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Chemically Stable Atomic-Layer-Deposited Al₂O₃ Films for Processability

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ABSTRACT: Atomic-layer-deposited alumina (ALD Al₂O₃) can be utilized for passivation, structural, and functional purposes in electronics. In all cases, the deposited film is usually expected to maintain chemical stability over the lifetime of the device or during processing. However, as-deposited ALD Al₂O₃ is typically amorphous with poor resistance to chemical attack by aggressive solutions employed in electronics manufacturing. Therefore, such films may not be suitable for further processing as solvent treatments could weaken the protective barrier properties of the film or dissolved material could contaminate the solvent baths, which can cause cross-contamination of a production line used to manufacture different products. On the contrary, heat-treated, crystalline Al₂O₃ has shown resistance to deterioration in solutions, such as standard clean (SC) 1 and 2. In this study, ALD Al₂O₃ was deposited from four different precursor combinations and subsequently annealed either at 600, 800, or 1000 °C for 1 h. Crystalline Al₂O₃ was achieved after the 800 and 1000 °C heat treatments. The crystalline films showed apparent stability in SC-1 and HF solutions. However, ellipsometry and electron microscopy showed that a prolonged exposure (60 min) to SC-1 and HF had induced a decrease in the refractive index and nanocracks in the films annealed at 800 °C. The degradation mechanism of the unstable crystalline film and the microstructure of the film, fully stable in SC-1 and with minor reaction with HF, were studied with transmission electron microscopy. Although both crystallized films had the same alumina transition phase, the film annealed at 800 °C in N₂, with a less developed microstructure such as embedded amorphous regions and an uneven interfacial reaction layer, deteriorates at the amorphous regions and at the substrate–film interface. On the contrary, the stable film annealed at 1000 °C in N₂ had considerably less embedded amorphous regions and a uniform Al—O—Si interfacial layer.

1. INTRODUCTION

Al₂O₃ deposited by atomic layer deposition (ALD) as a protective coating has attracted considerable interest in the past years.¹–⁴ ALD coatings in general are highly attractive due to the conformal nature of the deposited films. In principle, any geometry can be coated uniformly as long as the gaseous precursors are able to diffuse to the desired locations. Therefore, even geometries, such as pinholes and partly sealed cavities, can be protected. Protective ALD coatings can be applied in various areas such as (medical) microdevices,²⁵,⁶ and organic electronics.⁷ Besides utilizing ALD alumina films as protective coatings, they may also be used as functional and structural layers in microsystem manufacturing. For example, Al₂O₃ is known for its excellent stability as a plasma etching mask material in high-aspect-ratio micromachining.⁸,⁹ Al₂O₃ thin films can be exposed to various wet chemistries regardless of whether the films are utilized as protective coatings or as functional layers. Especially, the standard Radio Corporation of America (RCA) clean is highly relevant for commercial production of devices in a clean room environment.¹⁰,¹¹ The RCA clean is routinely applied in manufacturing to clean surfaces from contaminants. In addition to the water rinsing and drying steps, the RCA clean consists of standard clean 1 (SC-1, ammonium hydroxide and hydrogen peroxide), dilute hydrofluoric acid (HF), and standard clean 2 (SC-2, hydrochloric acid and hydrogen peroxide) solvent dips, which are all highly aggressive solutions. These solutions may deteriorate the coatings and hence either contaminate processing tools by introducing metallic contamination into the baths or decrease the barrier capability of the film. Contaminant Al on silicon wafers can cause deviation in the thermal oxidation rates of Si and fixed negative charge in the SiO₂, altering transistor performance.¹²,¹³ Cross-contamination is an especially large concern in foundry-type manufacturing where several different products may be processed within the same facilities. Therefore, Al₂O₃ that goes through processing...
should be fully stable and not dissolve into the cleaning baths. Furthermore, the redeposition of Al on Si has been shown to be directly proportional to the amount of contaminant Al in SC-1.13

