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Temperature-Dependent 4-, 5- and 6-Fold Coordination of Aluminum in MOCVD-Grown Amorphous Alumina Films: A Very High Field $^{27}\text{Al}$-NMR study

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ABSTRACT: The only easy way to prepare amorphous alumina is via thin film deposition. For this reason, the disorder in amorphous alumina has not yet been fully investigated. We have used very high-field (20 T) solid state $^{27}\text{Al}$ NMR spectroscopy to analyze the structural modifications of amorphous alumina thin films with deposition temperature ($T_d$). The films were deposited by metalorganic chemical vapor deposition in the $T_d$ range of 360–720 °C. Depending on $T_d$, film composition is either $\text{AlO}_x\text{(OH)}_{1-2x}$ (0 ≤ x ≤ 0.5) or $\text{Al}_2\text{O}_3$. From $^{27}\text{Al}$ 1D magic angle spinning (MAS) and 2D multiple-quantum magic angle spinning (MQMAS) NMR analyses, the films grown between 360 and 600 °C contain between 38 and 43 atom % of 5-fold coordinated aluminum sites ([5]Al). The percentages of [6]Al and [4]Al sites vary spectacularly, reaching their respective minimum (5 atom %) and maximum (54 atom %) around 515 °C. The analysis of a very thin film (85 nm) of $\text{Al}_2\text{O}_3$ reveals the presence of metallic aluminum at the interface with the substrate and suggests that the respective percentages of [4]Al sites slightly differ from those in thicker films. The observed $T_d$ dependence of amorphous alumina structure can be correlated with that of film properties previously reported, namely, Young’s modulus, hardness, and corrosion protection.

INTRODUCTION

Because of the well-known technological interest of alumina thin films in various domains, including catalysis, corrosion protection, and electrical insulation, insight into the influence of a given process on the atomic structure of the ceramic is a valuable key to process and properties optimization. This study was undertaken after observing that physical properties of amorphous aluminum oxide films grown by metalorganic chemical vapor deposition (MOCVD) depend on the deposition temperature ($T_d$). The films were prepared from aluminum tri-isopropoxide (ATI) at 0.67 kPa (5 Torr) over the temperature range 350–750 °C. Previous studies† had shown that films grown in the temperature range 350–415 °C are partially hydroxylated amorphous alumina, $\text{AlO}_{x+2}\text{(OH)}_{1-2x}$ with x varying from 0 (AlOOH) at 350 °C to 0.5 ($\text{Al}_2\text{O}_3$) for a deposition temperature above ca. 415 °C. Those grown between 480 and 650 °C are amorphous alumina ($\text{Al}_2\text{O}_3$), while around 700 °C, $\text{Al}_2\text{O}_3$, is embedded with nanocrystals of $\gamma-\text{Al}_2\text{O}_3$. Table 1 displays hardness and Young’s modulus for three films grown on Ti6Al4V titanium alloy at 350, 480, and 700 °C and for two films grown on silicon at 415 and 600 °C.‡ Although referring to films grown on two different substrates, these values suggest that the intrinsic mechanical properties of the films reach a maximum for a deposition temperature in the

Table 1. Composition, Hardness ($H$), and Young’s Modulus ($E$) of Alumina Films Deposited at Different Temperatures ($T_d$) on Metallic Substrates

<table>
<thead>
<tr>
<th>$T_d$ (°C)</th>
<th>350</th>
<th>415</th>
<th>480</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>Ti6Al4V</td>
<td>silicon</td>
<td>Ti6Al4V</td>
<td>silicon</td>
<td>Ti6Al4V</td>
</tr>
<tr>
<td>composition</td>
<td>a-AlOOH</td>
<td>a-Al2O3</td>
<td>a-Al2O3</td>
<td>a-Al2O3</td>
<td>a-Al2O3 + nano $\gamma-\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>$H$ (GPa)</td>
<td>5.8</td>
<td>7.8</td>
<td>10.8</td>
<td>11.2</td>
<td>~ 1</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>92</td>
<td>133</td>
<td>155</td>
<td>175</td>
<td>~ 10</td>
</tr>
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</table>

