

# Low-Temperature Deposition of Aluminum Oxide by Radical Enhanced Atomic Layer Deposition

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Aluminum oxide was deposited by radical enhanced atomic layer deposition using trimethylaluminum (TMA) and oxygen radicals in the temperature range 25-300 °C. The radicals were produced by dissociating oxygen gas in a remote microwave plasma discharge. Oxygen was mixed with argon which was also used as the carrier and purge gas. Films were grown on silicon, glass, and indium tin oxide coated glass substrates. Additional growth experiments were conducted on heat-sensitive materials: polyethene, polypropene, and wool. The time to complete one deposition cycle was nearly independent of the deposition temperature, being around 10 s for all deposition temperatures. Growth rates were between 1.5 and 2.9 Å per cycle, which is higher than what has been obtained with the TMA-H<sub>2</sub>O process in similar reactor conditions. The films were amorphous according to X-ray diffraction. The films were also very smooth; the surface root-mean-square roughness was less than 0.8 nm for 180 nm thick films. The films had breakdown fields, defined as the field corresponding to the leakage current density of 1  $\mu$ A/cm<sup>2</sup>, between 6 and 10 MV/cm, and dielectric constants between 6.5 and 8.1. The film impurity levels according to the refractive indexes at 580 nm were between 1.60 and 1.64.

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Aluminum oxide thin films have many applications, as  $Al_2O_3$  can be used as a dielectric, passivating, and protecting material. In electroluminescent thin-film displays aluminum oxide has all these roles. It is used as a passivation layer on glass to prevent sodium diffusion from glass to the thin-film structure, as a dielectric layer on top and bottom of the luminescent layer, and finally, an  $Al_2O_3$  layer encapsulates the whole thin-film structure.<sup>1-4</sup> Aluminum oxide is also known as a wear-resistant coating material and recently it has demonstrated excellent behavior in microelectromechanical devices.<sup>5</sup> Yet another new application for thin aluminum oxide films is as a thin-film magnetic head gap layer.<sup>6</sup> Aluminum oxide film can also improve the gas permeation properties of polymers.<sup>7</sup>

In microelectronics new high-*k* dielectric oxide materials to replace silicon dioxide have been extensively studied.<sup>8,9</sup> Aluminum oxide has good electrical properties such as wide bandgap (8.7 eV) and high electric field strength (8 MV/cm). The dielectric constant, however (k = 9), is only double to SiO<sub>2</sub>.<sup>6,8,10</sup> Al<sub>2</sub>O<sub>3</sub> is stable on bare silicon, which makes it an attractive material for gate dielectrics in metal-oxide-semiconductor (MOS) transistors.<sup>11-14</sup> Because of the stability, Al<sub>2</sub>O<sub>3</sub> can be deposited on bare silicon without the formation of a capacitance degrading interfacial SiO<sub>2-x</sub> layer.<sup>13,15</sup> An interfacial SiO<sub>2-x</sub> layer may be formed, however, by extrinsic reasons, such as oxidation by atmospheric oxygen after the deposition or by a strong oxidant during the deposition.<sup>13,14</sup> If the moderate *k*-value limits the use of pure Al<sub>2</sub>O<sub>3</sub> as gate oxide, it can be a component in a multilayer structure or solid solution with Zr, Hf, Ta, or rare earth oxides, for example.<sup>16-19</sup> Also, aluminate compounds, such as LaAlO<sub>3</sub>, have been considered potential high-*k* materials.<sup>20</sup>