ALD alumina has already displayed potential as a thin-film material with a low etch rate in a variety of solutions including SC-2,14 however, in general, the as-deposited ALD Al2O3 films tend to be amorphous15 and unstable in many solutions. For example, as-deposited ALD Al2O3 has been reported to be susceptible to water corrosion.15,16 Nevertheless, the etch rates of ALD alumina in different solutions have distinctly varied depending on the film deposition parameters and the annealing temperature.15 Both the deposition and the annealing temperature have been determined to be significant when fabricating chemically stable ALD alumina thin films.1,14 The elevated temperature treatments have caused the amorphous microstructure of ALD alumina to densify and to change its composition.16 Thermal treatments at elevated temperatures lead to phase transformations of alumina and to a reduced degree of hydration.17-19 The resulting microstructure may contribute to the chemical stability of the ALD alumina coatings. Consequently, crystalline ALD alumina films have been found resistant to H2SO414,20 high-purity water,1 KCl,1 KOH,1 SC-1, SC-2,14 and other chemicals relevant in microfabrication.14 However, none of the previous studies have analyzed in detail whether Al is nevertheless dissolved in minor quantities or whether some degree of damage is present in the films despite the films being apparently resistant to chemical attack. Furthermore, the microstructure of the stable, crystalline films has not been determined unambiguously and the deterioration mechanisms of unstable films are not comprehensively understood.

The objective of this study is to deposit and thermally treat ALD Al2O3 to obtain chemically stable films. The alumina films are tested in deionized water (DIW), SC-1, and HF cleaning solutions. The films are evaluated on the basis of changes in their thicknesses and refractive indices. The obtained etching rate data of soluble films may be exploited in micromachining too. The microstructures of the films are correlated with the chemical stability of the stable and unstable films. Furthermore, the degree of structural damage in the unstable films is evaluated with comprehensive scanning and transmission electron microscopy (TEM) studies. Finally, mass spectrometry (MS) is utilized to investigate the amount of solute Al contamination in the SC-1 and HF solutions.

2. RESULTS AND DISCUSSION

2.1. Al2O3 Films and Annealing. Al2O3 films were deposited from four precursor combinations. Table 1 presents information about the Al2O3 ALD films.

Table 1. Four Precursor Combinations of the ALD Al2O3 Films, Deposition Temperatures, and Deposition Results

<table>
<thead>
<tr>
<th>precursors</th>
<th>deposition temperature (°C)</th>
<th>growth per cycle (GPC) (nm/cycle)</th>
<th>nonuniformity (%)</th>
<th>thickness (nm)</th>
<th>refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>trimethylaluminum (TMA), H2O</td>
<td>450</td>
<td>0.07</td>
<td>1</td>
<td>102</td>
<td>1.66</td>
</tr>
<tr>
<td>TMA, O3</td>
<td>300</td>
<td>0.10</td>
<td>2</td>
<td>107</td>
<td>1.65</td>
</tr>
<tr>
<td>TMA, H2O, O3</td>
<td>300</td>
<td>0.10</td>
<td>1</td>
<td>103</td>
<td>1.65</td>
</tr>
<tr>
<td>AlCl3, H2O</td>
<td>450</td>
<td>0.07</td>
<td>18</td>
<td>89</td>
<td>1.65</td>
</tr>
</tbody>
</table>

“The measurements represent the average of 24 ellipsometry points from one wafer in each batch of 25 wafers. All films were visually inspected for deviations in color and obvious defects. Nonuniformities were calculated by subtracting the minimum value from the maximum and dividing by two times the average ( % nonuniformity = max − min 2ÅVÅC). Negligible standard deviations (SDs) were measured for the refractive indices but the errors can be approximated to be ± 0.01.

Most notably, the GPC values of the TMA-O3 and TMA-H2O-O3-based films were high compared to those of the films deposited at 450 °C. The GPC of a saturated TMA-H2O process at 300 °C has been reported to lie between 0.08 and 0.1 nm/cycle.14,21 However, TMA begins to decompose at around 370 °C, which could, in principle, induce chemical vapor deposition type film growth.22 However, it has been found that the increased temperature decreases the concentration of reactive OH groups at the surface of Al2O3.21 Therefore, it seems that the lower growth rate in the high-temperature processes is at least partly caused by the decreased number of reactive surface sites. Nevertheless, the GPC values and refractive indices are well in line with the previous research and comparable to those in similar processes.14 Finally, the nonuniformity of the AlCl3-based film was high and could be an issue in applications relying on strict thickness uniformity requirements.