During the initial phase of this study, the resistance to salt environment corrosion was comparatively studied for the three coated Ti6Al4V samples.§ From polarization curves in a 0.1 M NaCl solution and electrical impedance measurements after 1 h in the NaCl solution, the film deposited at 480 °C improved range 480–600 °C. The resistance to salt environment corrosion was comparatively studied for the three coated Ti6Al4V samples.§ From polarization curves in a 0.1 M NaCl solution and electrical impedance measurements after 1 h in the NaCl solution, the film deposited at 480 °C improved
corrosion resistance by 2 orders of magnitude with respect to the bare alloy. The other two films were by far less efficient.3

Such property variations are indicative of modifications of the amorphous structure upon changing Tdep. For the films of general formula a-AlOx(OH)y−2α, structural modifications are expected to accompany dehydroxylation from a-AlOOH to a-Al2O3. The question arises as to possible further structural modifications in a-Al2O3 for the films grown above 415 °C. Using 27Al magic angle spinning nuclear magnetic resonance (MAS NMR) experiments, Lee et al. recently showed that two a-Al2O3 films grown by physical vapor deposition (PVD) and atomic layer deposition (ALD) mainly consist of tetra-coordinated and penta-coordinated aluminum sites with a low content of hexa-coordinated aluminum sites.4,5 It is well-known that crystalline transition aluminas consist of [4]Al and [6]Al. However, a small amount (ca. 5%) of [5]Al was reported as surface species in γ-Al2O3 formed upon thermal decomposition of boehmite (γ-AlOOH).6–8

To our knowledge no study has so far addressed the influence of deposition temperature on the structure of amorphous alumina films grown from the vapor phase. Besides the interest in gaining information about process–structure relationship, the structure of an amorphous material is itself worth studying.

We present the results of very high-field (20 T) 27Al NMR structural investigations of MOCVD-processed alumina films between 350 °C (amorphous AlOOH) and 720 °C (a-Al2O3 with embedded nanocrystals of γ-Al2O3).

**Experimental Section**

**Sample Preparation.** Deposition experiments were performed in a custom-made, horizontal, hot-wall reactor described in a previous paper.7 The films were grown on 100 μm thick, (100) oriented silicon wafers. Six samples with targeted thickness of 0.5 ± 0.1 μm were prepared at 360, 420, 480, 550, 600, and 720 °C. Supercooled AT1 (Aeros Organics) was heated at 90 °C and carried to the deposition zone by bubbling with 99.9999% pure N2 as a carrier gas (Air Products). Fixed experimental parameters were as follows: total pressure, 0.67 kPa; N2 flow rate over ATI, 20 standard cubic centimeters per minute (sccm); and dilution N2 flow rate, 631 sccm. Three more samples with targeted thickness 0.1, 0.2, and 1 μm were also prepared at 480 °C in order to gain insight into possible structural evolution along the thickness of the alumina film. Film thickness, reported in Table 2, was determined from weight gain of the samples and by reflectometry using a UV–VIS reflectometer (Ocean Optics) and NanoCalc software. The samples, comprising the oxide film and the wafer, were then ground into a coarse powder for packing in the NMR sample container.

**Solid-State NMR.** All solid-state NMR experiments were carried out on a Bruker AVANCE III spectrometer operating at a magnetic field of 20.0 T (corresponding to 27Al and 1H Larmor frequencies of 221.5 and 850.1 MHz, respectively). Single resonance 27Al experiments were performed with a 2.5 mm MAS probe head. Double-resonance 2H−27Al experiments were performed with a 3.2 mm MAS probe head which increases the available volume of the powdered samples (42 μL for 3.2 mm versus 14 μL for 2.5 mm) at the cost of a lower spinning frequency.

The 27Al one-dimensional (1D) MAS spectra were recorded with a spinning frequency of 35 kHz. The excitation pulse length was 0.4 μs, i.e., a flip angle less than π/18 to ensure a quantitative 1D spectrum (radio-frequency field νRF = 35 kHz). The recycle delay was 20 ms (spin−lattice relaxation time T1 of ~200 ms, estimated with a saturation−recovery experiment on the most sensitive sample) and the number of transients was between 260K and 3 000K depending on the film thickness. The 27Al signal from the probe background was acquired using the same experimental conditions with the empty rotor (800K transients). After normalization according to the number of transients, it was subtracted from the baseline-corrected spectra.

