C to 1.0 Å/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 Å/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 Al₂O₃ films. Films deposited at 200 and 300°C were stoichiometric with a mass density of 3.0 g/cm³ and low C (~1 atom %) and H (~3 atom %) contents. At lower substrate temperatures, oxygen-rich films were obtained with a lower mass density and higher H-content. Remote plasma ALD produced uniform Al₂O₃ films with nonuniformities of less than ±2% over 200 mm diam substrates. Excellent conformity was obtained for films deposited in macro pores with an aspect ratio of ~8 (2.0–2.5 μm diam). Preliminary results on electrical properties of remote plasma deposited films showed high dielectric constants of 7.8 and 8.9 for as-deposited and forming gas annealed Al₂O₃, respectively.

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Manuscript submitted February 2, 2007; revised manuscript received March 5, 2007. Available electronically May 21, 2007.
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)3.15 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

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

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 \(^{4}\text{He}\) beam was applied in these measurements. The conformity of the remote plasma ALD process was examined for an 80 nm thick Al2O3 film deposited in 2–2.5 μm wide and ~19 μm deep silicon macropore structures. After sputtering a 2 mm platinum conductive layer for imaging purposes, high-resolution scanning electron microscopy (SEM) images using a FEI Nova NanoSEM 600 electron microscope revealed the conformity. 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 mm\(^2\)) were sputtered on the Al2O3 films using a shadow mask.

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 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.

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(CH$_3$)$_3$ dosing time of 20 ms, even though the delivery details and vapor pressure are similar for both H$_2$O and Al(CH$_3$)$_3$ [saturated vapor pressure of H$_2$O and Al(CH$_3$)$_3$ are $\sim$24 and $\sim$16 Torr at 25°C, respectively]. The relatively long time required to achieve saturation of the surface reactions is probably due to slow kinetics of the H$_2$O half reaction, which also explains the excellent uniformity of the thermal ALD process under all conditions studied. The nonuniformities were $<$1% as determined over 200 mm wafers. In addition, for shorter cycle times with reduced purging (and pumping) using high H$_2$O dosing times ($>$240 ms), a slightly decreased GPC was observed using the same Al(CH$_3$)$_3$ dose. Generally, one expects an increase in growth per cycle due to parasitic chemical vapor deposition (CVD) reactions when there is residual H$_2$O during Al(CH$_3$)$_3$ dosing. Yet, it is also possible that some Al(CH$_3$)$_3$ is consumed by parasitic CVD, at spots within the reactor that are more difficult to purge. In the remainder of this work a typical H$_2$O dosing time of 240 ms was used in the thermal ALD process of Al$_2$O$_3$. 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 H$_2$O dosing times.

Figure 4 shows the GPC of the remote plasma ALD process measured as a function of substrate temperature between 25 and 300°C. Data are also given for thermal ALD for substrate temperatures of 100, 200, 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 Al$_2$O$_3$ 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 H$_2$O 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 Al$_2$O$_3$, at increasing substrate temperature for remote plasma and thermal ALD (for substrate temperatures $>$200°C) is in line with observations reported in the literature for thermal ALD and plasma assisted ALD. This decrease is generally attributed to thermally activated recombination reactions of surface hydroxyl groups (–OH), the so-called dehydroxylation. Assuming that the reactive Al$_2$O$_3$ surface sites created during O$_2$ 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 Al$_2$O$_3$. It appears that the O$_2$ plasma is more effective as oxidant than H$_2$O, 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 Al$_2$O$_3$ 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-
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., \( \frac{[O]}{[Al]} = 1.88 \)) and slightly denser (i.e., \( 2.7 \pm 0.1 \) g cm\(^{-3} \)), as also shown in Fig. 5.

The results reported here show good agreement with the properties of the Al\(_2\)O\(_3\) films obtained in our home-built remote plasma ALD reactor under saturated conditions.\(^{16}\) Compositional data on radical-enhanced ALD yielded also similar trends but the films were more oxygen rich (\( \frac{[O]}{[Al]} = 1.81 \) at 100°C) and contained also more carbon, (2.3 atom % at 100°C).\(^{17}\) Other studies on plasma assisted ALD of Al\(_2\)O\(_3\) did not focus on film composition. For thermal ALD, the densities of the Al\(_2\)O\(_3\) films agree with values obtained by Groner et al.,\(^{26}\) 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 Al\(_2\)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 Al\(_2\)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 Al\(_2\)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.\(^{23}\)

Preliminary results of the electrical characterization of Al\(_2\)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

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**Figure 5.** (Color online) Material composition as a function of substrate temperature. (a) Mass density as determined from RBS and ellipsometry. (b) \( \frac{[O]}{[Al]} \) 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).

**Figure 6.** High-resolution SEM images of Al\(_2\)O\(_3\) deposited by remote plasma ALD in macropore structures with an aspect ratio of \( \sim 8 \) (diam: 2–2.5 μm, depth: 19 μm). The Al\(_2\)O\(_3\) was deposited using 700 ALD cycles.
O2 plasma was characterized and compared to the well-established Ck mally 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 Al2O3 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 de 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 ("Innova") project IS 044041. The research of W.M.M.K. was made possible by a fellowship from the Royal Netherlands Academy of Arts and Sciences.

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References