All films presented in Table 1 underwent a thermal treatment at 1000 °C in a vacuum furnace. Furthermore, the TMA-H2O-based films were also annealed at 600, 800, and 1000 °C in a N2 environment. Therefore, additional rows are present in the case of TMA-H2O in Table 2, which presents thickness and refractive index data of the annealed Al2O3 films.

Table 2. Thickness Decrease Data and Refractive Indices of the Alumina Films due to the Thermal Treatments

<table>
<thead>
<tr>
<th>sample</th>
<th>annealing temperature (°C)</th>
<th>annealing atmosphere</th>
<th>thickness decrease (nm)</th>
<th>refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA-H2O</td>
<td>1000</td>
<td>vacuum</td>
<td>6 ± 0</td>
<td>1.70</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td>1000</td>
<td>N2</td>
<td>7 ± 0</td>
<td>1.70</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td>800</td>
<td>N2</td>
<td>8 ± 0</td>
<td>1.70</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td>600</td>
<td>N2</td>
<td>−3 ± 1b</td>
<td>1.65</td>
</tr>
<tr>
<td>TMA-O3</td>
<td>1000</td>
<td>vacuum</td>
<td>7 ± 1</td>
<td>1.70</td>
</tr>
<tr>
<td>TMA-H2O-O3</td>
<td>1000</td>
<td>vacuum</td>
<td>7 ± 1</td>
<td>1.69</td>
</tr>
<tr>
<td>AlCl3-H2O</td>
<td>1000</td>
<td>vacuum</td>
<td>3 ± 9</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Each sample represents a complete wafer. The data were averaged from 24 ellipsometry points on each wafer. The thickness errors represent SDs (±1σ). Each film was measured before and after the thermal treatment. The refractive index errors can be approximated to be ±0.01. After 600 °C annealing, the TMA-H2O film had increased in thickness.
Table 3. Etch Rates Measured after the First Minute of Immersion in DIW at 38 °C (Vacuum-Annealed Films) and 50 °C (As-Deposited TMA-H2O), SC-1 at 80 °C, and HF at 21 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>annealing temperature (°C)</th>
<th>etch rate in 1000 0°H2O (nm/min)</th>
<th>etch rate in SC-1 0°H2O (nm/min)</th>
<th>etch rate in SC-1 0°HF (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA-H2O</td>
<td>1000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td>800</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td>600</td>
<td>19 ± 1</td>
<td>19 ± 1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>TMA-H2O</td>
<td></td>
<td>0.0</td>
<td>20 ± 0</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>TMA-O3</td>
<td>1000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TMA-O3</td>
<td></td>
<td>24 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMA-H2O-O3</td>
<td>1000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TMA-H2O-O3</td>
<td></td>
<td>21 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlCl3-H2O</td>
<td>1000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>AlCl3-H2O</td>
<td></td>
<td>24 ± 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“Empty space and hyphens indicate that no experiment was conducted (the etch rate columns) or that the film was in the as-deposited state (the annealing temperature column). The second reported values in the SC-1 etch rate column are from the N2 annealing experiment encompassing also a repeated as-deposited TMA-H2O-based film SC-1 etching experiment. All heat-treated samples used in the HF etch rate experiments were annealed in N2. The test was continued for 24 h after which the films showed a very minor thickness increase of ≤1 nm. The films started to swell after 60 min. The film started to swell after 15 min.

so thoroughly studied, it comes out as a more attractive precursor combination for ALD Al2O3 compared to the other precursor combinations in terms of being a more mature candidate for foundry-type manufacturing environments.

The thicknesses of the films decreased, except for the annealing at 600 °C in N2, whereas the refractive indices increased, indicating compaction of the films. The refractive index of bulk sapphire is above 1.75 at the wavelength of 632.8 nm. Values similar to these values have been reported after high-temperature treatments of ALD Al2O3 films. The large deviation in the thickness decrease of the AlCl3-based film stems from the originally high nonuniformity. The thicknesses and refractive indices of the films were measured over regular intervals. The thickness data after 1 min of immersion were used to construct the etching rates presented in Table 3. The chip sizes were 2 × 2 cm². Six ellipsometry measurements were taken from each chip.