The two-dimensional (2D) z-filtered 27Al multiple-quantum magic angle spinning (MQMAS) experiments11,12 were performed with a spinning frequency of 30 kHz, with triple-quantum (3Q) excitation and reconversion pulse lengths of 2.0 and 0.9 μs, respectively (νRF = 128 kHz). The z-filter duration was 3.3 ms, and the selective pulse length of the central transition was 7.5 μs (νRF = 10 kHz). Acquisition in the indirect dimension was synchronized with the spinning frequency13 and 12–14 t1 increments of 33.3 μs were collected with a recycle delay of 200 ms. The 3QMAS experiments lasted for about 3–4 days per sample. Among the four samples prepared at 480 °C, only the thinnest one was submitted to 3QMAS NMR because the amount of aluminum for the thinnest films (i.e., the smallest ratio alumina/wafer) would necessitate unpractical experimental times.

The 2H−27Al rotational echo double resonance (REDOR)14,15 experiments were performed for the films grown at 360, 420, and 480 °C with a spinning frequency of 24 kHz. The 27Al and 2H radio-frequency field strengths were νRF = 13 kHz (selective excitation of the central transition) and νRF = 52 kHz, respectively. The normalized difference signal due to dipolar dephasing (ΔS/S0) was obtained by acquiring separately reference (S0) and dipolar dephased (S) signals. The recycle delay was set to 0.5 s, and between 8K and 32K transients were collected for each dipolar dephasing and

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<tbody>
<tr>
<td>360</td>
<td>563 ± 73</td>
<td>32.9 ± 0.8</td>
<td>40.9 ± 0.7</td>
<td>26.2 ± 0.7</td>
<td>4.93</td>
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<tr>
<td>420</td>
<td>399 ± 78</td>
<td>45.6 ± 0.7</td>
<td>42.9 ± 0.5</td>
<td>11.5 ± 0.6</td>
<td>4.66</td>
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<tr>
<td>480</td>
<td>936 ± 84</td>
<td>53.6 ± 0.6</td>
<td>41.8 ± 0.4</td>
<td>4.6 ± 0.4</td>
<td>4.51</td>
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<tr>
<td>480*</td>
<td>600 ± 200</td>
<td>53.0 ± 0.6</td>
<td>41.6 ± 0.4</td>
<td>5.4 ± 0.4</td>
<td>4.52</td>
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<tr>
<td>480*</td>
<td>180 ± 10</td>
<td>53.7 ± 0.8</td>
<td>41.0 ± 0.6</td>
<td>5.3 ± 0.7</td>
<td>4.52</td>
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</tr>
<tr>
<td>480*</td>
<td>85 ± 7</td>
<td>50.7 ± 1.0</td>
<td>43.7 ± 0.7</td>
<td>5.6 ± 0.9</td>
<td>4.55</td>
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<tr>
<td>550</td>
<td>582 ± 78</td>
<td>53.3 ± 0.6</td>
<td>39.2 ± 0.5</td>
<td>7.5 ± 0.3</td>
<td>4.54</td>
<td></td>
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<tr>
<td>600</td>
<td>420 ± 81</td>
<td>46.5 ± 0.3</td>
<td>37.6 ± 0.3</td>
<td>15.9 ± 0.2</td>
<td>4.69</td>
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<td></td>
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<tr>
<td>720</td>
<td>578 ± 67</td>
<td>28.6 ± 0.6</td>
<td>12.2 ± 0.6</td>
<td>59.2 ± 0.5</td>
<td>5.31</td>
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</table>

* Asterisks (*) refer to the three extra samples prepared at 480 °C to study thickness structural effect. The errors in the simulations were determined using a Monte Carlo approach where for each spectrum 1000 data sets were generated from the model with added experimental noise and fitted using the same procedure. The standard deviations, σ, or the full width at half maximum, Δ, of the related Gaussian distribution (Δ = 2(2 ln(2))1/2σ), were used to estimate the uncertainties.