Atomic layer deposition (ALD) is an attractive thin-film deposition technique because it allows conformal deposition on structured surfaces.<sup>1,21</sup> Many of the applications mentioned above require conformal films. Al<sub>2</sub>O<sub>3</sub> has been deposited by ALD with many processes from which the one using trimethylaluminum (TMA) and water has been the most extensively studied.<sup>22-24</sup> This is probably the most successful ALD reaction and it operates at a very broad temperature range (30 - 500°C).<sup>7,24</sup> Alternatively, ozone and direct oxygen plasma have been used as an oxygen source in ALD of Al<sub>2</sub>O<sub>3</sub> from TMA,<sup>25-27</sup> and in one case the oxygen source has been aluminum metal oxide.<sup>15</sup> Stable thin-film growth can be achieved by the TMA-H<sub>2</sub>O process down to 30°C and the growth rate per cycle is higher than at elevated temperatures. However, the films grown at 100°C or less contain significant amounts of hydrogen.<sup>7</sup> It appears that the composition of the low-temperature films is close to AlOOH and they may even contain  $Al(OH)_3$ . Furthermore, the purging of water is very slow close to room temperature due to its polar nature. At 30°C deposition temperature the time required to purge water was as long as 180 s, which was almost 90% of the total ALD cycle time.<sup>7</sup> The slow purging of water makes the effective deposition rate low and can thus limit the feasibility of a process in potential applications.

In this paper Al<sub>2</sub>O<sub>3</sub> films are grown by ALD at low temperatures using oxygen radicals obtained from a remote plasma discharge. This paper aims to circumvent three problems of the known low-temperature Al<sub>2</sub>O<sub>3</sub> processes: (*i*) avoid possible substrate damage by energetic particle bombardment by using remote plasma, (*ii*) reduce the hydrogen content and (*iii*) decrease the cycle time by replacing water with oxygen radicals. The goal is to grow protective films on temperature-sensitive substrates like polymers and wool, and obtain a fast process with good film qualities even at low deposition temperatures.



**Figure 1.** Growth rate dependence on the TMA pulse length and the following purge time at room temperature,  $25^{\circ}$ C. The pulse time experiments were done with a purge time of at least four times the pulse time. The purge time experiments were done with a 0.5 s TMA pulse.

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Figure 2. Growth rate dependence on the oxygen pulse length at room temperature, 25 °C. The experiments were conducted using 0.5 s TMA pulse with 1 s purge period.

### **Experimental**

The growth experiments were carried out in a flow-type ALD reactor with inert gas valving.<sup>1</sup> The reactor had been modified to incorporate a remote microwave plasma source for radical generation.<sup>28</sup> The overall carrier and purge gas was argon (AGA, -99.98%) which was purified with Aeronex GateKeeper inert gas purifier to decrease the impurity levels below 1 ppb. TMA (Witco) was used as the aluminum precursor and it was kept at room temperature, 23°C. Oxygen radicals, produced from molecular oxygen gas (AGA, 99.99%) by the plasma discharge, were used as the oxygen source. Aluminum oxide was grown on several substrate materials: n-type silicon, borosilicate glass, and indium tin oxide (SnO<sub>2</sub>:In, ITO) coated glass. Also, some highly heat-sensitive substrate materials were used: polyethene, polypropene, and wool.

Film crystallinities were studied with grazing incidence X-ray diffraction (GIXRD). Film density and interface roughness were measured using X-ray reflectivity (XRR). Both measurements were conducted with a Bruker-axs D8 Advance diffractometer/ reflectometer operated in parallel beam geometry. For some samples, also the film thickness was determined with XRR measurements. For the majority of samples either the film thickness was too large or the density difference between the film and the substrate was too small, and the XRR curves could not be modeled. Film thicknesses and refractive indexes were determined by fitting optical reflectance spectra measured within a wavelength range of 370 - 1100 nm using a Hitachi U-2000 spectrophotometer.<sup>29</sup>

To measure leakage current densities and capacitances of the films, aluminum oxide films were grown on sputter-deposited ITO



Figure 3. Growth rate and film density dependence on the deposition temperature.



Figure 4. Film composition according to TOF-ERDA as a function of deposition temperature.

films at four different temperatures ranging from room temperature to 300°C. The top electrodes were aluminum dots, evaporated through a shadow mask. The evaporation was done with an Instrumentti Mattila IM-1992 electron-beam evaporator using aluminum pellets (99.99% Al, Cerac) as the source material. A Keithley 2400 SourceMeter was used for measuring the leakage current densities. Capacitance measurements were done with an HP4284A LCR meter using a 100 kHz measuring frequency. The breakdown voltage and dielectric constant were measured from several electrodes, and the reported values were obtained from at least three electrodes.