The etching data show that none of the as-deposited films were stable during the RCA cleaning as the etch rates in SC-1 and HF are on the order of 20 nm/min. The films annealed at 1000 °C in both atmospheres and additionally the TMA-H2O film annealed at 800 °C in N2 seem to be stable over a short period of time of similar magnitude as in cleaning baths. The etch rates of the stable films rounded to 1 nm did not show apparent etching in SC-1 and HF after 1 min; however, the ellipsometry showed thickness decreases of some angstroms, indicating that a surface layer, such as a contaminant carbon or hydroxylated layer, had been etched.

Furthermore, prolonged exposure of 60 min to SC-1 and HF started to impose optical changes on the TMA-H2O film annealed at 800 °C in N2. The TMA-H2O annealing series etching results are visualized in Figure 3, which presents the thickness change and refractive index data in graphs. The film annealed at 800 °C was not fully stable, indicated by the slight increase in thicknesses and the decrease in refractive indices from the vacuum-annealed films because the high number of blisters (Figure 2) distorted the results. Nevertheless, the roughnesses of the films increased due to the annealing. Furthermore, as shown in Figure 2, bright circular defects, blisters, appeared on all of the films after the vacuum annealing. The optical micrographs were identical for all films with the same treatments, that is, vacuum-annealed; blistered films showed white dots and nonblistered films, including annealed and as-deposited films, displayed a deep shade of blue with no obvious defects. Blisters did not appear after the nitrogen atmosphere annealing, and the optical micrographs were identical to those of as-deposited films. Blisters have been observed in various other studies too. The blisters are caused by the local delamination and subsequent bulging of the film. Stress and any gases trapped at the film–Si interface probably play a role. Therefore, a vacuum atmosphere may exacerbate the driving force of the blister formation. Further efforts were placed on characterizing the TMA-H2O films annealed in nitrogen because the nitrogen atmosphere annealing did not cause blistering.

2.2. Chemical Stability. The chemical stability of the films was investigated by immersing them into various solutions typically employed in wafer cleaning (DIW, SC-1, and HF). The thicknesses and refractive indices of the films were measured over regular intervals. The thickness data after 1 min of immersion were used to construct the etching rates presented in Table 3. The chip sizes were 2 × 2 cm². Six ellipsometry measurements were taken from each chip.

The etching data show that none of the as-deposited films would be stable during the RCA cleaning as the etch rates in SC-1 and HF are on the order of 20 nm/min. The films annealed at 1000 °C in both atmospheres and additionally the TMA-H2O film annealed at 800 °C in N2 seem to be stable over a short period of time of similar magnitude as in cleaning baths. The etch rates of the stable films rounded to 1 nm did not show apparent etching in SC-1 and HF after 1 min; however, the ellipsometry showed thickness decreases of some angstroms, indicating that a surface layer, such as a contaminant carbon or hydroxylated layer, had been etched.

Furthermore, prolonged exposure of 60 min to SC-1 and HF started to impose optical changes on the TMA-H2O film annealed at 800 °C in N2. The TMA-H2O annealing series etching results are visualized in Figure 3, which presents the thickness change and refractive index data in graphs. The film annealed at 800 °C was not fully stable, indicated by the slight increase in thicknesses and the decrease in refractive indices from the vacuum-annealed films because the high number of blisters (Figure 2) distorted the results. Nevertheless, the roughnesses of the films increased due to the annealing. Furthermore, as shown in Figure 2, bright circular defects, blisters, appeared on all of the films after the vacuum annealing. The optical micrographs were identical for all films with the same treatments, that is, vacuum-annealed; blistered films showed white dots and nonblistered films, including annealed and as-deposited films, displayed a deep shade of blue with no obvious defects. Blisters did not appear after the nitrogen atmosphere annealing, and the optical micrographs were identical to those of as-deposited films. Blisters have been observed in various other studies too. The blisters are caused by the local delamination and subsequent bulging of the film. Stress and any gases trapped at the film–Si interface probably play a role. Therefore, a vacuum atmosphere may exacerbate the driving force of the blister formation. Further efforts were placed on characterizing the TMA-H2O films annealed in nitrogen because the nitrogen atmosphere annealing did not cause blistering.
after 60 min of immersion in both SC-1 and HF. The effects are slightly more pronounced in HF.

The concentrations of the dissolved Al in the SC-1 and HF etchants were analyzed with inductively coupled plasma MS (ICP-MS). Table 4 presents these results.