Table 2. Thickness, [8]Al Percentages (atom %), and Averaged Aluminum Coordination Number (CN) for Films Obtained at Different Deposition Temperatures (Tdep)
reference experiment to ensure a good signal-to-noise ratio. Each REDOR experiment lasted between 2.5 and 4.5 days.

All spectra were referenced with respect to a 1 M solution of Al(NO₃)₃. 1D and 2D spectra were simulated using the Dmfit software.¹⁶

## RESULTS AND DISCUSSION

### Influence of Deposition Temperature

Figure 1 and Figure 2 illustrate the 1D quantitative ²⁷Al spectra and their respective 2D 3QMAS ²⁷Al spectra for the six investigated Tₜd values, respectively. Using the very high magnetic field (20.0 T) allows the improvement of the spectral resolution and a clear identification of the tetra-, penta-, and hexa-coordinated aluminum sites ([n]Al with n = 4, 5, or 6). Their line shapes are characteristic of a typical amorphous structure as seen in alumina-containing glasses.¹⁶ The simulation of such NMR spectra is based on the “Czjzek” model (or Gaussian isotropic model) which considers that the local structure of the [n]Al sites may be described as a purely statistical disorder of environments, with a joint probability distribution of the principal value Vzz of the EFG tensor and of the quadrupolar asymmetry parameter ηQ.⁻¹⁷⁻¹⁹ The NMR parameters deduced from this model are the averaged isotropic chemical shift (δiso), the chemical shift distribution (ΔCS), and the averaged quadrupolar constant (C_Q). As shown recently²⁰ for ²⁷Al, δiso is mainly governed by chemical modifications of the second coordination sphere, while ΔCS and C_Q measure the distortion (bond lengths and/or angles) of the AlO₄ tetrahedra; C_Q is, for example, correlated with the mean tangent of the absolute deviation of the tetrahedral ZO–Al–O bond angles from the ideal value of 109.47°.

As the 3QMAS spectra have fully separated the three [n]Al sites (Figure 2), they were first simulated in order to obtain primary sets of optimized values of δiso, ΔCS and C_Q (Tables S1 and S2 in the Supporting Information). Nevertheless, the 3QMAS experiment efficiency is known to strongly depend on the strength of the quadrupolar couplings and particularly filter out the strongest ones. The optimized C_Q values are usually underestimated, even at high magnetic fields. Hence, the 1D ²⁷Al MAS spectra were reconstructed by optimizing nine parameters (δiso, C_Q, amplitude) while keeping the ΔCS values as issued from the 3QMAS experiment. The percentage of each [n]Al site was calculated from line shape integration of the central transition. All the optimized values are summarized in Table 2.

Figure 3 shows the evolution with Tₜd of the percentages of [n]Al sites (Figure 3a) and of ΔCS (Figure 3b). The respective percentages of tetra- and hexa-coordinated sites vary with opposite trends. The [4]Al content increases from 33% for Tₜd = 360 °C up to 53% for Tₜd = 480 °C; at the same time, the [6]Al content decreases from 26% to 5%. For Tₜd = 550 °C, the respective percentages have values that are nearly the same as those for 480 °C, suggesting that the maximum of [4]Al sites and the minimum of [6]Al sites occur at ∼515 °C. From 360 to 515 °C, the [5]Al content is at its highest with values between 40% and 43%. It can be noticed that the [4]Al percentages measured for Tₜd = 480 °C (and 550 °C) compare well with

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**Figure 1.** One-dimensional ²⁷Al MAS spectra of the central transitions of the three [n]Al sites for films deposited at different temperatures. Black circles and red lines represent the experimental and reconstructed spectra, respectively. The gray lines refer to the different contributions of the reconstructed spectrum; asterisks (*) show the spinning sidebands of the external transitions. The center bands were simulated with Gaussian line shapes accounting for the line widths and intensities of their neighboring spinning sidebands.