The impurity content of the films was analyzed by time-of-flight elastic recoil detection analysis (TOF-ERDA).<sup>30</sup> The presence of  $Al_2O_3$  on the polymers and wool was verified by scanning electron microscopy (SEM) using a Zeiss DSM 962 electron microscope, and energy-dispersive X-ray spectroscopy (EDX) using a Link ISIS spectrometer. Fourier-transform infrared spectroscopy (FTIR) performed with a Perkin Elmer Spectrum GX spectrophotometer in transmission mode was used to study the aluminum oxide phases and the chemical nature of the impurities.

### **Results and Discussion**

 $Al_2O_3$  films could be grown on all substrate materials tested. The growth was successful on even the most sensitive polymer and wool without damaging the substrates. The TMA source length was varied to study its effect on the film growth rate (Fig. 1) at room temperature. The saturation of growth rate occurred with TMA pulse length of 0.5 s. The purge period following the TMA pulse had to be at least of equal length with the TMA pulse, otherwise some growth occurred in chemical vapor deposition (CVD) mode (Fig. 1). The growth rate at room temperature saturated even with a 3 s oxygen radical pulse (Fig. 2). This is the shortest controlled oxygen radical pulse time that can be obtained, because the discharge column extends slowly from the microwave plasma source.<sup>28,31</sup> Increasing the oxygen pulse length increases the area of saturated growth, because the source is point-like. The 5 s pulse time used in the majority of experiments already results in large enough diameter (about 3 cm)

# Table I. Film composition according to TOF-ERDA at four different deposition temperatures.

Deposition - temperature (°C)	Film composition (atom %)			
	Al	0	Н	С
25	25	56	15	3.8
100	32	58	7.8	2.3
200	38	59	2.5	1
300	40	59	0.8	0.15



Figure 5. Infrared absorption spectra of aluminum oxide films grown utilizing (a)  $H_2O$  and (b-e) O-radicals as the oxygen precursor. The film deposition temperatures were (a) 150, (b) 25, (c) 100, (d) 200, and (e) 300°C.

for easy characterization of the film properties. The purge period following the oxygen pulse was 3 s, which is required to allow the flow through the plasma source to stop. The dependence of saturated film growth rate on substrate temperature was also studied (Fig. 3).

The time required to complete one ALD cycle at room temperature was 10 s, whereas the cycle time for TMA-H<sub>2</sub>O process at room temperature was about 200 s, largely because of the need for a long, 180 s purge period after the water pulse.<sup>7</sup> The growth rate at room temperature in the present process was 0.29 nm per cycle, which is considerably higher than the highest rate of 0.19 nm/cycle reported for the TMA-H<sub>2</sub>O process.<sup>32</sup> The growth rate decreased with increasing deposition temperature: at 100 and 200°C the growth rate was 0.23 nm/cycle and at 300°C, 0.15 nm/cycle. The decreasing growth rate with increasing growth temperature can be somewhat attributed to increasing density (Fig. 3). The thickness values obtained with UV-visible (UV-vis) and XRR measurements agree very well: the differences between the values obtained by these two techniques were less than 5%. Refractive indexes obtained by UV-vis measurements were between 1.60 and 1.64 at 580 nm wavelength for samples grown at 25 and 300°C, respectively. The values are similar to what has been obtained with the TMA-H<sub>2</sub>O process.2

According to XRD the as-deposited films were amorphous, which is an expected result for  $Al_2O_3$  grown by ALD. The films were smooth according to the XRR measurements: the surface root mean square (rms) roughness values were below 0.8 nm for about 180 nm thick films.



Figure 6. Leakage current vs. electric field for  $Al_2O_3$  grown at room temperature, 25°C.