Four observations can be made from the ICP-MS results. First, both as-deposited and 600 °C annealed samples showed the same concentrations of Al in the etchants as expected due to the complete dissolution of the films. Second, both reference solutions contained Al. In the case of the SC-1 experiment, N2 annealing crystallized the TMA-H2O films into the monoclinic 0-alumina at 800 and 1000 °C. The reported phase transformation temperatures of the 0 phase correspond to those used in this study.26 Another possibility, with respect to the transformation temperature, could be the 0 → k phase, which provided a reasonable fit to the XR data, although not as good as the 0 fit (see Figure S4). The thermal treatments caused densification and increased surface roughness of the films at 800 and 1000 °C (Table S5). The films became polycrystalline with a preferred orientation because many of the strong peaks expected for an isotropically oriented powder were absent in the grazing incidence XR (GIXR) geometry scans (see Figure S4). The density fits of the X-ray reflectivity (XRR) at 800 and 1000 °C correspond to the reported density of the 0 phase, whereas the k phase should have a considerably higher density (3.98 g/cm3).26 Finally, the XRR roughness values can be seen to increase after crystallization.

TMA-H2O-based Al2O3 films were imaged with scanning electron microscopy (SEM). The imaged films included the as-

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**Table 4. ICP-MS-Measured Al Concentrations in SC-1 and HF after 10 min of Etching Each Sample**

<table>
<thead>
<tr>
<th>sample</th>
<th>Al concentration in SC-1 (µg/L)</th>
<th>Al concentration in HF (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>500 ± 200</td>
<td>400 ± 100</td>
</tr>
<tr>
<td>600 °C</td>
<td>500 ± 200</td>
<td>400 ± 100</td>
</tr>
<tr>
<td>800 °C</td>
<td>80 ± 20</td>
<td>60 ± 20</td>
</tr>
<tr>
<td>1000 °C</td>
<td>80 ± 20</td>
<td>70 ± 20</td>
</tr>
<tr>
<td>reference</td>
<td>80 ± 20</td>
<td>60 ± 20</td>
</tr>
</tbody>
</table>

"Reference" means that the solution was kept in the beaker for 10 min without any sample. The solutions were prepared separately for each experiment. SC-1 temperature was 80 °C, and HF was at room temperature (21 °C). Chip sizes were 3 × 3 and 2 × 2 cm² in SC-1 and HF, respectively. The error limits represent the expanded uncertainty and were calculated with a 95% confidence interval (2σ).
Table 5. Density and Roughness Values Obtained from the XRR Measurements

<table>
<thead>
<tr>
<th>sample</th>
<th>density (g/cm³)</th>
<th>surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>3.25</td>
<td>0.50</td>
</tr>
<tr>
<td>600 °C</td>
<td>3.25</td>
<td>0.50</td>
</tr>
<tr>
<td>800 °C</td>
<td>3.55</td>
<td>1.30</td>
</tr>
<tr>
<td>1000 °C</td>
<td>3.65</td>
<td>1.20</td>
</tr>
</tbody>
</table>

“Error in all of the values comes mainly from the inaccuracy of the fit and is ±0.05 units.

The surfaces of the nitrogen atmosphere annealed films had developed features that were observable in SEM, with the morphology being rougher in the case of 1000 °C annealing. Figure 3 showed that the films annealed at 800 °C and submerged for 1 h in the SC-1 or HF had measurable changes in their thicknesses and clear changes in their refractive indices. The SEM images further revealed clear changes in these films: the films had changed surface characteristics (pronounced contrast differences) and nanocracks (Figure 5c,e). The increased contrast at the surface may originate from changes in surface topography and material density. The decrease in the refractive indices and the increase in thicknesses indicate that the films have become less dense. If the films have undergone hydroxylation or other structural changes, the films may have expanded in volume, causing cracking. ALD Al₂O₃ films tend to be in a biaxial tensile stress in their as-deposited state at room temperature. Additional stress caused by the volume expansion of hydroxide products together with the internal stress of the films may be the root cause for the nanocracks. Nevertheless, it is obvious that although only small changes were observed with ellipsometry, the prolonged aggressive solvent exposure had caused structural changes in the 800 °C annealed films. On the contrary, no nanocracks, or any change in the ellipsometry data, were observed in the films annealed at 1000 °C in N₂. However, HF seems to have attacked the 1000 °C annealed film in localized areas on the surface. It is unclear whether the dark or light contrast areas, or neither, represent the original surface. It is possible that the films that have obvious contrast changes at the surface (Figure 5c,e,f) have undergone a dissolution–precipitation process theorized by Correa et al. That is, the less dense surface of the films may have reacted with the solutions forming aluminum hydroxides, which have subsequently precipitated on the surfaces of the films.