**Figure 2.** Two-dimensional ²⁷Al 3QMAS spectra of the films deposited at different temperatures. Black and red lines refer to experimental and simulated spectra, respectively.

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**Figure 3.** Evolution of the percentages of [n]Al sites (Figure 3a) and of ΔCS (Figure 3b) with Tₜd. The respective percentages of tetra- and hexa-coordinated sites vary with opposite trends. The [4]Al content increases from 33% for Tₜd = 360 °C up to 53% for Tₜd = 480 °C; at the same time, the [6]Al content decreases from 26% to 5%. For Tₜd = 550 °C, the respective percentages have values that are nearly the same as those for 480 °C, suggesting that the maximum of [4]Al sites and the minimum of [6]Al sites occur at ∼515 °C. From 360 to 515 °C, the [5]Al content is at its highest with values between 40% and 43%. It can be noticed that the [4]Al percentages measured for Tₜd = 480 °C (and 550 °C) compare well with
those measured by Lee et al. for two aluminum oxide films prepared by PVD and ALD. In the 550–720 °C range, the [6]Al content increases to 59% and the [4]Al and [5]Al contents decrease to 29% and 12%, respectively.

The average isotropic chemical shift δiso does not present any significant evolution with Td, consistent with the fact that there are no chemical variations in the aluminum second coordination sphere (i.e., only Al atoms). The average values of C$_{Q}$(4) and ΔCS between the three [n]Al sites show the same hierarchy whatever the temperature of deposition: C$_{Q}$(4)[Al] > C$_{Q}$(5)[Al] > C$_{Q}$(6)[Al]; ΔCS(4)[Al] > ΔCS(5)[Al] > ΔCS(6)[Al]. The same trend was observed for rare-earth aluminosilicates and may therefore be related to polyhedra-specific distortions. Figure 3b shows that ΔCS is maximal for a Td more or less half-way between 480 and 550 °C for each coordination number. This suggests that the utmost structural disorder corresponds to the highest rates of [4]Al and [5]Al sites.

**Influence of Film Thickness.** Figure 4 presents the 1D quantitative $^{27}$Al spectrum in the frequency range 1450–1850 ppm for four films of different thickness processed at T$_{d}$ = 480 °C. The spectrum of the thinnest (~85 nm) film clearly reveals a peak corresponding to metallic aluminum $^{27}$Al at 1650 ppm. Increasing film thickness results in the decrease of the relative intensity of this peak. It was verified that this peak does not show up on a 1D $^{27}$Al spectrum recorded with the bare silicon substrate as a reference, thus confirming that metallic aluminum formed during alumina growth.

The NMR parameters (δiso and C$_{Q}$) do not vary significantly with film thickness. The respective [6]Al contents do not vary either for the three thicker films (180, 600, and 984 nm). The [4]Al and [5]Al contents in the thinnest film (85 nm), are slightly but significantly different from those in the thicker films. This film is probably not thin enough to discriminate between surface and bulk [n]Al environments. Consequently one cannot exclude that the distribution of [n]Al sites does slightly differ from that in the thicker films prepared at the same temperature.

The intensity of the line corresponding to metallic aluminum increases in proportion as thickness decreases, suggesting that $^{27}$Al forms at the silicon/alumina interface; calculated $^{27}$Al relative populations $^{27}$Al/(Al$_{3}$ + $^{27}$Al) (CT for central transition only; $^{27}$Al lines reconstructed with a Gaussian shape) are 1.8%, 1.0%, and 0.3% for oxide thicknesses of 85, 180, and 600 nm, respectively. If metallic aluminum were dispersed in the bulk, this ratio should be constant.