Figure 7. Leakage current vs. electric field for Al<sub>2</sub>O<sub>3</sub> grown at 300°C.

The impurity contents of the films decreased steadily with increasing temperature and the impurities were exclusively carbon and hydrogen (Fig. 4). Based on the film composition (Table I), the film grown at 25°C would seem to be close to AlOOH. Films grown at 100°C and above are more clearly Al<sub>2</sub>O<sub>3</sub> but with CH<sub>3</sub> impurities. However, based on the FTIR measurements (Fig. 5), all samples were similar, even the one grown at 25°C, and contained only features associated to Al<sub>2</sub>O<sub>3</sub> and not AlOOH.<sup>33</sup> The only difference between the samples is in the intensity of the very broad AlO-H stretch between 2600 and 3800 cm<sup>-1</sup>,<sup>34</sup> which increases with decreasing deposition temperature. Thus, as the sample grown at 300°C is nearly pure Al<sub>2</sub>O<sub>3</sub> (Table I) and the sample grown at 25°C displays similar FTIR spectrum, the latter seems to be Al<sub>2</sub>O<sub>3</sub> also. The exact chemical nature of the impurities in the sample grown at 25°C, however, remains unclear.

As a general trend, the leakage current densities decreased with increasing deposition temperature as did the breakdown fields (Fig. 6-8). Breakdown field was defined as the field causing a 1  $\mu$ A/cm<sup>2</sup> current density. No clear trend could be observed, however, for the behavior of the dielectric constant (Fig. 8). For the sample grown at room temperature the breakdown field was 5.8 MV/cm and the dielectric constant,  $\varepsilon$ , was 7.4. For the sample grown at 100°C the breakdown field increased to 9.2 MV/cm but the dielectric constant was only 6.5. For the sample grown at 200°C the breakdown field did not change much, being 9.5 MV/cm, but the dielectric constant increased to 8.1. Finally, for the sample grown at 300°C both values remained nearly the same: the breakdown field increased slightly to 10 MV/cm and dielectric constant was 7.8.



Figure 8. Breakdown voltage and dielectric constant as a function of deposition temperature. The breakdown voltage values are within an error range of 5% and dielectric constant 1%.



Figure 9. SEM images of wool before and after deposition. The left image is the fiber without  $Al_2O_3$  at 500 times magnification, and on the right is the one with  $Al_2O_3$  at 1000 times magnification.

The film growth on polymers and wool was verified by EDX analysis: all polymers, including two different types of Teflon substrates and wool, exhibited strong signals from aluminum whereas the nondeposited reference substrates did not. Additionally, EDX measurements gave an upper limit for the growth rate of  $Al_2O_3$  on polyethene and Teflon. The growth rate was slightly higher than on silicon, but this may be explained by porosity or roughness of the substrate. Nevertheless, EDX measurements confirm at least qualitatively that the growth rate is more or less the same on polyethene and Teflon as on silicon. SEM images revealed that the most sensitive substrate material used, wool, exhibited very similar surface features before and after deposition (Fig. 9). This indicates that the process is gentle enough even if it uses oxygen radicals as the oxygen source. In related studies done in our laboratory, it was found that wool burns almost instantly in oxygen plasma but can withstand some exposure to oxygen radicals. In this light, it seems that the aluminum oxide being deposited protects the wool beginning already from the first deposition cycles.

# Conclusions

 $Al_2O_3$  could be successfully grown at room temperature on several substrate materials including heat-sensitive polymers and wool. The cycle times at room temperature were very fast compared to the TMA-H<sub>2</sub>O process, and further improvement may be expected with a different reactor plasma source design. Also, the electrical properties were already good for the films grown at room temperature and improved steadily with increasing growth temperature with the best values obtained at 300°C. The successful growth at room temperature on polymers without destroying them makes this process interesting for gas permeation application, for example. The hydrogen content is high for films deposited at room temperature but is still much lower than in the TMA-H<sub>2</sub>O process at 33°C and up to deposition temperatures close to 100°C.

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