The evolution of structure and the degree of damage in the films was further investigated by preparing cross-sectional TEM samples of the films in Figure 5. Figures 6–9 present the most relevant observations. The as-deposited TMA-H₂O film was found amorphous, as expected based on the literature (Figure 6). However, the native oxide of Si was not resolved at the interface in contrast to the literature. ALD Al₂O₃ had undergone a dissolution–precipitation process theorized by Correa et al.

Figure 5. SEM surface micrographs of TMA-H₂O films after various treatments. The 800 °C (a) and 1000 °C (b) annealed films displayed a distinct difference in their surface morphology. The 800 °C annealed films in SC-1 (c) and HF (e) after 60 min had developed cracks and distinct differences in the surface contrast. The 1000 °C annealed films in SC-1 (d) and HF (f) after 60 min did not display cracks. The inset in (f) displays the boundary area of the two different contrast zones. Note that image (f) has a considerably different magnification compared to that of the other images to highlight the relevant observations.

Figure 6. TEM images of the H₂O-TMA as-deposited sample. (a) Bright-field (BF) TEM taken with the smallest objective aperture selecting the zero-order beam to increase the diffraction contrast. (b) HRTEM image at the Si–Al₂O₃ interface. (c) HRTEM image at the Al₂O₃ surface. The film is clearly amorphous based on the images (a–c). No distinct phase contrast arising from a Si native oxide was seen in image (b).
The thickness of the interfacial layer has remained at sub-10 nm after 1000 °C annealing. In their study, the ALD alumina films were crystallized on Si(111) substrates at over 1000 °C with a constant thickness along the lamella, whereas the layer was found uniform in the sample annealed at 1000 °C.

Interdiffusion had taken place at the higher temperatures (i.e., at least at 800 and 1000 °C), and an Al-Si-O compound had formed between the crystalline alumina and Si (see Figure S7). The surface of the sample seems to have amorphized due to Ga damage, which is why no surface image was included here.

The preferential orientation of the films was investigated with SAED and HRTEM. Figures 7 and 8 show that the films annealed at 800 and 1000 °C had crystallized with a preferred orientation of stacked θ-Al2O3|201⟩ planes on the Si|002⟩ surface. In the SAED patterns of Figure 7a inset and Figure 8b, the θ 201 reflections are not completely aligned with the Si 002 reflections, indicating some rotation of the preferentially oriented grains. Therefore, the GIXRD scans (i.e., nonsymmetrical XRD scans) also showed the 201 peaks as the area that is illuminated in XRD is much larger compared to that in SAED, leading to a higher probability of illuminating the highly tilted grains too. Finally, the d spacings of the 201 reflections were calculated based on the Si 002 type reflections, that is, the length measurement was calibrated with the Si unit cell, which gave a good match to the d spacing of the 201 θ XRD peak.

The film annealed at 800 °C and tested in SC-1 for 1 h showed bright areas extending across the film in the bright-field images (Figure 9). The bright contrast was broadened at the Si interface. These areas obviously scattered the electron beam less compared to that from the rest of the film. The interfacial reaction layer was highly modified at these areas compared with the film annealed at 800 °C that had not undergone testing in SC-1 (HRTEM images of Figure 7 vs Figure 9). Furthermore, the DF STEM in Figure 9 showed similarly that the film had undergone alterations at localized points at the substrate.
interface with some of the areas having clear but narrow paths toward the film surface. It is reasonable to assume that the locations where a clear path toward the surface was seen correlate with the nanocracks observed in the SEM topography images. The dark areas in the DF STEM images indicate regions that scatter the electron beam less, meaning either lower Z number elements and/or lower density such as amorphous regions. Therefore, it is reasonable to assume that those areas have reacted with the SC-1 solution, resulting in an amorphous reaction product. Likewise, the HRTEM images of the SC-1-treated sample (Figure 9b,c) showed no lattice fringes in the reacted areas (both visual and fast Fourier transform inspection were used).