**Interpreting Coordination Variation.** As was mentioned in the Introduction, previous studies concluded that films grown between 350 and 415 °C are amorphous hydroxylated alumina $^{α}$-AlOO$_{1-x}$(OH)$_{x}$ with $x$ varying from 0 (a-ALOOH) for T$_{d}$ = 350 °C to 0.5 (a-Al$_{2}$O$_{3}$) for T$_{d}$ above ca. 415 °C. This result was obtained from a series of different films by (i) measuring the O/Al ratio comparatively to a standard sample of $^{α}$-Al$_{2}$O$_{3}$ through three different techniques, namely, energy dispersion and Rutherford backscattering spectroscopies and electron probe microanalysis (EDS, RBS, and EPMA, respectively) and (ii) measuring surface and volume hydrogen contents through elastic recoil detection analysis (ERDA). Moreover, Fourier transform infrared transmission spectroscopy showed a wide OH absorption band in the 3500 cm$^{-1}$ region for films deposited at 350, 380, and 415 °C; this band did not show up for a film prepared at 480 °C. In the same way, thermogravimetric analyses (TGA, DTG) showed mass
loss attributable to dehydroxylation for films deposited at 350 and 380 °C and no significant mass loss for $T_d = 480 \, ^\circ C$.\textsuperscript{1}

The $^{[1]H}\gamma^{27}Al$ REDOR experiment enables the probing of the spatial proximities (not specifically chemical bonds) between aluminum and hydrogen in the sample. The REDOR curves, i.e., $\Delta S/S_0$ as a function of the dephasing time, can be separated into two main domains: $\Delta S/S_0$ first increases and then reaches a plateau which, assuming that the experiment is perfect, corresponds to the amount of $[4]Al$ sites having protons nearby.\textsuperscript{2,5} Early dephasing times notably exhibit the nearest hydrogen neighbors for aluminum. The REDOR curves (Figure 5) confirm the presence of hydrogen in the proximity of the $[6]Al$ sites for the films deposited at 360 and 420 °C. Considering first the effect of $T_d$, $\Delta S/S_0$ is always higher for 360 °C than for 420 and 480 °C, regardless of the $[6]Al$ site and the dephasing time. This is consistent with the formation of fewer OH groups per $[6]Al$ site as $T_d$ increases. Then the variation of $\Delta S/S_0$ as a function of the aluminum coordination shows the hierarchy $\Delta S/S_0([6]Al) > \Delta S/S_0([5]Al) > \Delta S/S_0([4]Al)$ for each film. This suggests that the H atoms are more numerous and/or closer to hexa-coordinated aluminum ions than to any other. This is illustrated with bayerite Al(OH)$_3$ for which the REDOR curve grows faster than any of the amorphous aluminas (Figure 5) because of the presence of six $[6]Al$ ions. This OH groups can possibly create hydrogen bonds $[6]Al–OH...O-[6]Al$ ($n = 4, 5,$ or 6) with neighboring polyhedra; but the resulting H-to-$[6]Al$ distances are larger than the intraoctahedron H-to-$[6]Al$ distances.

The presence of hydrogen in the films prepared at 480 °C is questionable because $\Delta S/S_0$ becomes significant after a long dephasing time (1.5 ms). This suggests that hydrogen is either present in a small amount in the bulk or may come from surface-adsorbed water. In the sample submitted to ERDA analysis,\textsuperscript{4} the hydrogen content was 0.9 atom % in the bulk and 5.1 atom % on the surface. The drop in octahedral sites from $\sim27\%$ for $T_d = 360 \, ^\circ C$ to $\sim5\%$ for $T_d = 480 \, ^\circ C$ most likely ensues from dehydroxylation. From Figure 3a, it is difficult to decide whether the percentage of $[6]Al$ sites presents a true minimum at about 510 °C or reaches a plateau at 480 °C (same comment for the maximum of the percentage of $[4]Al$ sites). In any case, one can consider that there are virtually no OH groups in the structure for $T_d = 480 \, ^\circ C$.