The film annealed at 1000 °C has more developed grains with less defects and grain boundaries compared to those in the film annealed at 800 °C. It is thermodynamically beneficial for small grains to grow, for which the increased temperature provides the kinetics. The increased density indicated by XRR also supports such notions. Furthermore, the grain boundaries themselves may have become denser and with less impurities, such as residual carbon arising from the TMA precursor during deposition, after 1000 °C annealing compared to 800 °C annealing. Nonetheless, the most noticeable difference between the samples annealed at 800 and 1000 °C is that the number and size of the embedded amorphous regions have considerably decreased (Figure 7c vs Figure 8e). Therefore, we propose that in the 800 °C annealed film the solvents diffuse through the less stable grain boundaries/amorphous regions extending from the surface of the film to the substrate interface. The solvents then react both at the amorphous regions and at the interface. For example, Oda and Yoshio have shown that the corrosion of ceramic α-Al2O3 mainly proceeded at the grain boundaries by the dissolution of SiO2 and Na2O impurities.

The reaction product is less dense and will cause the refractive index to decrease although the effect on the thickness of the film is only some nanometers. The reactions inside the amorphous regions and at the interface likely also caused some volumetric increase, which in turn caused cracking visible in the SEM images; however, some of the secondary electron contrast may also come from the different density of the reacted boundaries.

3. CONCLUSIONS

ALD Al2O3 films were shown to be unstable in the amorphous state in DIW and SC-1, whereas heat-treated, crystalline Al2O3 films showed stability in DIW, SC-1, and HF. The crystalline films were realized by annealing alumina, deposited from TMA and H2O at 450 °C, at 800 and 1000 °C. The films crystallized with a preferential orientation to the monoclinic β-Al2O3 phase, where the {201̅} planes were stacked on the (100)Si substrate. However, although the 800 °C annealed film was apparently stable according to the ellipsometry measurements during the first minutes of immersion, electron microscopy showed nanocracks on the film after 60 min of exposure to SC-1 and HF. On the contrary, the film annealed at 1000 °C was completely stable and its surface was unaffected after 60 min in SC-1, and with little modification after 60 min in HF. The deterioration of the 800 °C annealed film had taken place at embedded amorphous regions and at the substrate—film interface. The 1000 °C N2-annealed film, fully stable in SC-1 and with minor reaction with HF, did not show dissolved Al in ICP-MS within the precision of the test setup. The films should be crystallized to process ALD Al2O3 in a manufacturing environment with strict requirements of purity levels. In addition, the crystalline quality needs to be sufficient (volumetric ratio of amorphous regions to crystalline regions should be minimized). Such requirements impose limitations in terms of thermal budget as the lowest possible crystallization temperature may require long annealing times to drive the crystallization of Al2O3 films to a sufficient fraction to preserve it from degradation. Furthermore, if the ALD Al2O3 is used as a barrier layer, it would be likewise beneficial to drive the grain growth to the complete thermodynamic equilibrium. Crystallization kinetics studies of ALD Al2O3 would provide beneficial knowledge required to fully control the grain nucleation and growth.

4. EXPERIMENTAL SECTION

4.1. ALD and Annealing. Four different precursor combinations based on TMA, AlCl3, H2O, and ozone were used in the ALD of the Al2O3 films. All of the films were deposited in a batch reactor (Beneq P400A) with 25 wafers in each run. The films were dual-side deposited on 150 mm single-side-polished (100)Si wafers with the native oxides. Three of the processes were binary, TMA-H2O, TMA-O3, and AlCl3-H2O, with alternating pulses of the metal precursor and the oxygen source. A purge cycle was applied between each step. One process, TMA-H2O-O3, was a ternary process without a purge sequence between the H2O and O3 pulses. The deposition temperatures were selected to produce as high purity films as possible and were ≥300 °C in all cases. The impurity content depends on the deposition temperature, with a higher temperature usually leading to a higher purity in the case of ALD Al2O3 as long as the deposition is carried out.
within the process window for the particular set of precursors.\textsuperscript{36,37}

The annealing tests were conducted in two parts. A fresh film/wafer was used in each test, that is, no film endured two sequential temperature treatments. First, all of the Al$_2$O$_3$ films were annealed for 1 h (dwell time at the maximum temperature) at 1000 °C under high vacuum (HV) conditions ($p_{\text{tot}} < 10^{-6}$ mbar) in a furnace (Webb Red Devil M). The heating ramp rate was 10 °C/min, and cooling was achieved through natural heat dissipation. Second, one of the films (precursor combinations) was selected for a set of thermal treatments based on its as-deposited quality (e.g., low nonuniformity), thermal behavior (e.g., increase in refractive index), and etching experiments (low etch rate in SC-1). The set consisted of annealing at temperatures of 600, 800, and 1000 °C for a 1 h dwell time in a N$_2$ environment. The N$_2$ environment was dictated by the furnace (PEO-603) that was used due to its higher purity classification within the research facilities. Furthermore, nitrogen is an inert gas well-suited for crystallization experiments because it is not expected to react with oxides that are more stable than the corresponding nitride compounds (e.g., Al$_2$O$_3$ vs AlN). The heating ramp rate was 15 °C/min, and the cooling rate was 13 °C/min.

### 4.2. Etching Experiments

The etching experiments were carried out in a fume hood inside a clean room. Borosilicate beakers (Schott Duran) were utilized in precleaning steps, DIW, and SC-1 experiments, whereas beakers made of polypropylene were used in experiments involving HF. The sample holder in all of the experiments was ethylene tetrafluoroethylene. Before the immersion into the etchant, the samples were prewashed in acetone, isopropanol, and DIW for 5 s in each solution. The etch was kept at a desired temperature using a hot plate. The temperature of the heated etchants (i.e., not HF) was monitored using a thermometer. The samples were rinsed in DIW and dried with a nitrogen blow gun after the etching experiments.

The SC-1 solution consisted of 500 mL of DIW and 100 mL of aqueous NH$_4$OH (29 wt % NH$_3$). The liquids were mixed in a glass beaker and heated on a hot plate to a sub-target temperature. Aqueous H$_2$O$_2$ (140 mL, 30%) was added after that, and the complete solution was heated to the target temperature. The SC-1 temperature was 80 °C except when the activation energy of the etching mechanism was studied. The HF solution was prepared by mixing 500 mL of DIW and 10 mL of aqueous HF (50 wt % HF) in a plastic beaker at room temperature (21 °C). DIW experiments were conducted at 38 and 50 °C.

### 4.3. Thin-Film and Solvent Characterization

Ellipsometry (Plasmos SD2300) was used to measure the thicknesses and refractive indices of the films. A He–Ne laser (632.8 nm) was used as the light source. The angle of incidence was fixed to 70°.

An AFM (Digital Instruments Dimension 3100) was used to characterize the surface roughnesses of the films before and after annealing in the HV environment. Optical microscopy was used to visually inspect for defects on the films. Especially of interest were possible cracks or other similar defects after the thermal treatments. SEM (Zeiss Sigma VP) surface characterization was conducted using an in-column secondary electron detector at a 2 kV acceleration voltage.

GIXRD at the grazing angle of $\omega = 0.6^\circ$ and XRR analyses were carried out with an X-ray diffractometer (Rigaku SmartLab) equipped with a 9 kW rotating Cu anode source.

The incident beam was monochromated using a multilayer mirror and a Ge(220) double-bounce monochromator in both the GIXRD and XRR measurements. The measured XRR curves were fitted using in-house-developed software.\textsuperscript{38} The fitting routine was used to extract the thicknesses, densities, and roughnesses of the films. Some etched samples were selected based on the SEM characterization for further TEM inspection. The thin foil preparation was performed using focused ion beam (FIB, FEI Quanta 3D 200i and Helios NanoLab 600) systems. TEM studies were conducted at 200 kV (JEOL JEM-2800).

ICP-MS (Thermo Fisher Scientific iCAP Q) was carried out to analyze the solute Al in the SC-1 and HF solvents used to etch the films. Nitric acid (HNO$_3$) digestion was used in the sample preparation to assure that the aluminum in the solvents was in the ionic form. Measurements were carried out using the SFS-EN ISO 17294-2 standard.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00443.

AFM images, Arrhenius plot, thickness decrease plots, XRD plots, XRR fits, SEM images of the TMA-H$_2$O films (as-deposited and as-deposited after 45 min in DIW), STEM-EDX maps of the TMA-H$_2$O film annealed at 1000 °C in N$_2$ (PDF)

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Notes

The authors declare no competing financial interest.

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### REFERENCES