**Coordination and Physical Properties.** Hardness and Young’s modulus for films prepared at 350, 420, and 480 °C (Table 1) increase with $T_d$ and therefore with the decreasing content in hydroxyl groups. The averaged Al coordination number $CN$ decreases from 4.93 for $T_d = 360 \, ^\circ C$ to 4.52 for $T_d = 480 \, ^\circ C$ (Figure 3a). The ensuing increasing covalent character may account for the observed increase in film hardness and Young’s modulus (Table 1). The collapse of these two properties for $T_d$ between 600 and 700 °C (Table 1) might well indicate the progressive formation of crystals, thus leading to a bi-phasic amorphous/crystalline structure. It is recalled that embedded nanocrystals of $\gamma$-alumina were observed in the TEM for $T_d = 700 \, ^\circ C$ while no such crystals formed for $T_d = 550 \, ^\circ C$.\textsuperscript{1} The structure of $\gamma$-alumina is made of tetrahedral (T) and octahedral (O) Al ions, with the ratio O/T ≥ 2. Therefore crystals can form only in zones where (i) tetrahedral and octahedral ions are segregated from penta-coordinated ions and (ii) there are enough octahedral ions with respect to tetrahedral ions: from the data in Table 2, for $T_d = 550, 600,$ and 720 °C, O/T = 0.14, 0.36, and 2.20, respectively. Formation of such segregated zones as a prelude to nanocrystals may account for hardness and Young’s modulus starting to decrease for $T_d$ as low as 600 °C. Further experiments are needed to specify the onset.

As reported in the Introduction, films deposited at 480 °C on Ti6Al4V proved to be 2 orders of magnitude more protective against salt corrosion than those deposited at 350 and 700 °C. This observation is consistent with the fact that the most disordered structure occurs for $T_d$ around 500 °C. The most disordered structure, hence the most amorphous one, is less propitious to grain boundary formation; hence, it is the most efficient as a diffusion barrier.

**CONCLUSION**

This very high-field (20 T) NMR study was conducted on thin films that were no more than a few hundred nanometers thick.
It provides new insights into the structural variation with deposition temperature of MOCVD amorphous alumina films. The presence of as much as 40% of penta-coordinated aluminum in amorphous aluminum oxide thin films was first established by Lee et al. for two films prepared by PVD and ALD. With the experimental conditions used in the present study, such a high Al content has proven to be sustainable over 350–600 °C, i.e., a wide range of T$_d$. It concerns not only the Al$_2$O$_3$ oxide deposited between 480 °C (42%) and 600 °C (38%) but also diversely hydroxylated aluminum oxyhydroxides AlO$_{1+x}$(OH)$_{2-x}$ from x = 0 (AlOOH for T$_d$ = 350 °C) to x = 0.5 (Al$_2$O$_3$, for T$_d$ ~ 480 °C). Al and Al contents vary spectacularly with T$_d$. For 350 < T$_d$ < 480 °C, the Al content increases from 30% up to 53% and the Al content decreases from 30% down to 5%. Between 480 and 550 °C, they are almost constant. Then, for 550 < T$_d$ < 720 °C, they vary reversely up to 59% for Al and down to 29% for Al. The Al content is 38% for T$_d$ = 600 °C and 11% for T$_d$ = 720 °C.

The “most amorphous” structure is that of Al$_2$O$_3$ grown between 480 and 550 °C and corresponds to the maximum of Al and Al and the minimum of Al contents. This is an important structural feature for the properties of alumina as a diffusion barrier and is confirmed by preliminary results concerning the high corrosion protection potential of a film grown at 480 °C in comparison with that of two films grown at 350 and 700 °C.

Several other issues remain to be explored. In particular, the preparation of films with different thicknesses at 480 °C revealed the formation of metallic aluminum at the interface between the silicon substrate and the deposit. Correlatively, the thinnest film had a distribution of Al sites slightly different from that of thicker films.

Variations of Young’s modulus and hardness of a few films prepared at different temperatures between 350 and 700 °C seem to fit with the distribution of Al sites. This encouraging observation needs to be reinforced by further mechanical studies of a greater number of various samples. Detailed investigation is in progress to better specify these structure–property correlations.

Regarding applications in catalysis, MOCVD-deposited amorphous alumina appears a promising material because the temperature of deposition allows tuning of the content both in OH groups and in 4-, 5, and 6-coordinate aluminum, i.e., in Bronsted and Lewis sites. Particularly, the role of 5-coordinate Al$^{1+}$ as binding sites for preparing active metal catalyst phases on alumina has been recently proposed.

## ACKNOWLEDGMENTS

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## REFERENCES


